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Kearsey, Timothy

# MULTI-PROXY PALAEOCLIMATE RECONSTRUCTION OF THE PERMIAN–TRIASSIC MASS EXTINCTION EVENT

by

**TIMOTHY KEARSEY**

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# MULTI-PROXY PALAEOCLIMATE RECONSTRUCTION OF THE PERMIAN–TRIASSIC MASS EXTINCTION EVENT

TIMOTHY KEARSEY

The Permian/Triassic (P/Tr) boundary is widely assumed to have been a time of extreme environmental upheaval and change. In the terrestrial realm, a negative anomaly in $\delta^{13}C$ isotope values has been reported from organic carbon in Antarctica, Australia, India and Madagascar, and from marine carbonate in the Karoo Basin. However, these sections are all from southern palaeolatitudes.

Analysis from the Permian–Triassic terrestrial sedimentary record of the South Urals, in Russia, comprising of many Aridisol and Vertisol horizons has revealed that, like the Southern Hemisphere, there is a dramatic change in paleosol morphology across the P/Tr boundary linked to a shift from meandering rivers to conglomeratic alluvial fans. Most of the paleosols include pedogenic carbonates at different stages of development, both above and below the P/Tr boundary. By the Triassic there is evidence of depressed water tables and increased seasonality. Analyses of the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ signatures of these pedogenic carbonates have revealed a number of negative excursions in $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ in the Late Permian, including a negative excursion in the mid-Changhsingian, the first time such an event has been recorded in a terrestrial environment. Associated with this excursion are indicators of increasing extremes of climate, including pedogenic dolomite, which suggest a dramatic change in climate up to the P/Tr boundary. Equally, there is an increase in the range of precipitation, suggesting that what caused this mid-Changhsingian event also had a profound effect on the atmosphere.

There is also evidence, in the form of the $\delta^{18}O_{carb}$ excursion, of a rise in temperature just prior to the onset of the conglomeratic alluvial fan deposits, which mark the P/Tr boundary in Russia. Although in the Russian paleosols this excursion could be explained by a rise in the effect of seasonal rain or atmospheric temperature, estimates from unaltered brachiopods from the Italian Dolomites confirm that there is a rise in temperature and suggests that this is in the region of 7-8°C. These paleosols also record a dramatic rise in $pCO_2$ in the Earliest Triassic similar to what has been recorded in stomatal records across this period suggesting a dramatic input of $CO_2$ in to the atmosphere.

# Contents

## List of Figures

## List of Tables

### Chapter 1



### Chapter 2

## List of Equations

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# Chapter 1. Introduction

## 1.1 Rationale

The end-Permian mass extinction event is recognised as being the greatest mass extinction of the whole Phanerozoic (Hallam and Wignall 1997; Benton and Twitchett 2003; Erwin 2006). Estimates of the extinction suggest 80-96% marine species became extinct, and a similar or greater loss in the terrestrial realm (Benton 1995; Hallam and Wignall 1997). Studies have suggested that the extinction was in the order of $10^{4-5}$ years (Rampino *et al.* 2000; Twitchett *et al.* 2001) and that the $\delta^{13}C$ excursions, which are linked to the mass extinctions, also only lasted for <10,000years (Retallack and Jahren 2008).

The causes of the mass extinction are still strongly debated and no one mechanism has yet been shown to explain all the evidence. There has been some proposed evidence for an impact event at the Permian/Triassic (P/Tr) boundary based on both chemical data, such as extraterrestrial helium trapped in fullerenes, and a possible impact structure in Bedout in north western Australia (Becker *et al.* 2001; Becker *et al.* 2004). However, both these lines of evidence have been highly criticised (Koeberl *et al.* 2004; Renne *et al.* 2004; Wignall *et al.* 2004; Farley *et al.* 2005; Müller *et al.* 2005). A kill mechanism which has long been proposed as causing the end Permian mass extinction is the Siberian Traps. These are continental flood basalts (Bryan and Ernst 2008) which cover an area of over 2,300,000km$^3$, although this estimate does not take into account erosion since their emplacement (Reichnow *et al.* 2002). They represent the biggest continental flood basalt event in the Phanerozoic (Hallam and Wignall 1997) and have been linked to a vast input of carbon dioxide into the atmosphere which caused dramatic global warming (e.g. Wignall 2001; Kidder and Worsley 2004; Twitchett 2007).

Krull and Retallack (2001) have observed extremely negative $\delta^{13}C$ values of –46.2‰ from paleosol-derived organic carbon from Graphite Peak in Antarctica, just before the P/Tr boundary (as defined by Collinson *et al.* 2006). They interpret this as being caused by methanotrophic bacteria, which are supposed to be present in high abundance due to the presence of high atmospheric methane levels. This methane was thought to have been generated from the destabilisation of methane clathrates (Erwin 1993; Krull and Retallack 2001). However, clathrates as the source of this methane has been recently questioned (Berner 2002; Payne and Kump 2007; Retallack and Jahren 2008). Instead it is proposed that the methane was produced by the Siberian Traps intruding into the extensive carbon-rich sediment found in the Siberian basin metamorphosing the coal and producing methane (Erwin 2006; Krull and Retallack 2006; Retallack and Jahren 2008).

It has also been suggested that there may have been multiple causes of the extinction (Erwin, 1993; 2006, so-called 'Murder on the Orient Express' hypothesis). This envisages many, or all, of the above mechanisms causing, or having an impact upon, the extinction event (e.g. Kidder and Worsley 2004) which were either triggered by the Siberian Traps (Wignall 2007; Twitchett 2007) or methane production related to some other factor, such as a mantle plume, which caused both the events (e.g. Heydari *et al.* 2008). To resolve the lack of consensus, it is important to assess the different environmental, sedimentological and geochemical evidence for climate change across the P/Tr boundary to see if there are any gaps in our understanding that might lead to a resolution of this debate.

## 1.2 Environmental and sedimentological variation

### *1.2.1 Sedimentological evidence*

There was a significant change in environment across the P/Tr boundary. The evidence for dramatic climate change across the P/Tr boundary in terrestrial sequences is especially marked. The most striking is the sudden change in facies from quiescent meandering river systems to braided river and conglomeratic fans (Newell *et al.* 1999; Ward *et al.* 2000). This shift to coarser-grained facies concurrent with the P/Tr boundary has been observed in the Karoo Basin of South Africa (Ward *et al.* 2000), Antarctica (Retallack and Krull 1999, Retallack 2005a), Australia (Retallack 1999; Michaelsen 2002) India (Sarkar *et al.* 2003), the Iberian ranges of Spain (Arche *et al.* 2005; Benito *et al.* 2005) and the South Urals of Russia (Newell *et al.* 1999; Benton *et al.* 2004). This global distribution is taken to suggest that the cause is not the result of localised changes in uplift and deposition rates, rather it is thought to be caused by a major die-off of rooted plant life causing destabilisation of the surface and resulting in dramatic erosion in highland source areas (Ward *et al.* 2000; Retallack 2005a).

It has also been observed that in all sections that span the P/Tr boundary that there is no coal in the earliest Triassic (Retallack *et al.* 1996; Michaelsen 2002; Retallack *et al.* 2005) and this is thought to be due to an extinction of coal floras (Retallack *et al.* 1996). An increase in global aridity is inferred through the Permian (Ziegler *et al.* 1997; Roscher and Schneider 2006).

In both Antarctica and the Karoo Basin it has been inferred that there is a significant increase in mean annual precipitation (Retallack and Krull 1999; Retallack *et al* 2003). This is not, however, a globally consistent picture as in Australia it has been observed that there was a drop in precipitation from the latest Permian and earliest Triassic to the Early Triassic

(Retallack 1999). Rises in precipitation are linked to an abrupt increase in chemical weathering observed at Graphite Peak in Antarctica, suggested by increased leaching of the soil recorded in geochemical ratios (Sheldon.2006). This is similar to physical leaching observed in the boundary breccias found in Australia (Retallack 1999). Also the identification of berthierine in the earliest Triassic Antarctica paleosols suggests a reducing environment in the paleosols, possibly caused by methane oxidation in the atmosphere (Sheldon and Retallack 2002; Retallack *et al.* 2006).

It is important to identify global similarities and differences in the evidence, in order to show which factors were acting regionally and which require a global explanation. This is important in understanding the global significance of any particular factor in explaining the cause of the P/Tr mass extinction.

### *1.2.2 Isotopic evidence*

It has been observed globally that the Permian mass extinction is coincident, or just before or after a marked negative excursion in $\delta^{13}C$ isotope values in both marine and terrestrial sections (e.g. Erwin 1993; Kidder and Worsley 2006; Erwin 2006, Krull and Retallack 2006; Gorjan *et al.* 2008; Retallack and Jahren 2008). Variation in $\delta^{13}C$ has been linked to many of the environmental effects of the extinction as well as changes in atmospheric carbon dioxide ($pCO_2$). It has also been linked to changes in the input of terrestrial carbon into marine sections and upwelling of anoxic bottom waters, in marine sections (Foster *et al.*1997; Ekart *et al.* 1999; Kidder and Woresley; Algeo *et al.* 2007) and the presence of methane in the atmosphere (Krull and Retallack 2001).

| Location | Material | Excursion (‰, VPDB) | | | Source |
|---|---|---|---|---|---|
| | | $\delta^{13}C_{carb}$ | $\delta^{18}O_{carb}$ | $\delta^{13}C_{org}$ | |
| British Columbia | Kerogen | - | | -3.0 | Wang *et al.* 1994 |
| Gartnerkofel-1, Austria | Carbonate and Kerogen | -3.4 | -3.0 | -15.9 | Magaritz *et al.* 1991; Magaritz *et al.* 1992 |
| Japan | Carbonate and Kerogen | -2.0 | | -1.4 | Musashi *et al.* 2001 |
| Meshian, China | Carbonate | -8.0 | | | Yin *et al.* 2001 |
| Abadaeh, Iran | Carbonate and Kerogen | -5.1 | | -3.2 | Heydari *et al.* 2000 |
| Emarat, Iran | Carbonate | -4.9 | | | Baud *et al.* 1989 |
| Nammal Gorge, Pakistan | Carbonate | -4.4 | | | Baud *et al.* 1996 |
| Soverashan, Armenian | Carbonate | -3.5 | | | Baud *et al.* 1989 |
| Wadi Wasit, Oman | Carbonate | -3.5 | | | Krystyn *et al.* 2003 |
| Jameson Land, East Greenland | Carbonate and Kerogen | -8.5 | | -10.5 | Twitchett *et al.* 2001 |
| Heping, China | Carbonate | -6 | | | Krull *et al.* 2004 |
| Dolomites, Italy | Carbonate | Between -1 to -3 | | | Korte and Kozur 2005 |
| Gerennavar, Hungary | Carbonate | -2.6 | | | Korte and Kozur 2005 |
| Slovenia | Carbonate and Kerogen | -12.5 | -5.3 | -6.5 | Dolenec *et al.* 1999, 2001 |
| Nhi Tao, Vietnam | Carbonate | -3 | | | Algeo *et al.* 2007 |
| Tesero, Italy | Carbonate | -2 | -3 | | Magaritz *et al.* 1988 |
| Northern India | Carbonate | -4 | -6.0 | | Baud *et al.* 1996 |
| Dicksonland, Spitsbergen | Kerogen | | | -8.5 | Wignall *et al.* 1998 |
| Sverdrup Basin, Arctic Canada | Kerogen | | | -6.5 to -3.5 | Grasby and Beachamp 2008 |

**Table 1.1 A summary of the carbon and oxygen isotopic excursion across the Permian/Triassic boundary in marine sections.**

The $\delta^{13}C_{carb}$ carbonate anomaly is recorded globally (Table 1.1) both in equatorial localities such as the Italian Dolomites to high latitudes such as Spitzbergen (Table 1.1; Retallack and Krull 2006). Equally it has been observed both in organic carbon in deep waters settings (cf. Wang *et al.* 1994) and shallow marine settings (cf. Magaritz *et al.* 1992). There is a variation in the relative sizes of the excursion globally (Table 1.1). Grasby and Beauchamp (2008) suggest that some of this may simply reflect local basin-scale processes. In their study in the Sverdrup Basin, Arctic Canada, they observe that $\delta^{13}C_{org}$ organic values decrease progressively from –6.5‰ on the basin margin to –3.5‰ in the basin centre. However, others

have argued that the global variation is more to do with the relative impact of the extinction event than localised variation (Retallack and Krull 2006; Retallack and Jahren 2008).

| | | Excursion (‰, VPDB) | | | |
|---|---|---|---|---|---|
| **Location** | **Material** | **$\delta^{13}C_{org}$** | **$\delta^{13}C_{carb}$** | **$\delta^{18}O_{carb}$** | **Source** |
| Commando Drift Dam, Karoo | Nodular carbonate, Organic carbon | no trend | -2 | | Coney *et al.* 2007 |
| Eddystone, Australia | Organic carbon | -3.2 | | | Morante 1996 |
| Xinjiang Province, China | Organic carbon | many excursions | | | Metcalfe *et al.* 2008 |
| Raniganj Coalfield, India | Organic carbon | -13.8 | | | de Wit *et al.* 2002 |
| Talcher Coalfield, India | Organic carbon | -8.8 | | | de Wit *et al.* 2003 |
| Morondava, Madagascar | Organic carbon | -7.9 | | | de Wit *et al.* 2004 |
| Graphite Peak, Antarctica | Organic carbon | -22.2 | | | Krull and Retallack 2000 |
| Portal Mountain, Antarctica | Organic carbon | -3 | | | Retallack *et al.* 2006 |
| Raniganj Coalfield, India | Organic carbon | -9 | | | Sarkar *et al.* 2003 |
| Bethulie, Karoo | Nodular carbonate | | -10 | -1 | MacLoed *et al.* 2000 |
| Bethulie, Karoo | Vertebrate teeth and tusks | | -1.9 | -0.53 | MacLoed *et al.* 2000 |
| Karoo Composite | Nodular carbonate | -2 | -12 | | Ward *et al.* 2005 |

**Table 1.2 The carbon and oxygen isotopic excursion across the Permian / Triassic boundary in terrestrial sections.**

There are far fewer terrestrial isotope studies (Table 1.2) than marine, however, their significance is in many ways more important as they represent a direct interaction with climate and the atmosphere rather than being buffered by ocean chemistry (Krull and Retallack 2001; de Wit *et al.* 2002). Thus, they will be directly influenced by the proposed extinction mechanism such as the input of volcanogenic carbon dioxide or methane (de Wit *et al.* 2002). Terrestrial isotope excursions have been recorded in other locations globally (Table 1.2, Figure 1.1) including in South Africa, Australia, India and China.

Three types of material have been used as proxies to record $\delta^{13}C$ in terrestrial sequences: organic matter, vertebrate teeth and carbonate nodules. The $\delta^{13}C$ values of these all record subtly different things. Soil organic carbon records the composition of organic matter

preserved in a soil, which chart atmospheric $\delta^{13}C$ that is assimilated into and fractionated by plants (Arens *et al.* 2000) recording variation over a matter of years (Retallack and Jahren 2008). Vertebrate teeth record the isotopic composition of the animal's diet when it the organism is growing teeth (Thackeray *et al.* 1990; MacLeod *et al.* 2000) On the other hand, paleosol carbonate in nodules can take thousands of years to form and thus represents a time-averaged signal (Liu *et al.* 1996; Retallack 2001a; Alonso-Zarza 2003). The values from the Karoo Basin, from organic matter, carbonate nodule (Ward *et al.* 2000; Coney *et al.* 2007) and vertebrate tusks (MacLeod *et al.* 2000), show excursions in both $\delta^{13}C$ and $\delta^{18}O$ at the P/Tr boundary. However, it has been argued that at least the pedogenic carbonate values may represent local soil conditions rather than atmospheric variation because some of these soils show strong evidence of being waterlogged (Tabor *et al.* 2007).

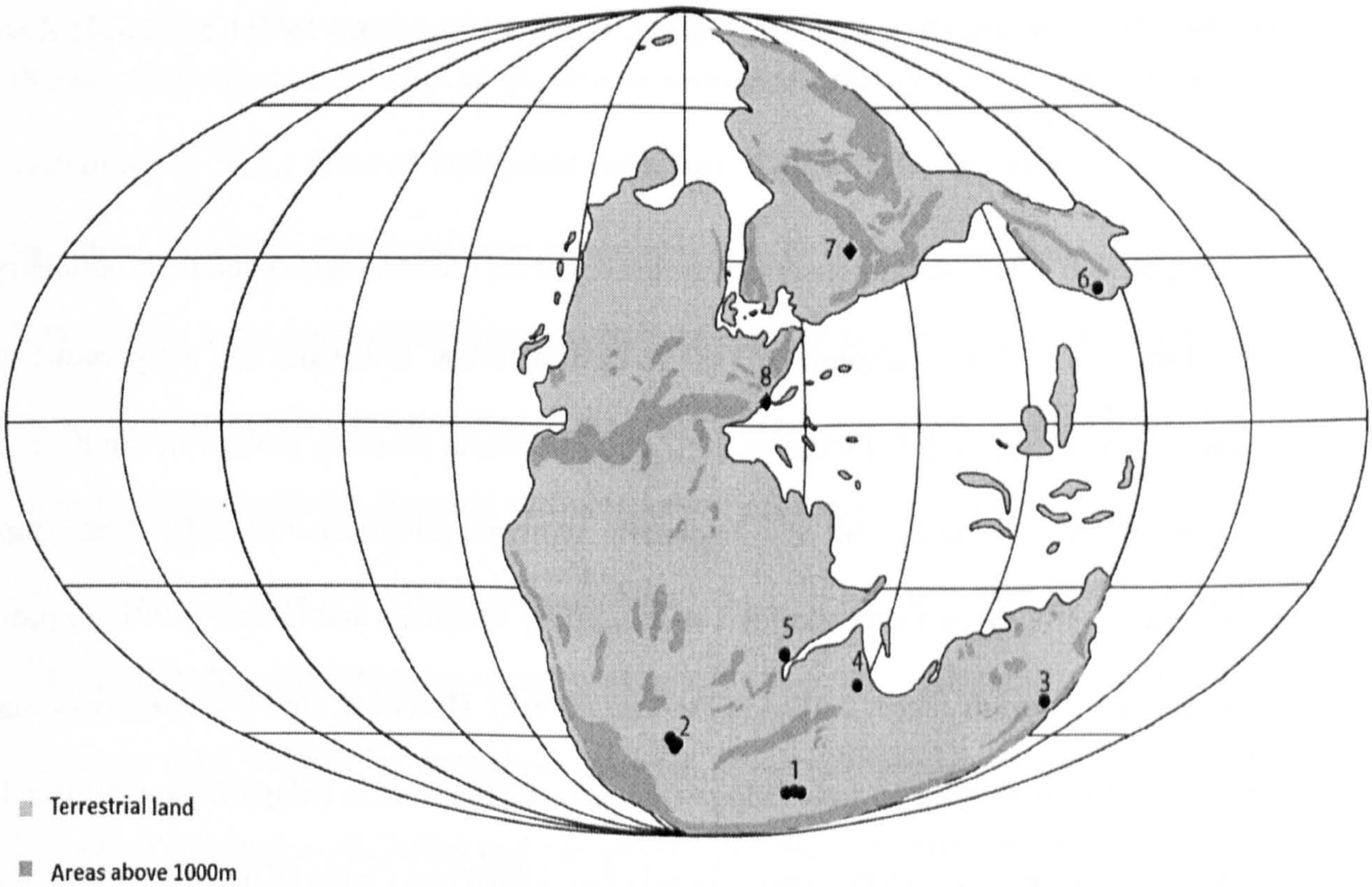


**Figure 1.1 Terrestrial P/Tr isotope sections 1. Antarctica (e.g. Krull and Retallack 2001), 2. Karoo basin, South Africa (MacLeod *et al.* 2000; Ward *et al.* 2005), 3. Australia (e.g. Morante 1996), 4. India (e.g. deWit *et al.* 2002), 5. Madagascar (e.g. deWit *et al.* 2002), 6. North China (Metcalfe *et al.* 2008). Field areas investigated in this study 7. South Urals of Russia and 8. Marine sections from the Italian Dolomites. (base map adapted from Rowley 2008, Changhsingian 252Ma).**

The $\delta^{13}C$ and $\delta^{18}O$ excursions have been observed to be greater at high latitudes in the southern hemisphere (Table 1.2). Studies in North China have failed to show any organic carbon anomaly (Metcalfe *et al.* 2008) and as yet there have been no studies into terrestrial pedogenic carbonate from the northern hemisphere or studies that investigate as far into the late Permian as has been studied in Antarctica and Australia (cf. Morante 1996; Krull and Retallack 2001; Metcalfe *et al.* 2008).

## 1.3 Temperature and $pCO_2$ changes

One of the main indicators of a rise in temperature across the Permian/Triassic boundary comes from the terrestrial realm. It has been observed that there was a migration of thermophilic plants and a change in paleosols in the high latitudes of both the northern and southern hemispheres (Retallack 1999, 2002, Retallack and Krull 1999 Looy 2001; Retallack and Krull 2006).

The negative $\delta^{18}O$ excursion observed in some marine sections across the P/Tr boundary is linked to a 5-6°C rise in temperature (Magaritz and Holser 1991) and this temperature is often quoted in the literature (cf. Twitchett 2007 and references therein). However, the P/Tr $\delta^{18}O$ excursions may also be a result of a diagenetic overprint (Heydari *et al.* 2001; Hass *et al.* 2006), especially as the Gartnerkofel-1 core used by Magaritz and Holser (1991) to produce this estimate is heavily recrystallised (Twitchett 2007). However, this $\delta^{18}O$ excursion has also been recorded in sections in Italy (Magaritz *et al.* 1988), Austria (Magaritz and Holser 1991), Slovenia (Dolenec *et al.* 1999), India (Baud *et al.* 1996) and China (Xu *et al.* 1986) which may also suggest that it is a global event rather than a localised diagenetic overprint. In the analysis of their data Magaritz and Holser (1991) conclude that a similar negative $\delta^{18}O$ shift could also be caused by a decrease in salinity.

The study of the isotopic composition of fossil carbonate shells such as brachiopods has the potential to avoid some of these issues because they form in equilibrium with seawater and so represent a direct interaction with the water chemistry (Auclair *et al.* 2003). Fossil brachiopods, due to their low-Mg calcite composition, which is a diagenetically more stable polymorph of calcite, have the potential to preserve a primary isotopic signal (Auclair *et al.* 2003). Korte *et al.* (2005a,b) carried out studies into brachiopod variation through the Permian and Triassic to investigate coeval isotopic variation of seawater and palaeotemperature. However, crucially, they found no unaltered brachiopods from the earliest Triassic (Korte *et al.* 2005b) and do not compare the brachiopod records and bulk rock values from the same locality.

Pedogenic carbonate nodules can be used to investigate changes in palaeotemperature though variation in $\delta^{18}O_{carb}$ value of pedogenic carbonate. This is based on the principle that $\delta^{18}O$ in terrestrial sediments is derived from meteoric water (Dworkin *et al.* 2005; Prochnow *et al.* 2006). It has been demonstrated that the oxygen isotopic composition of unaltered soil carbonates is directly related to that of the ambient meteoric water, and the $\delta^{18}O$ of the meteoric water is itself a function of fractionation during precipitation and atmospheric temperature (Cerling and Quade 1993; Mack *et al.*, 1991). It may therefore be possible to use $\delta^{18}O_{carb}$ of pedogenic carbonate to estimate palaeotemperature (Dworkin *et al.* 2005; Prochnow *et al.* 2006). This technique has been effectively used in paleosols from the late Triassic (Prochnow *et al.* 2006) and across the Cretaceous/Tertiary boundary (Dworkin *et al.* 2005) but has not yet been applied to the Permian/Triassic boundary.

The $\delta^{13}C$ composition of pedogenic carbonate from paleosols can also be used to calculate atmospheric $pCO_2$ although this depends on the paleosol not being formed in non-

waterlogged conditions (Cerling 1984; Cerling 1991; Ekart *et al.* 1999). This technique has been applied to paleosols from the early Guadalupian and Middle Triassic in India and a ~500ppmV rise in $pCO_2$ across this interval has been inferred (Ghosh *et al.* 2001).

## 1.4 Aims

The aims of this project are to investigate changes in climate, precipitation, stable isotopes, temperature and carbon dioxide variation through the Late Permian and Early Triassic recorded in sections in the northern hemisphere. It will focus on paleosols from terrestrial sections in the South Urals of Russia and compare them to previously published studies from Southern Hemisphere to ascertain whether the recorded changes are global.

### *1.4.1 Objectives*

- To investigate paleosols from the South Urals of Russia and to determine the environment of their formation and how they vary both laterally and vertically in stratigraphic section across the South Urals basin.
- To study the stable isotope composition of pedogenic carbonate from the paleosols, determine the effects of diagenesis and other influences on the carbonate, and assess whether recorded changes are the result of changes in atmospheric conditions or localised soil waters.
- To use the information gained from the paleosols and the isotope results to investigate changes in precipitation and temperature through the P/Tr boundary.
- To study the stable isotope composition of brachiopods from the Italian Dolomites across the P/Tr boundary to produce estimates for atmospheric $\delta^{13}C$ compositions and accurate palaeotemperature estimates which can be compared with the results from the South Urals to test the validity of the paleosol estimates.

- To use the isotopic information from both the Italian brachiopods and Russian pedogenic carbonate to investigate variations in $pCO_2$.
- To compare these results with those recovered from other terrestrial and marine studies across the P/Tr boundary.

# Chapter 2. Methodology

## 2.1 Introduction

The data and samples used in this study were collected during four field seasons; two investigating the terrestrial sequence of the South Urals of Russia in 2004 and 2006, and two in the Italian Dolomites investigating terrestrial and marine sections in 2006 and 2007. The field localities are described in the relevant results chapters (Chapters 3 and 6). The Russian field seasons were as part of the Bristol–Plymouth–Saratov Expedition, headed by Prof Mike Benton, Dr Richard Twitchett, Misha Surkov and Dr Valentin Tverdokhlebov. The author was not present on the 2004 Russian field season and thus the samples collected from that year (labelled 04.--. --) were not sampled by the method described below.

This chapter describes the methods used both in the field and laboratory analysis for further discussion of the techniques used see Chapters 4 and 6. This chapter also discusses the mathematical and statistical techniques used in Chapters 4 and 5. For discussion of the palaeotemperature equations and how they were generated see Chapter 5.

## 2.2 Field methods

### *2.2.1 Paleosol field methodology*

All paleosols identified in this study were logged using a standardised field methodology, base on methods suggested by Retallack (1997, 2001). Paleosols were initially identified on 1) their presence within terrestrial sequences; 2) the presence of root traces or evident mud cracking which would suggest subaerial exposure; 3) the presence of mottling and/or carbonate nodules. The paleosols were named using a three-letter locality code (i.e.

Sambullak = SAM) and a number referring to that paleosol horizon (Table 2.1). Where subsequent analysis has revealed that a paleosol is actually part of a stacked sequence of paleosols, or for time reasons in the field they were grouped as one unit, the names are subdivided using alphabetic symbols (i.e. KOR1a, KOR1b). The paleosols from the Boyevaya Gora section are labelled KOR as the field name for this locality was Korolki (the Korolki ravine is only part of the Boyevaya Gora exposure).

| Locality | Locality code |
|---|---|
| Boyevaya Gora | KOR |
| Sambullak | SAM |
| Tuyembetka | TUY |
| Krasnogor | KRA |
| Vozdvizhenka | VOZ |
| Petropavlovka | PET |
| Mescheryakovka | MES |

**Table 2.1 Locality codes for Russian samples collected for isotope analysis.**

In the field, once a paleosol had been located, the top of the horizon was identified and the paleosol profile was logged from there down at centimetre scale. Grain size changes through these profiles were identified and noted, along with other features such as: the presence and shape of nodules and their composition (i.e. carbonate, siderite or other); the nature, depth of penetration, and preservation of root traces; the shape and nature of the ped; evidence of desiccation and pedogenic slickensides (identified on the basis of being restricted to horizons within a paleosol); and other pedogenic features such as relict bedding.

All of these features were graphically represented on the field logs with emphasis on accurate scaled representation, especially with reference to depth within the horizon, rather than stylisation. Colour changes and mottling were recorded with reference to a Munsell colour chart (Rock Color Chart 1991) and noted next to relevant part of the field log. 10% hydrochloric acid was used to identify the presence of carbonate in a paleosol and to track its

changes with depth. Each horizon was photographed with a Kodak Z740 digital camera and any relevant, remarkable or unidentifiable features within the profile were also photographed and notes were made on the logs of the position of the photographs.

The majority of the paleosols identified in the field areas contain pedogenic carbonate nodules. As the carbonate nodules were to be used for stable isotope analysis particular attention was given to them. Each paleosol carbonate (Bk) horizon was classified on the level of carbonate development (after Machette 1985; Retallack 2001a, Alonso-Zarza 2003) (Table 2.2). Each carbonate horizon was logged in detail with the exact location and pattern of the carbonate within the horizon described on the log. Notes were also made of the presence of root traces, mottling and other features in the carbonate horizon and how they interacted with the carbonate present.

| Stage | Soil development in gravel | Soil development in sand, silt or clay |
|---|---|---|
| I | Thin discontinuous coatings on and under clasts | Dispersed powdery and filamentous carbonate |
| II | Continuous, coating around and between clasts; more discontinuous carbonate beyond main horizon | Few to common carbonate nodules and powdery carbonate between the nodules |
| III | Carbonate a continuous layer enveloping clasts; less pervasive carbonate beyond main horizon | Carbonate a continuous layer of coalescing nodule, some nodules and powdery carbonate beyond horizon |
| IV | Upper part of solid carbonate layers with a weakly developed platy or lamellar structure capping less pervasively calcareous parts of the profile | |
| V | Platy or lamellar cap to the carbonate layer strongly expressed in places, brecciated and pisoliths of carbonate | |
| VI | Brecciation and recementation as well as pisoliths common in association with the lamellar upper layer | |

**Table 2.2 Bk horizon classification used in the field based on that of Retallack (2001).**

Within nodular carbonate horizons a minimum of four nodules was collected. The precise height and location of each nodule within the paleosol was recorded. Within nodule horizons >10cm thick, nodules were taken from equal spacing through the nodular horizon. Where possible, samples were taken laterally within a horizon to quantify the lateral isotopic

variation. Sections made of continuous carbonate (Stage III – VI, see Table 2.2) were sampled from equal spacing though the carbonate horizon. Samples of the material from around the nodules and other prominent non-carbonate horizons in the paleosol were also collected for thin sectioning and bulk rock analysis. Each sample had its orientation recorded and was placed in a separate labelled sample bag to avoid cross-contamination in transport.

Each paleosol was plotted on a stratigraphic section which was logged using standard sedimentary methods (in Russia this was undertaken by Dr Andy Newell and Dr Richard Twitchett). The local sedimentary facies and structures were described to give context to the paleosols. At each section, the strike and dip of the beds were recorded.

### *2.2.2 Paleosol classification*

Classification of paleosols is crucial for comparison of different sections, both across and within basins, and to interpret the palaeoclimatic and palaeoenvironmental variation (Kraus 1999). It has been suggested that soil classification is best undertaken in the field (Retallack 1997). However, classification of paleosols has been much debated in the literature, and there are many different proposed classification schemes.

The disputes arise primarily because there is an already established system for classification of modern soils (Soil Survey Staff 1999 and the Food and Agriculture Organisations schemes; see Retallack 2001a and reference there in). Using a paleosol classification system based on this makes it easier to draw comparisons with modern soils (Kraus 1999). Problems arise, however, as many features used to classify modern soils are destroyed or altered by diagenesis and so this detailed classification can prove problematic when applied to paleosols (Mack *et al* 1993; Retallack 2001a; Krasinikov and Calderón 2006). Equally it has been debated

whether it is appropriate to apply modern names and terms to ancient soils as confusions may arise (Daham and Holliday 1998; Nettleton *et al.* 1998; Nettleton *et al.* 2000).

Some authors use the system proposed by Mack *et al.* (1993) (refined by Mack and James 1994) which is based purely on field observations. This has been proposed to provide a systematic approach to paleosol classification which can be uniformly applied to paleosols of all ages (Mack *et al.* 1993). However, many authors feel that this is over simplistic and makes it hard to compare with modern analogues, thus diminishing the environmental information that can be gained from them (Kraus 1999; Retallack 2001a).

Other authors prefer the system proposed by Retallack (1993, 1994, 1997, 2001a) which advocates a simplified use of the United States Department of Agriculture (USDA) soil classification scheme (Soil Survey Staff 1999). This is based on 19 diagnostic sub-surface horizons (Retallack 2001a) which can be broken down into 11 principal soil orders (Retallack 1993). Other authors have also proposed an altered version of USDA classification; either altering the Soil Survey Staff (1999) scheme to make it relevant to paleosols (Nettleton *et al.* 1998; Nettleton *et al.* 2000) or using a different modern classification (i.e. the World Reference Base for Soil Resources as proposed by Krasinikov and Calderón 2006).

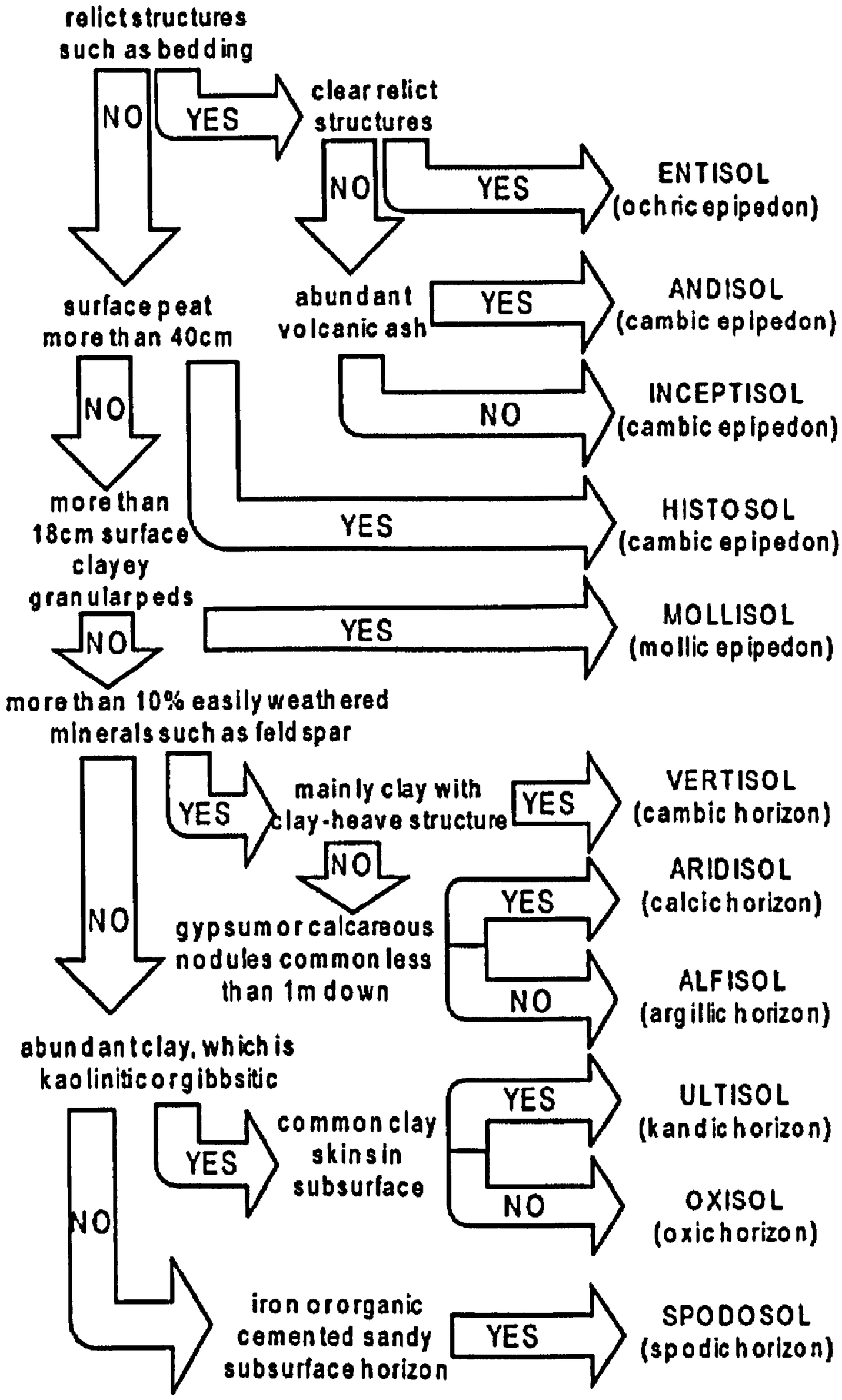


**Figure 2.1Soil classification key proposed by Retallack (1993) used for field classification.**

In the field the simplified classification key proposed by Retallack (1993) was used (Figure 2.1). There was an emphasis on observed field structure (such as carbonate nodules, pedogenic slickensides etc.) to avoid the pitfalls inherent in misclassifying horizons which may have been altered by diagenesis and burial (cf. Daham and Holliday 1998).

### *2.2.3 Marine rocks field methodology*

The marine limestones identified in the Italian Dolomites (see Chapter 6 for field localities) were sampled for bulk stable isotope analysis. Also any brachiopod fossil- rich beds were identified and brachiopod samples were collected for stable isotope analysis. Limestone sections were logged at a scale of 1:10 (at Tesero and the section around the Bellerophon/Werfen Formations contact at Val Brutta) and the longer sections (the whole of the Bellerophon Formation exposed at Val Brutta) at 1:50. Sections were logged using the methods described by Tucker (2003) and Tucker and Wright (1990). Limestones were classified in the field using Dunham's classification scheme (Dunham 1962; Tucker and Wright 1990). Clastic rocks were classified using the standard sedimentary grain size classification devised by Udden and Wentworth (Tucker 2001). Any sedimentary features (cross beds, ripples, stylolites etc.) were marked on the log using standardised symbols (after Tucker 2003) and any other detail was recorded in notes next to the logs. Those sections logged at 1:10 were sampled every 10cm and those logged at 1:50 were sampled for isotopic analysis every 100cm, or where exposure allowed. At all field localities bulk rock samples of between 10 and 100g were taken (depending on lithology and exposure) and care was taken to take samples big enough to avoid areas of weathering or surface alteration.

Beds containing brachiopod fossils were sampled and the exact positions of the fossils within each bed were recorded.

## 2.3 Laboratory methods

The laboratory work for this project was primarily carried out by the author, from preparation to running of the analysis, at the University of Plymouth. The only exceptions to this were the cathodoluminescence microscopy, which was carried out by the author and Miss Nikita

Jacobsen, at Camborne School of Mines in Falmouth, and the isotopic composition of organic carbon isotope analysis which were performed by Dr Neil Ogle at Queen's University, Belfast.

### 2.3.1 Stable isotope analysis methods

The fractionation of stable isotopes is due to thermodynamic properties of the atoms based on the relative atomic masses of which they are composed (Faure 1986). Thus, factors such as changes in temperature, atmospheric carbon dioxide, the introduction of gas in the biosphere and metabolic effects will be recorded in biogenic and non-biogenic isotopic changes in $\delta^{13}C$ and $\delta^{18}O$ carbonate material (Brownlow 1996). For this study, interest was focused on the effects of changes in atmospheric and oceanic conditions (such as temperature and carbon dioxide) on carbonate in brachiopod fossils and in pedogenic carbonate from paleosols.

All results in this study were described as an isotopic ratio between the two stable isotopes ($^{13}C/^{12}C$ and $^{18}O/^{16}O$) and as a deviation from a standard by delta values ($\delta$) in per mil (‰) (Brownlow 1996):

$$\delta\,‰ = \left(\frac{isotopic\ ratio\ for\ sample}{isotopic\ ratio\ for\ standard} - 1\right) 1000 \qquad (2.1)$$

Isotope results were measured relative to Vienna Pee Dee Belemnite (VPDB). To convert values to Vienna Standard Mean Ocean Water (VSMOW) the equation of Coplen *et al.* (1983).

$$\delta^{18}O_{VSMOW} = (1.03039\ \delta^{18}O_{VPDB}) + 30.39 \qquad (2.2)$$

All stable carbon and oxygen carbonate analyses were carried out on a GV Instruments Isoprime mass spectrometer with a Gilson Multiflow carbonate auto-sampler at the University of Plymouth. The carbonate powders were reacted with 100% phosphoric acid at 90°C for 1 hour. The evolved $CO_2$ was then sampled, passed through a Thermal Conductivity Detector (TCD) and then into an Isotope Ratio Mass Spectrometer (IRMS). Any results below 1.2 nA were removed from the dataset and rerun. The results were calibrated against VPDB using the international standard NBS-19 (National Bureau of Standards 19 published values; $\delta^{13}C$ = 1.95‰ $\delta^{18}O$= –2.20‰), IAEA -CO-8 (International Atomic Energy Agency -CO-8 published values; $\delta^{13}C$ = –5.75‰ $\delta^{18}O$= –22.67‰), and IAEA-CO-9 (International Atomic Energy Agency -CO-9 published values; $\delta^{13}C$ = –45.12‰ $\delta^{18}O$= –15.28‰). To correct for daily drift within individual isotope runs NBS-19 and an internal lab standard which were placed after every ten unknown samples. These standards were used to correct for any drift that occurred within a run by comparing analysed standard values with the published values and using this difference to correct the daily offset for the unknown samples. The average measured values for NBS19 $\delta^{13}C$ = 2.00‰ (±0.45‰ 1σ std) $\delta^{18}O$ = -2.50‰ (±0.49‰ 1σ std) for all analyses carried out over a 3 year period (for full list of all standards run see appendix A2.6).

In this study three types of carbonate material were analysed in the mass spectrometer: marine and terrestrial carbonate bulk rock samples, pedogenic carbonate and brachiopod fossils. These materials were prepared using the following methods.

### *2.3.2 Carbonate bulk rock preparation*

The marine bulk samples from the Italian Dolomites and terrestrial carbonate samples from the South Urals of Russia for stable isotope analysis were prepared as follows. 1) Each bulk sample or nodule was cut in half and one side was retained for petrographic analysis. 2) The other half was cleaned in an ultrasonic bath for 5 minutes to remove any weathered surface

material. 3) The cut face was then sampled with a microdrill (0.75mm diameter) taking samples of between 300-500μg from the fine fraction carbonate areas avoiding any fossil material and sparry calcite. For the carbonate nodules, material drilled from the most homogeneous area of micrite from the centre of the nodule. 4) The resulting powders were placed in a sealed sample vial and weighed. They were then run on the IRMS using the method described in Section 2.3.1.

### *2.3.3 Pedogenic carbonate nodules*

Robinson *et al.* (2002) noted considerable isotopic variation between the micritic and sparry parts of pedogenic nodules, thought to be related to changes in the source of the calcite-forming water (Robinson *et al.* 2002; Quast *et al.* 2006). However, it has been suggested that the spar-forming waters can overprint the micritic values without altering the texture of the micrite (Quast *et al.* 2006). Therefore, for every nodule that contained both spar and micritic material, both were sampled separately to compare the values and to test for overprinting. They were prepared and analysed using the method described above. When determining the experimental error between the micritic and sparry component of a carbonate nodule (see Chapter 4) the isotopic standards from the precise run containing both spar and micrite analysis was used to calculate the experimental error to account for long term drifts in the analysis. These daily offsets values can be found in Appendix A2.6.

### *2.3.4 Fossil preparation*

Seven articulate brachiopods, including representatives of *Janiceps, Comelicania,* and *Orbicoelia,* were analysed from Val Brutta and one from Tesero in the Italian Dolomites (see Chapter 6). The brachiopods were cleaned and sectioned longitudinally across the shell. All samples were photographed under both a petrographic and cathodoluminescence (CL)

microscope. This latter technique was used to provide an estimate of the degree of diagenetic alteration. The areas of the shell were divided into four categories depending on the amount of luminescence displayed under cathodoluminescence (following the method of Mii *et al.* 1997). These categories were: (a) NL: Non-Luminescent, and showing clear internal structure; (b) NL+SL: Non-Luminescent with Slightly Luminescent areas, showing clear internal structure, and >50% non-luminescence by area, but with some luminescence in places; (c) L+SNL: Luminescent and Slightly Non- Luminescent shells, with <50% Non Luminescence by area; and (d) L: those areas that were completely luminescent. A microdrill (0.75mm diameter) and a binocular optical microscope were used to drill samples from individual layers identified by the CL and petrographic microscopy in transects both across and along the length of each shell (see Appendix A4.4). The carbonate powders were analysed for $\delta^{13}C$ and $\delta^{18}O$ using the same method as that used for the bulk rock analysis.

Some brachiopods were encased in silt sediment. To remove this sediment the samples were treated with white spirit (following the method of Brasier 1980). This involves removing as much sediment around the fossil as possible mechanically, drying in an oven for 24 hours at 40°C, then removing the sample from the oven and placing it in a beaker with just enough white spirit to cover the sample and leaving it for 30 minutes to 8 hours. The white spirit is then removed and replaced with hot distilled deionised water and left to break down the sample. Finally, the fossil was placed in an ultrasonic bath of distilled deionised water until all remaining sediment was removed.

### *2.3.5 $\delta^{13}C$ Organic carbon analysis*

The organic carbon component of the rock was liberated by dissolving 4-5g of sample in 5ml of 10% hydrochloric acid (HCl) which was left for at least 24 hours or until any reaction had

ceased. The sample was then washed in ultra-pure deionised water and filtered through a non-organic filter. The filtrate was then dried in a petri dish for 5hrs at 30°C before any organic matter was picked out and placed in a sterile sample vial and sealed prior to being sent away for analysis. All organic carbon was analysed at the Stable Isotope Facility, Environmental Engineering Research Centre, Queen's University, and Belfast on a SerCon ABCA Isotope Ratio Mass Spectrometer with ANCA Combustion/Reduction interface by Dr Neil Ogle. Unfortunately only three samples contained enough organic carbon to generate accurate analyses. All of these were from the Sambullak section (Chapter 4, 6).

### *2.3.6 X-Ray diffractometer methods*

X-ray diffraction (XRD) analysis was used to investigate the mineral composition of carbonate from both Italy and Russia. The powder XRD analyses were conducted on a Phillips PW 1729 X-ray generator at the University of Plymouth, using an X'Pert Quantify computer interface. A Cu anode source was used with generator settings of 30kV and 40mA. Computer-based mineral identification of the traces was achieved using X'Pert High Score identification software. Manual identification was completed with reference to the Joint Committee on Powder Diffraction Standards (1971) index. Samples of crystalline calcite and dolomite from the Plymouth University's mineral collection were also run to verify the results of both the computer and manual identification results. The identification of crystalline calcite and dolomite was verified using calcite and dolomite specific stains (see below).

Samples to be analysed on the XRD were drilled from the same stub as the stable isotope analysis. 1-2g of material was drilled using a 1mm drill bit. In all cases, the sample for analysis was taken from as close as possible to the isotope analysis sample. All samples were placed in their own glass vials to avoid cross-contamination between samples. The powder

was compacted on a silica slide and placed in the machine for analysis. In cases where counts were recorded for the 100% 2°0 peak were ≤ 100counts the sample was rearranged on the slide and re-run.

### 2.3.7 ICP OES methods

Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) was used to determine the trace elemental composition of the brachiopod fossils used in this study. All analyses were conducted at the University of Plymouth on a Varian 725-ES ICP OES. The elements Al, Fe, Mg, Mn, Na, S and Sr were investigated as these have been successfully used to determine the level of alteration in brachiopod shells (Mii *et al.* 1997; Brand *et al.* 2003; Korte *et al.* 2005; van Gelden *et al.* 2006). 20-50mg of the shell and bulk rock material from each sample was reacted with 20% nitric acid in 10ml dilutions. The resulting solution was analysed for the proportions of major elements present by calibrating against standard solutions. The run was calibrated for the elements to be investigated by using dilutions of standard solutions for Al, Fe, Mg, Mn, Na, S and Sr.

### 2.3.8 Cathodoluminescence methods

Cathodoluminescence (CL) has been shown to be an indicator of diagenetic alteration in fossil brachiopod shell (Veizer 1983; Mii *et al.*1997; Korte *et al.* 2005a, b, Tomašových and Farkaš 2005). This is because the activation of cathodoluminescence is primarily by $Mn^{2+}$ which is associated with altered carbonate, and inhibited by $Fe^{2+}$ associated with unaltered carbonate (Veizer 1983). It has been suggested that cathodoluminescence may be used to assess alteration of paleosol carbonate (Budd *et al.* 2002, Williams and Krause 1998). However, the rapidly changing redox potentials in soils during pedogenesis (Dworkin *et al.* 2005) and the

large amounts of free iron oxides in the rock obscure the cathodoluminescence of carbonate paleosols (Dr Gregory Price, *pers. comm.*).

The brachiopods were cleaned and sectioned longitudinally across the shell. These sections were mounted on glass slides using optical resin and the slides were then surfaced polished on a Petropol Buehler using 0.3μm aluminium oxide.

CL photography was carried out at Camborne School of Mines in Falmouth using a CITL CL MK3A Luminscope. The samples were placed in a vacuum chamber under an electron gun emitting a cathode-ray which was set at ~450μA and ~10kv. The sections were photographed through a petrographic microscope. All analyses were carried out by the author apart from brachiopod TS1 which was photographed by Miss Nikita Jacobsen.

### *2.3.9 SEM microprobe methods*

A Scanning Electron Microscope (SEM) was used to investigate the crystal shape and elemental composition of the dolomitic and calcitic carbonate nodules. The scanning electron microscope images were analysed on a Jeol Jsm-6100 SEM at the University of Plymouth, using an Oxford Inca X-Ray analysis system to identify the elemental components of different crystals. This method of element identification is energy-dispersive X-ray spectroscopy (EDS) and was used to identify the relative levels of O, Mg, Ca and Si.

Samples were prepared by taking the thin section side of a carbonate nodule (the opposite of that used for the IRMS and XRD analysis) and mounting it on a glass slide. The slide was then polished with 0.3μm aluminium oxide on a Petropol Buehler, until the sample was 1mm

thick. These slides were then coated with a layer of carbon before being introduced into the SEM.

## 2.4 Petrographic slide preparation

Petrographic thin sections were made of both the Italian and Russian material. In the case of the Russian material many of the samples were so poorly lithified that they had to be injected with paraloid or encased in resin to stabilise them for thin sectioning. The non-calcareous samples taken in Russia were so poorly consolidated it was impossible to produce thin sections of them. All sections that were taken were mounted on glass slides using optical resin and ground down using a Precision Lapping and Polishing Machine to a thickness of 30μm with 25μm silicon carbide powder. The slide was then protected by a cover-slip.

*Stains – Dickson's stain*

Dickson's stain method was used to identify the presence of calcite in the thin sections (Dickson 1966). The method used is that proposed by Allman and Lawrence (1972), as listed below (Table 2.3). The etch solution is 1000ml of 1.5% hydrochloric acid solution. Staining solution 1 is produced in two parts; part A is 0.2g alizarin red S and 100ml 1.5% HCl solution; part B is 2g potassium ferricyanide and 100ml 1.5% HCl solution. Staining solution 2 is 0.2g alizarin red S dissolved in 1.5% HCl solution 100ml.

| Procedure | | Time | Carbonate | Result |
|---|---|---|---|---|
| Stage 1 | Etch solution | 10-15sec | Calcite ferroan calcite | Considerable etch |
| | | | Dolomite ferroan dolomite | Negligible etch |
| Stage 2 | Staining solution 1 3 part A and 2 parts B | 30-45 sec Medium stain 40 sec Light stain 30 sec | Calcite | Very pale pink to red depending on optical orientation |
| | | | Ferroan calcite | Very pale pink to red, pale blue to dark blue; the two superimposed give mauve–purple–royal blue |
| | | | dolomite | no colour |
| | | | Ferroan dolomite | Pale to deep turquoise depending on ferrous content |
| Stage 3 | Staining solution 2 | 10-15 sec Medium stain 15 sec Light stain 10 sec | calcite | Very pale pink–red |
| | | | Ferroan calcite | Mauve–purple–royal blue |
| | | | dolomite | No colour |
| | | | Ferroan dolomite | Pale to deep turquoise |

**Table 2.3 Dickson's staining technique (after Allman and Lawrence 1972).**

*Stains – Alkaline alizarin red S*

Alkaline alizarin red S is a dolomite-specific stain which stains dolomite purple and leaves calcite unstained. It was used in both the carbonate nodules from Russia and the Italian samples to identify the presence of dolomite in thin section.

The method is based on that proposed by Miller (1988). The staining reagent is produced by: (a) dissolving 0.2g of alizarin red S in 25ml methanol in a small beaker over a hot water bath; (b) carefully dissolving 30g sodium hydroxide pellets in 70ml water.

The staining procedure is: (a) add 15ml of the 30% NaOH solution to the alizarin red solution and bring to the boil; (b) immerse the thin section in boiling reagent for at least five minutes; (c) add a few drops of methanol to compensate for evaporation; (c) rinse in distilled water.

## 2.5 Mathematical methods

Both mathematical and statistical techniques were used in this project. The mathematical techniques were used in modelling the palaeotemperature equations, while statistical techniques were applied to the Russian data to determine the significance of the isotope excursions seen between the isotope results from nodules from different paleosol horizons.

### *2.5.1 Temperature equations*

Dworkin *et al.* (2005) and Prochnow *et al.* (2006) created a palaeotemperature equation combining the relationship between mean annual ambient temperature (MAT) and the $\delta^{18}O$ composition of calcite in soil (Friedman and O'Neil 1977), and the relationship between $\delta^{18}O_p$ and MAT in modern terrestrial environments (Fricke and O'Neil 1999; Dworkin *et al.* 2005) to produce a cubic function. When these equations have been solved for zero (Dworkin *et al.* 2005; Prochnow *et al.* 2006) the palaeotemperature estimate is the value at which the curve of the equations cuts the $x$ axis. However, cubic functions can have three possible solutions for $x$ (see Figure 2.2), so there can be up to three temperatures that satisfy these equations, though not all of these may be physically possible in the real world.

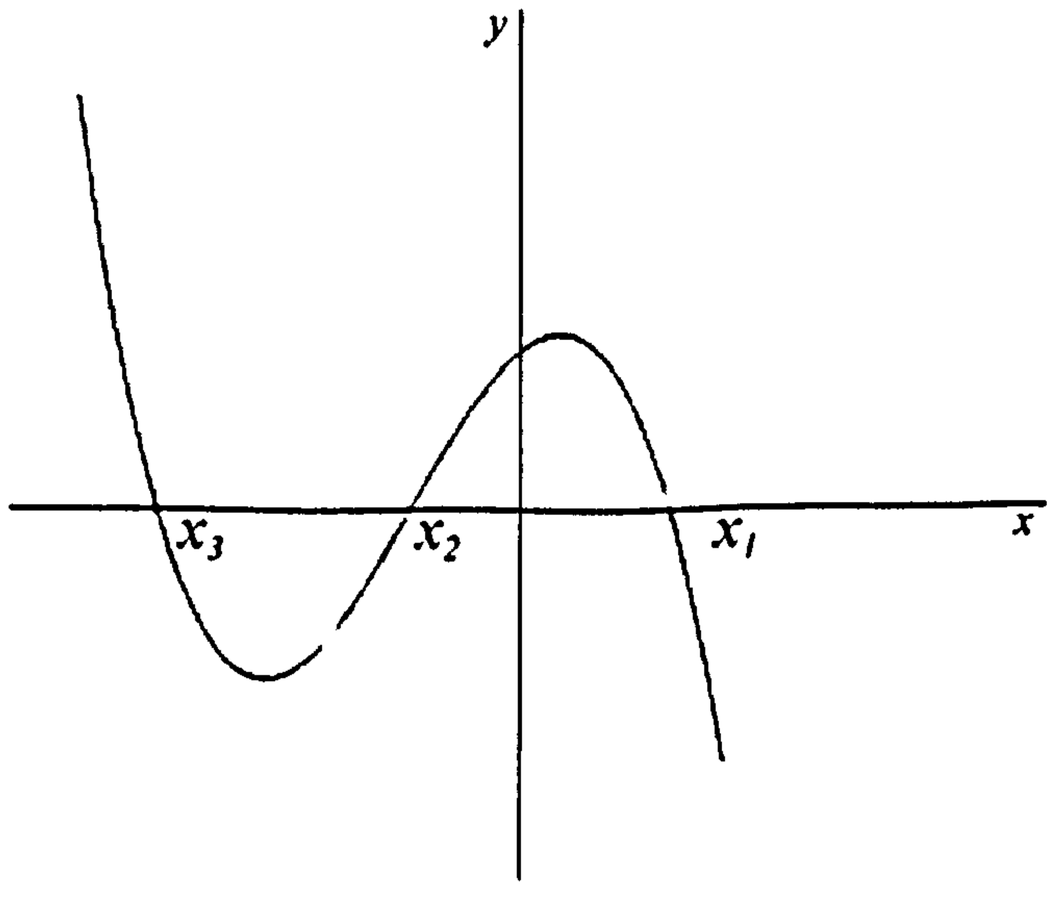


**Figure 2.2 A theoretical cubic function showing the three points at which it cuts the $x$ axis.**

### 2.5.2 Solving cubic equations

The method used in this study to solve cubic equations is as follows. Assuming the cubic equation is as follows (after Woan 2000):

$$ax^3+bx^2+cx+d=0 \ (a\neq 0) \tag{2.3}$$

Where $x$ is variable and $a$, $b$, $c$, $d$ are real constants. To solve this equation for $x$ the following intermediate definitions $p$, $q$ and $D$ must first be calculated

$$p=\frac{1}{3}\left(\frac{3c}{a}-\frac{b^2}{a^2}\right) \tag{2.4a}$$

$$q=\frac{1}{27}\left(\frac{2b^3}{a^3}-\frac{9bc}{a^2}+\frac{27d}{a}\right) \tag{2.4b}$$

$$D=\left(\frac{p}{3}\right)^3+\left(\frac{q}{2}\right)^2 \tag{2.4c}$$

If $D\geq 0$ then the following intermediate definitions must also be calculated

$$u=\left(\frac{-q}{2}+D^{1/2}\right)^{1/3} \tag{2.5a}$$

$$v = \left(\frac{-q}{2} \cdot D^{1/2}\right)^{1/3} \tag{2.5b}$$

$$y_1 = u + v \tag{2.5c}$$

$$y_{2,3} = \frac{-(u+v)}{2} \pm i\,\frac{u-v}{2}\,3^{1/2} \tag{2.5d}$$

If $D<0$ then the following intermediate definitions must also be calculated

$$\varphi = \arccos\left[\frac{-q}{2}\left(\frac{abs(p)}{3}\right)^{-3/2}\right] \tag{2.6a}$$

$$y_1 = 2\left(\frac{abs(p)}{3}\right)^{1/2}\cos\frac{\varphi}{3} \tag{2.6b}$$

$$y_{2,3}=-2\left(\frac{abs(p)}{3}\right)^{1/2}\cos\frac{\varphi\pm\pi}{3} \tag{2.6c}$$

Then the roots of equation (A) are as follows:

$$x_n=y_n-\frac{b}{3a} \tag{2.7}$$

### 2.5.3 Application

*Solution for where D<0*

Using the spatial relationship described by Dworkin *et al.* (2005) (equation 5.8a, see Chapter 5) as an example:

$$-0.50T^3+(\delta^{18}O_{carb}+152.04)T^2-2.78\times10^6=0 \tag{5.8a}$$

the values for *a, b, c, and d* and *x* are as follows:

$a$ = -0.50

$b$ =($\delta^{18}O_{cc}$+ 152.04)

$c$ = 0

$d$ = –2.78×10$^6$

$x$ = $T$

Then using the value for $\delta^{18}O_{carb}$ = 30.39‰ (‰, VSMOW) (which is equal to 0‰, VPDB) the first the intermediate definitions *p*, *q* and *D* must first be calculated.

| *a* | *b* | *c* | *d* | *p* | *q* | *D* |
|---|---|---|---|---|---|---|
| -0.5 | 182.43 | 0 | -2.78E+06 | -44374.2732 | 1.96E+06 | -2.27E+12 |

**Table 2.4 The calculated intermediate definitions for the equation (3a) with inputs of δ18OcarbVSMOW = 30.39‰.**

Table 2.4 shows the input values and the intermediate definitions created by equations (2.4a), (2.4c), and (2.4d). As $D<0$ equation (5.8a) was used to calculate $\varphi$ and equation (2.6b) and (2.6c) was used to produce $y_1$, $y_2$ and $y_3$. From these results equation (2.7) was used to calculate $x_1$, $x_2$ and $x_3$ (MAT in °K). These was converted to °C using the conversion °C = °K – 273.15 (Bureau International des Poidset Mesures 2008) (Table 2.4).

| | $\varphi$ | $y$ | $x$ (°K) | $x$ (°C) |
|---|---|---|---|---|
| 1 | 2.147615 | 183.53 | 305.15 | 32.15 |
| 2 | 2.147615 | 110.24 | 231.86 | -41.14 |
| 3 | 2.147615 | -242.90 | -121.28 | -394.28 |

**Table 2.5 Values for the three different *x* intercepts in both °K and °C.**

Three possible temperatures are produced: $x_1$ = 32.25°C; $x_2$ = –41.14°C and $x_3$ = –394.28°C (Table 2.5). The value for $x_3$ can be easily discounted as, being below 0°K, it is physically impossible. Equally the value for $x_2$ is also very cold and there is no evidence of ice wedging in any of the sections so this can be discounted. Thus, the value for $x_1$ can be taken as the palaeotemperature estimate.

*Solution for where D≥0*

When $D \geq 0$ there is only one real root ($x_1$) as the other two are ($x_2$, $x_3$) are complex roots (Figure 2.3) and do not have real solutions (Woan 2000). Thus, in these circumstances only one temperature estimate can be generated. The temporal relationship described by Dworkin *et al.* (2005) (equation 5.8b) is an example of an equation where $D \geq 0$.

$$-0.22\,T^3 + (\delta^{18}O_{carb} + 61.99)\,T^2 - 2.78\times10^6 = 0 \qquad (5.8b)$$

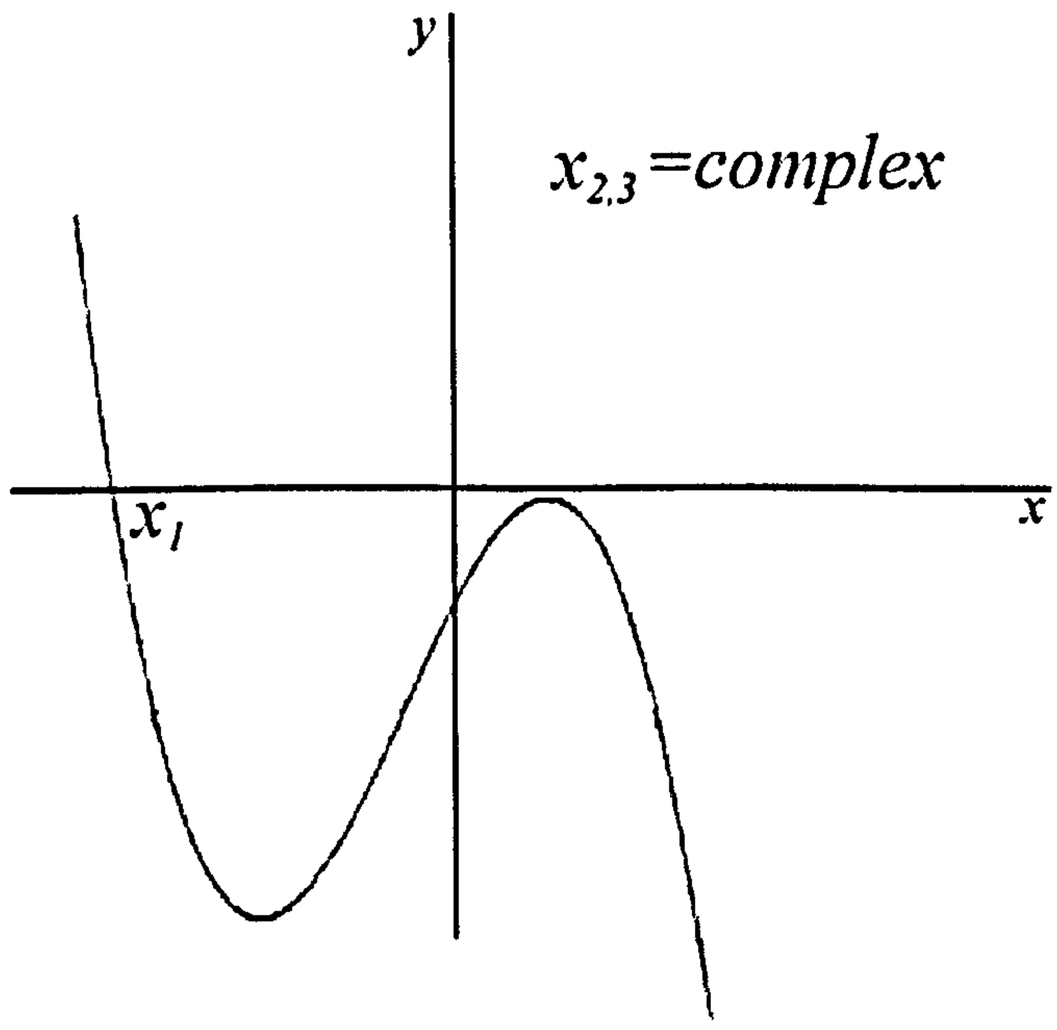


**Figure 2.3 A cubic solution when $D \geq 0$, there is only one real root, the other two are complex roots.**

Again using the value for $\delta^{18}O_{carb}$ VSMOW = 30.39‰ (which is equal to 0‰ $\delta^{18}O_{carb}$ VPDB) first the intermediate definitions *p*, *q* and *D* must first be calculated (Table 2.6).

| *a* | *b* | *c* | *d* | *p* | *q* | *D* |
|---|---|---|---|---|---|---|
| -0.22 | 92.85 | 0 | -2.78E+06 | -59374.1219 | 7.07E+06 | 4.74E+12 |

**Table 2.6 The calculated intermediate definitions for the equation (5.8b) with inputs of $\delta^{18}O_{cc}$ VSMOW = 30.39‰**

In this case as $D \geq 0$ rather than using equations (2.6a, 2.6b, 2.6b) the equations (2.4a), (2.4b) and (2.4c) are needed to solve the intermediate definitions $u$, $v$, and $y_1$ respectively. Equation (2.6) was uses to calculate $x_1$ (temperatures in °K). This was converted into °C using the conversion °C = °K – 273.15 (Bureau International des Poidset Mesures 2008).

| | $u$ | $v$ | $y$ | $x$ (°K) | $x$ (°C) |
|---|---|---|---|---|---|
| 1 | -110.72 | -178.73 | -289.466 | -148.78 | -421.78 |

**Table 2.7 Values for $x_1$ intercepts in both °K and °C.**

To solve for $y_2$ and $y_3$ the equation (2.2e) has the value $i$ which is an imaginary number and thus the roots are not real solutions (Woan 2000; Dr S. Kearsey *pers. comm.*). Thus, these values can be discounted in this study.

As all palaeotemperature solutions were produced using Microsoft Excel 2007 it was a useful check to ensure that substituting the derived temperature solutions back into the cubic function produced zero values.

### *2.5.4 Mathematical problems with estimates*

Problems occur with the palaeotemperature equations if the $D$ value changes from $<0$ to $\geq 0$ within the experimentally measured values for $\delta^{18}O_{carb}$. This occurs with the summer/winter rainfall equation produced from the data from the Saratov weather station (IAEA/WMO, 2008) (Equation 5.8c)

$$-0.28\,T^3 + (\delta^{18}O_{carb} + 92.24)\,T^2 - 2.78\times10^6 = 0 \qquad (5.8c)$$

(see Chapter 5 for how this equation was created)

This equation changes from $D<0$ to $D\geq0$ at $\delta^{18}O_{cc}$ values of -10‰ (VPDB) and below, as a result the predicted temperature jumps from 6°C to -409°C (Figure 2.4). This is because the cubic function changes from having three points where it cuts the $x$ axes (Figure 2.2) to having only one (Figure 2.3). As –409°C is obviously an unrealistic value it can be said that for $\delta^{18}O_{carb}$ values of –10‰ (VPDB) and below, the initial equations cannot be a valid model of the processes at that locality.

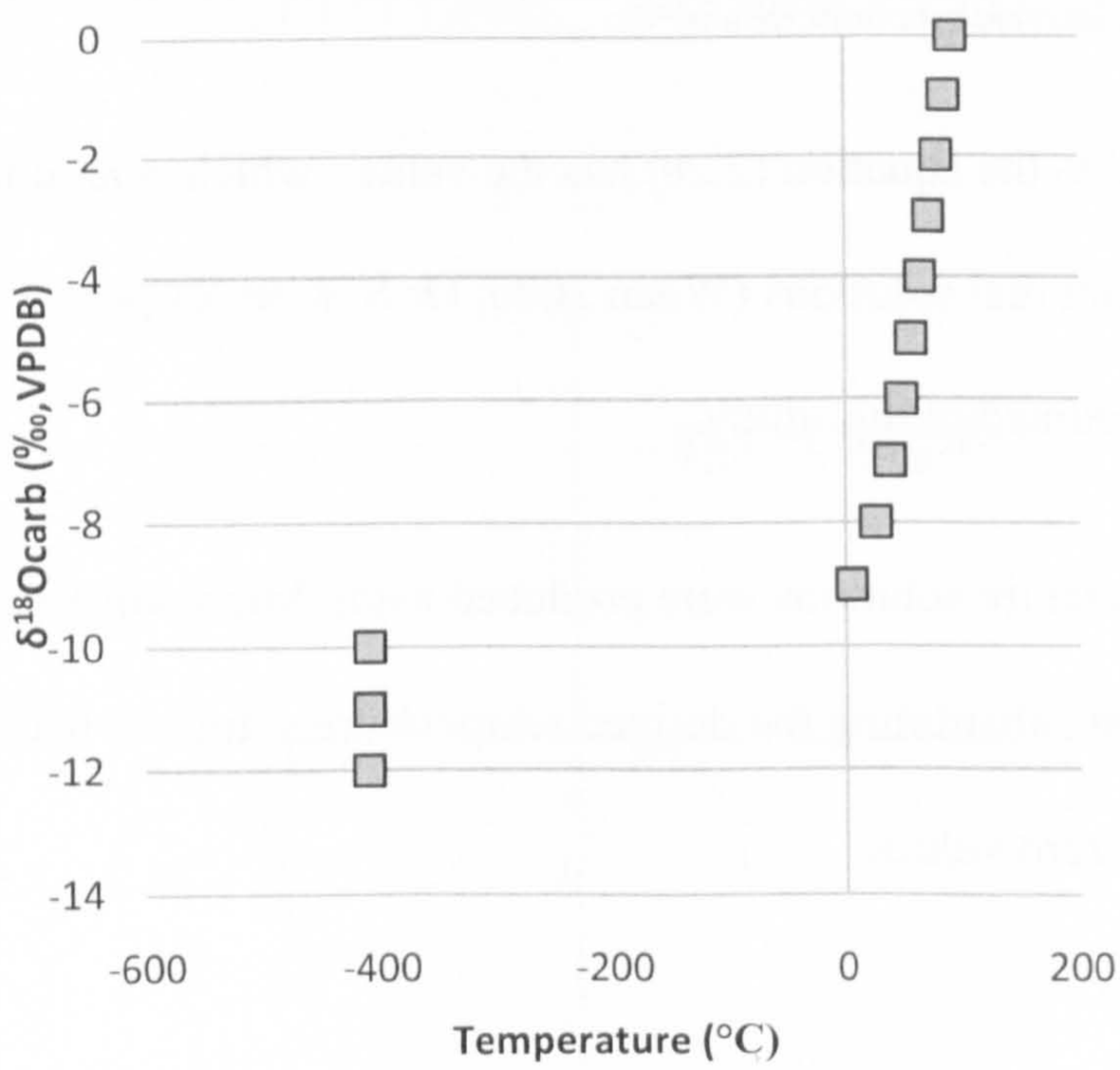


**Figure 2.4 Palaeotemperature estimates for equation (5.8c) using $\delta^{18}O_{cc}$ values from 0‰ to -12‰ VPDB. Note the sudden negative jump in the palaeotemperature estimates resulting from $D<0$ to $D\geq0$.**

## 2.5.5 Statistical methods

It is observed that there was a lot of variation in the isotopic composition of different nodules in certain paleosols (Chapter 4). It is important to determine if these variations in the isotopic signal through time represent true excursions, or are just an increase in the range of values from the mean. This assumes that results from different nodules within a paleosol represent an average of the isotopic composition of the soil water for the entire time that soil was active.

This assumption may become problematic if there is significant environmental change for the period that a soil is active creating a large spread of isotopic values in one paleosol. The isotopic variation of nodules within a paleosol does not always show a normal distribution (Figure 2.5) and thus parametric statistics such as Student's t-test cannot be used (Rana Moyeed *pers. comm.*)

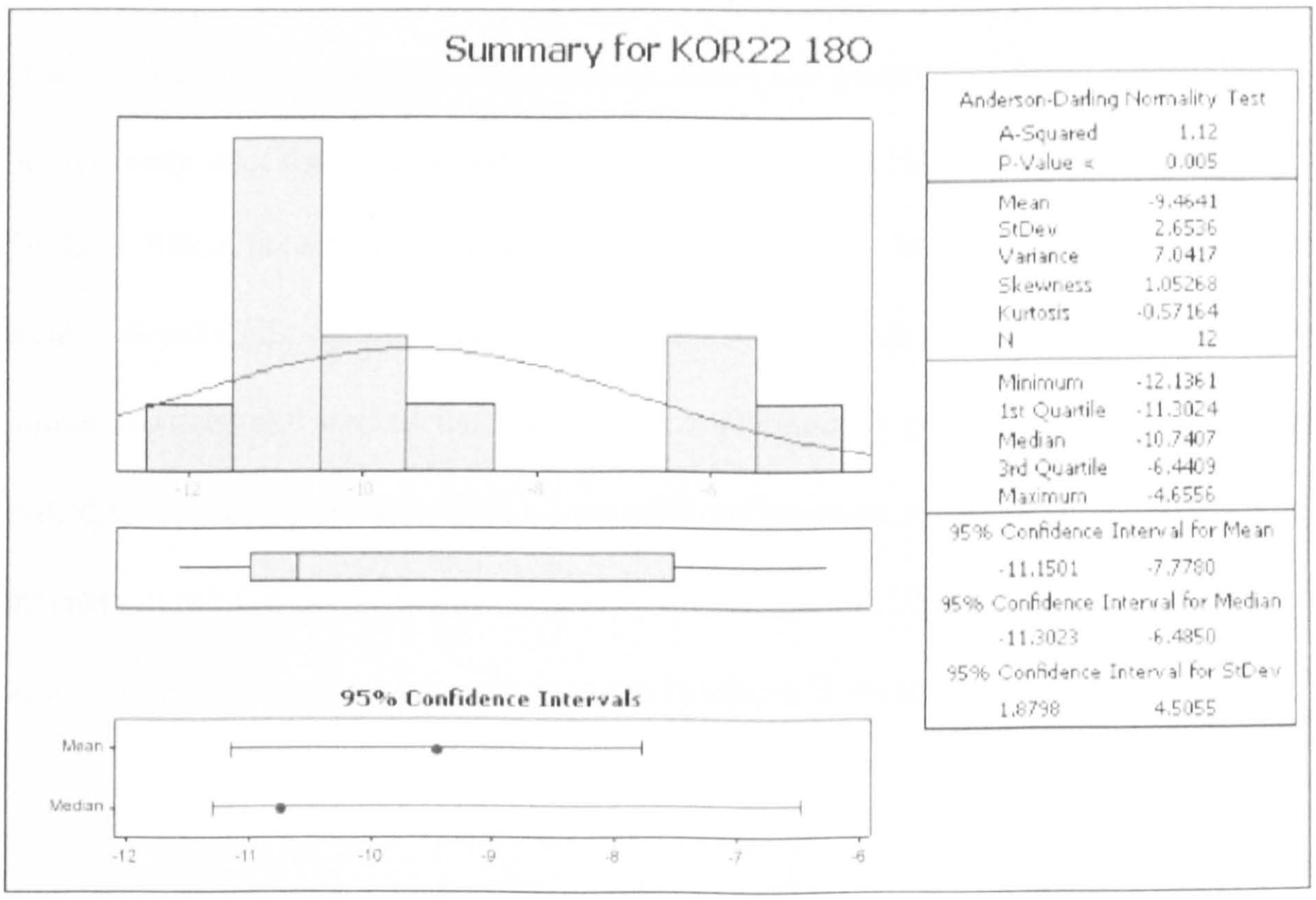


**Figure 2.5 Graphical statistical summary for the $\delta^{18}O$ values from paleosol KOR 22 at Boyevaya Gora showing a non-normal distribution.**

To investigate the significance of an isotope excursion between paleosols the Mann-Whitney test was used. This is a non-parametric test which has a null hypothesis that the two data sets are from the same population. The underlying assumptions in the Mann-Whitney Test are that: 1) both samples are random samples from their respective populations; 2) there is mutual independence between the two samples; 3) that the results are continuous measurements (Conover 1980).

All statistical analyses were conducted using the statistical program Minitab 15.1.0.0. Below a $p \leq 0.1$ it is statistically likely that the null hypothesis is invalid (to a 90% confidence interval) and the two datasets are from separate populations (Dr R. Moyeed *pers. comm.*; Conover 1980).

# Chapter 3. Paleosols of the South Urals, Russia

## 3.1 Introduction

Paleosols are a direct product of environmental influences and thus are extremely useful in investigating changes in climate (Retallack 1994; 1997; 2001). Previous studies into paleosols in Antarctica at the P/Tr boundary have identified a dramatic ecosystem reorganisation relating to changes in root traces (Retallack 2007) and poorly developed paleosols immediately after the P/Tr boundary (Retallack and Krull 1999; Krull and Retallack 2000; Sheldon 2006). Investigations into paleosols in the Karoo Basin, South Africa have recorded weakly developed paleosols just after the boundary and a change from shallow calcareous nodules to deep and well focused calcic horizon (Retallack *et al.* 2007). This is thought to be linked to a change from an arid to a semi-arid environment across the boundary and an increase in rainfall in the earliest Triassic (Retallack *et al.* 2007). However, similar detailed observations have not yet been made in the Northern Hemisphere.

## 3.2 Geological background

The Upper Permian to Lower Triassic strata of the South Urals consist of 1000 metres of terrestrial fluvial siliciclastic rocks. The exposure is largely restricted to streams cut in low relief, grass-covered terrain and small escarpments (Newell *et al.* 1999; Surkov *et al.* 2007; Dr A. Newell and Dr R. Twitchett, unpublished field data, T.K. personal observations). The overall palaeogeography of the area is a foreland basin to the Ural mountain range which was active through the Permian-Triassic periods. As such it is part of a major north–south linear depocentre that extends for some 2500km across mainland Russia from the Arctic to the Aral Sea (Newell *et al.* 1999; Tverdokhlebov *et al.* 2002).

The depocentre was formed by flexure of the European craton, as a result of the Ural orogenic event to the east (Zonenshian *et al.* 1984). The basin was active from the Mid-Carboniferous through to the Early Triassic. The earliest Carboniferous rocks consist of marine turbidites which sit directly on the orogenic platform, and the sedimentary package above consists of two shallowing upwards sequences starting with deepwater turbidites and finishing with shallow marine limestones (Puchkov 1997; Newell *et al.* 1999). The first cycle ends in the Sakmarian (Early Permian) and the second ends in the Kazanian (Early Permian) (Newell *et al.* 1999 Puchkov 1997).

Above, in the Tatarian, the sequence contains mostly alluvial red beds consisting of a variety of facies types: mudflat and floodplain interbedded sheet sandstones and mudstones, sandy distributary, small gravelly channels, and large gravelly channel systems (Newell *et al.* 1999; Tverdokhlebov *et al.* 2005; Surkov *et al.* 2007). Of these, the floodplain deposits show extensive paleosol development ranging from isolated root traces to indurated pedogenic calcretes (Newell *et al.* 1999; T.K. personal observations). The P/Tr boundary is marked by 'thick conglomerates' which are laterally extensive and up to 15m thick (Newell *et al* 1999; Tverdokhlebov *et al.* 2002; Tverdokhlebov *et al.* 2005). In the eastern sections these conglomerates comprise of 15m of erosionally-based conglomerates comprising of multiple, lenticular storeys containing gravel and cobble rounded clasts of up to 20cm sourced from the Ural Orogen (Newell *et al.* 1999; Tverdokhlebov *et al.* 2002). The conglomerate units are thought to be associated with a major fluvial conduit from an intra-orogen source deep in the Ural Mountains forming braided pattern channels at low flows similar to modern megafans (Newell *et al.* 1999; Benton *et al.* 2004).

The Late Permian and Early Triassic strata are unthrusted, and have been uplifted to their current position by post-depositional salt movement (Brunet *et al.* 1999 Newell *et al.* 1999; Newell *pers. comm.*). As such they are ideal for palaeoclimate and isotopic studies as they are more likely to retain their original isotopic values rather than a later diagenetic overprint.

### *3.2.1 Stratigraphic position*

As discussed by other authors (Newell *et al.* 1999; Tverdokhlebov *et al.* 2002; Tverdokhlebov *et al.* 2005; Taylor *et al.* 2009) there has been much confusion about the stratigraphic positioning of Russian strata with respect to the international stratigraphic framework. Most of this confusion arises from the fact that traditional Russian stratigraphic units are not directly comparable with international units. The Russian system breaks both lithology and geological time into Svitas and Gorizonts (Tverdokhlebov *et al.* 2005). Gorizonts are the major regional stratigraphic units in the Russian system but, rather than referring to lithostratigraphic packages, they are defined primarily on their palaeontological characteristics (Tverdokhlebov *et al.* 2005). Svitas, on the other hand, are largely lithostratigraphic units and are defined by a mix of field lithological and biostratigraphic criteria (Tverdokhlebov *et al.* 2002). The Tatarian is divided into the Urzhumian, Severodvinian and Vyatkian Gorizonts, with the Vyatkian representing the uppermost Permian Gorizont (Figure 3.1). This is divided into two Svitas: the Kutulukskaya in the Volga–Ural Anticlise and the Kulchumovskaya in the Cis-Ural Trough (Tverdokhlebov *et al.* 2005). The Lower Triassic is divided into the Vetlugian Super Group, comprising the Vokhmian, Rybinskian, Sludkian, Ust-Mylian and the Yarenskian Gorizonts. These correspond to the Kopanskaya, Staritskaya, Kzylsaiskaya, Gostevskaya and Petropavlovskaya Svitas (Figure 3.1) (Tverdokhlebov *et al.* 2002).

| Period | Epoch/ Stage | Gorizont | | Svita |
|---|---|---|---|---|
| TRIASSIC | Olenekian | Yarenskian | | **Petropavlovskaya** |
| | | Vetlugian Supergorizont | Ust-Mylain | **Gostevskaya** |
| | | | Sludkian | **Kzylsaiskaya** |
| | | | Rybinskian | **Staritskaya** |
| | Induan | | Vokhmian | **Kopanskaya** |
| PERMIAN | Lopingian | Tatarian | Vyatkian | **Kulchumovskaya** |
| | Guadalupian | | Severodvinian | **Vyazovskaya** |
| | | | Urzhumian | **Urzhumian** |

**Figure 3.1 Stratigraphy of the Cis-Ural Trough (adapted from Tverdokhlebov *et al.* 2002, 2005).**

Wardlaw *et al.* (2004) suggest that the top of the Tatarian in Russia corresponds to the top of the Guadalupian. Thus, they suggest there is a gap of approximately 11 million years between the youngest Permian rocks and the oldest Triassic rocks in Russia. Others, however, disagree

Tverdokhlebov *et al.* (2005) assign the beds below the thick conglomerates that cap the Permian succession to the Late Tatarian and the beds directly above this unit as Induan based on both and vertebrate fossils and microfossils (Tverdokhlebov *et al.* 2005). Furthermore, from both tetrapod and ostracod evidence, the Vyatkian Gorizont is inferred to be of equivalent age to the *Dicynodon* Assemblage Zone of South Africa (i.e. Changhsingian) (Benton *et al.* 2004; Surkov *et al.* 2007; Benton 2008). This interpretation implies that the Upper Tatarian is Changhsingian in age and within a million years of the P/Tr boundary (Tverdokhlebov *et al.* 2005).

There has been some debate over whether the multi-storey conglomerates represent the latest unit of the Permian or the youngest unit of the Triassic. Newell *et al.* (1999) suggested that because they sit below a structural unconformity they should be included in the Tatarian. Biostratigraphic studies, however, suggest the break in facies marks the P/Tr boundary and that the conglomerates are basal Triassic in age (Benton *et al.* 2004; Surkov *et al.* 2007).

This second interpretation has been further strengthened by recent magnetostatigraphic studies. Taylor *et al.* (2009) have shown that it is possible to correlate sections across the field area using a polarity transition from Reverse-Normal polarity zone which falls, in those sections where it is exposed, just before the onset of the thick conglomerates. They correlate the Russian magnetostratigraphic sections to the global correlation produced by Steiner (2006) in which the P/Tr boundary falls just after the start of this Normal. Thus, not only does this suggest that the Russian sections include almost all of the Late Permian (Lopingian), but also confirms that the thick conglomerates are the basal Triassic and the P/Tr boundary falls at, or just before, this facies change (Taylor *et al.* 2009).

### *3.2.2 Studied sections*

In total 7 sections were identified and the paleosols within them studied; Vozdvizhenka (51° 42.651'N, 56° 23.034'E), Tuyembetka (51° 55.318'N, 56° 19.616'E), Sambullak (51° 52.922'N, 56° 13.098'E), Krasnogor (51° 33.378'N, 56° 4.820'E), Petropavlovka (52° 1.970'N, 55° 38.110'E) Mescheryakovka (51° 22.755'N, 55° 16.884'E ), Boyevaya Gora (51° 17.883'N, 54° 54.569'E) (Figure 3.2). Of these sections Boyevaya Gora, Sambullak, Tuyembetka, Vozdvizhenka and Krasnogor all contain the boundary between the Tatarian and Early Triassic marked by the dramatic change to multi-storey conglomerates, while Mescheryakovka and Petropavlovka are Early Triassic sections (Figure 3.3).

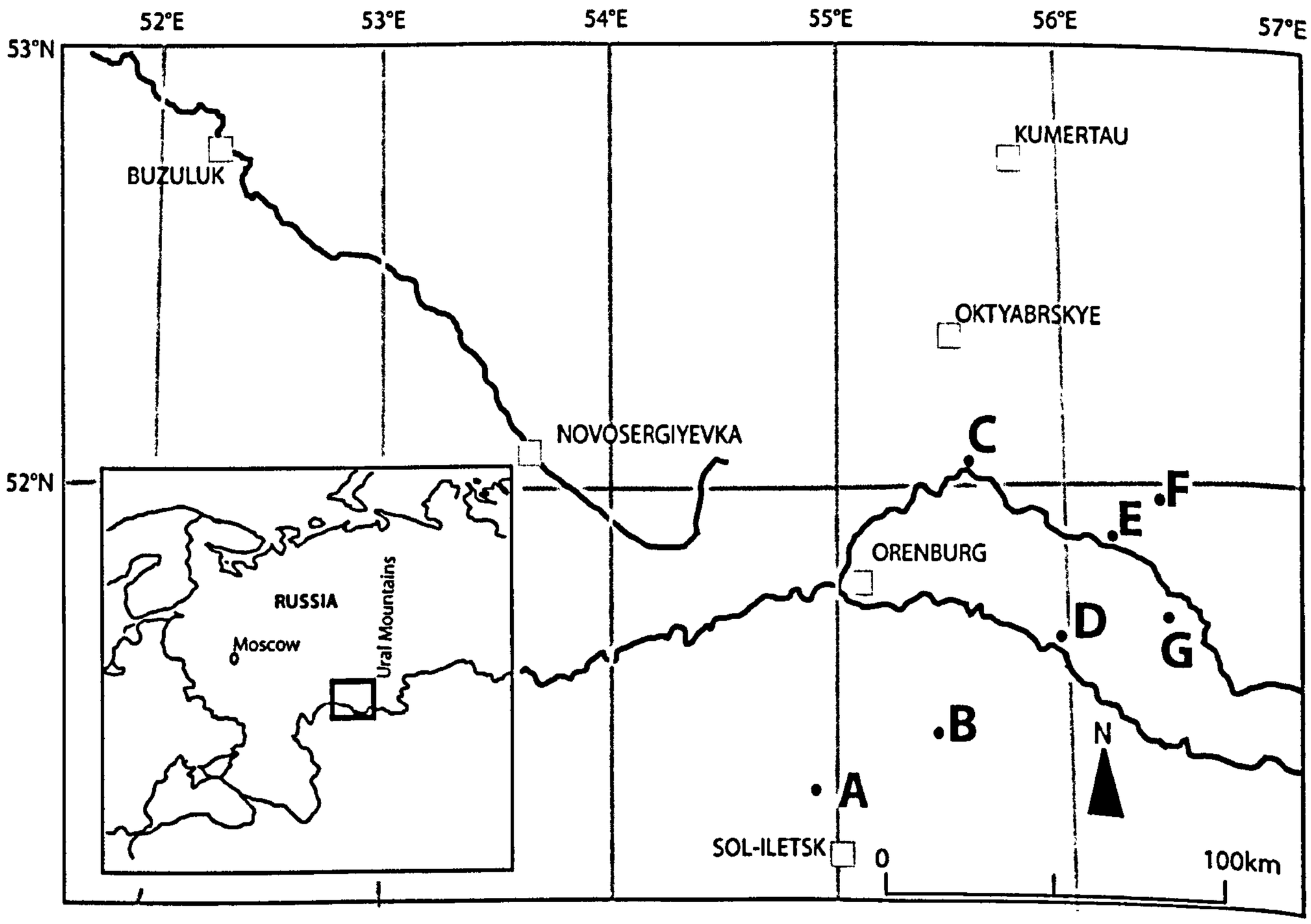


**Figure 3.2 Field area in Southern Urals. A) Boyevaya Gora, B) Mescheryakovka, C) Petropavlovka, D) Krasnogor, E)Sambullak, F) Tuyembetka and G) Vozdvizhenka. The black lines represent major rivers (figure adapted from unpublished map by A. Newell).**

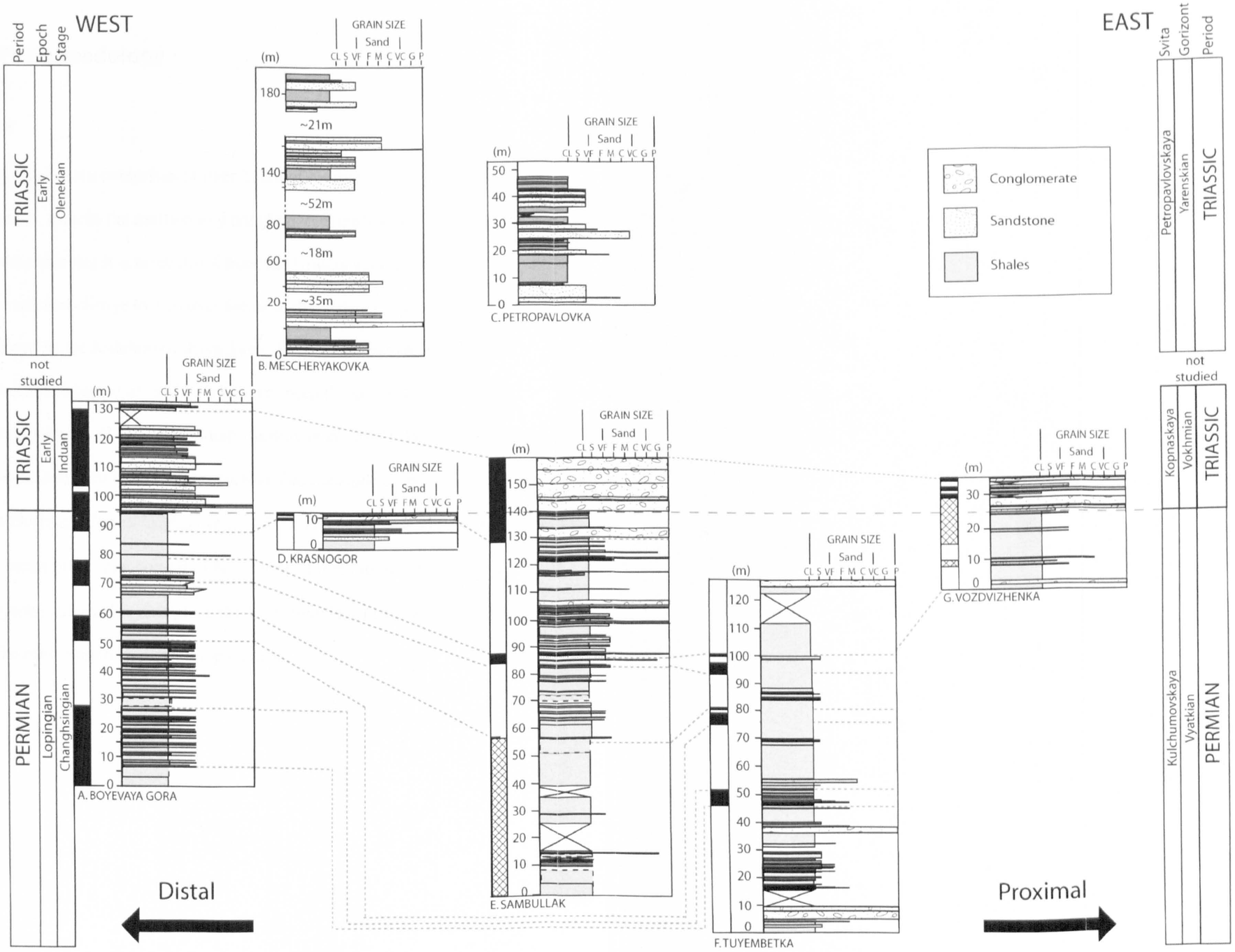


**Figure 3.3 The stratigraphic position of all the sections studied in Russia. Sections A, D, E, F, G, are correlated using magnetostratigraphy defined by Taylor *et al.*(2008).The positioning of Triassic sections B and C is based on palaeontological data (Tverdokhlebov *et al.* 2002) Sections are arranges West to East across the basin, how the Svitas correspond to the global stages and epochs can be seen in Figure 3.1. (Sedimentological logs from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

## 3.3 Field results: Palaeopedology

### *3.3.1 Boyevaya Gora*

The section studied at Boyevaya Gora comprises of over 132m of mudstones, siltstones, sandstones and conglomerates. It lacks the multi-storey conglomerate units seen in the east of the basin, probably due to the fact that it is more distal from the Uralian source (Surkov *et al.* 2007). However, there is a marked change to a coarser facies in the early Triassic. The lower part of the section is attributed to the Kulchumovskaya Svita, Vyatkian Gorizont by fish scales and skull bones (Tverdokhlebov *et al.* 2005). It has also been the site of large therapsid footprints interpreted as being produced by a dicynodont (Surkov *et al.* 2007). The section above the facies break has yielded vertebrate remains such as *Tupilakosaurus* and others of Early Triassic, Vokhmian Gorizont affinity (Surkov *et al.* 2007). The latest Permian fossils are found 22m below the facies break, and consist of both tetrapod remains and fish scales (Surkov *et al.* 2007). Magnetostratigraphic data place the P/Tr Boundary just below the facies break (Taylor *et al.* 2009) confirming the palaeontological data.

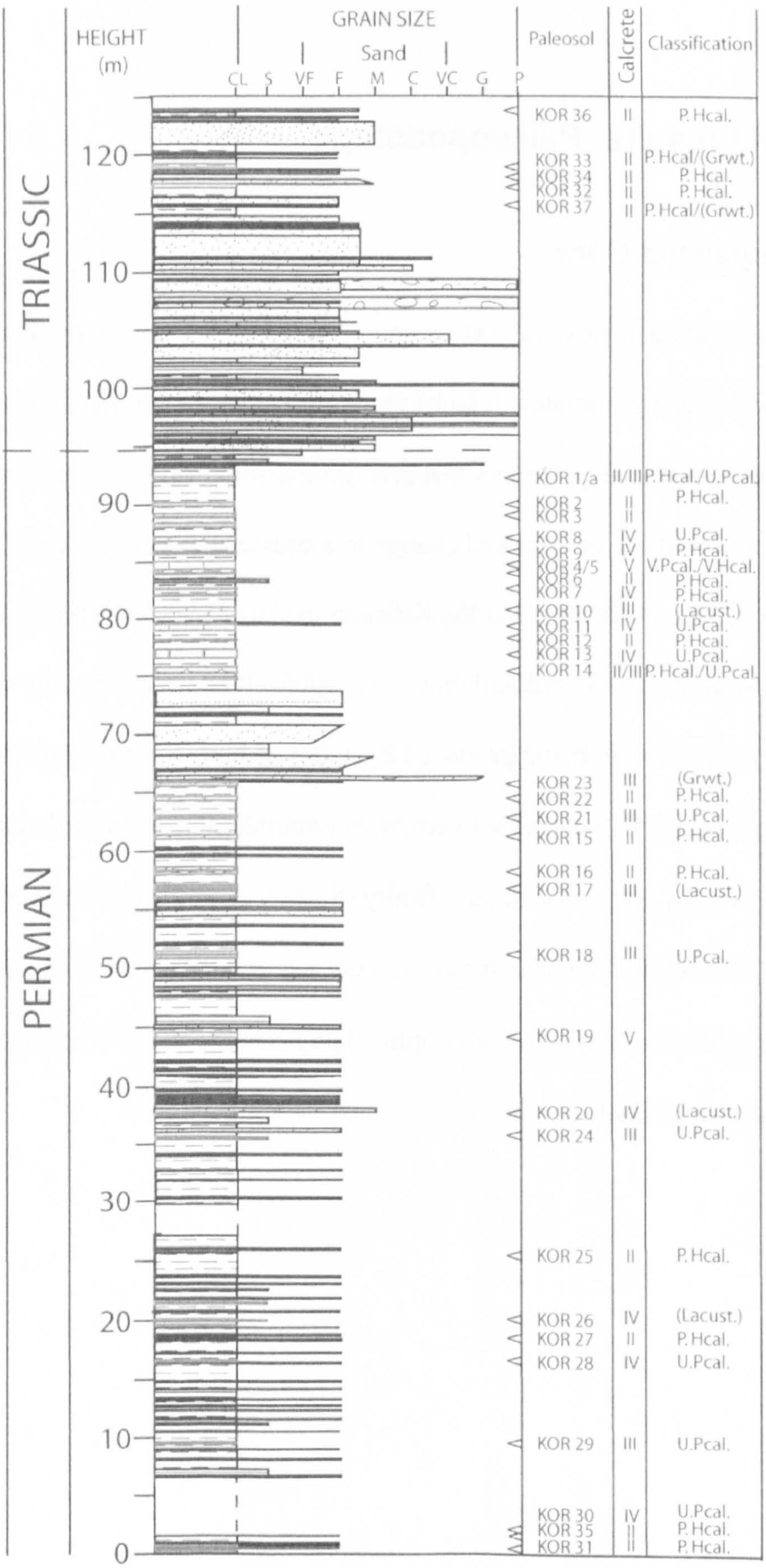


**Figure 3.4 The studied section at Boyevaya Gora. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols (see Table 2.2). Note the high density of soils just below the P/Tr boundary (Sedimentological for log from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

In total 37 paleosol horizons were identified at Boyevaya Gora (Figure 3.4, for individual paleosol descriptions see Appendix A1.1), interbedded with minor sand and gravel channels and associated over bank deposits. The thickness of the paleosols ranges from 15cm to 137cm. The more developed calcrete profiles appear to be marginally thicker (e.g. KOR 4) than the less developed paleosols (e.g. KOR 6), although this may be because the more developed calcretes are more resistant to erosion and compaction. Four of these paleosols (KOR 14) are part of stacked sequences where the paleosols below have been partially overprinted by the paleosols above producing compound horizons as described by Kraus (1999) in a period of steady deposition where the rate of sedimentation roughly matched the rate of deposition. Overall the paleosols are a uniform colour of 10R (ranging from moderate orange pink–10R 7/4 to greyish red –10R 4/2), although those above the P/Tr boundary show a marked colour change to 5GY (grey yellow).

All the paleosols have a grain size of either clay or silt and all but two (KOR 36 and KOR 9) have recorded root traces, although for some the rooting is restricted to the A horizon. These root traces primarily take the form of in fills of reddened clay, possibly formed by the oxidation of the original organic matter of the root (as suggested by Retallack 2001a), and are 2-6mm in width and have an obvious tapering and branching structure (Figure 3.5A). This would suggest an oxygenated environment and would explain the lack of preservation of organic matter.

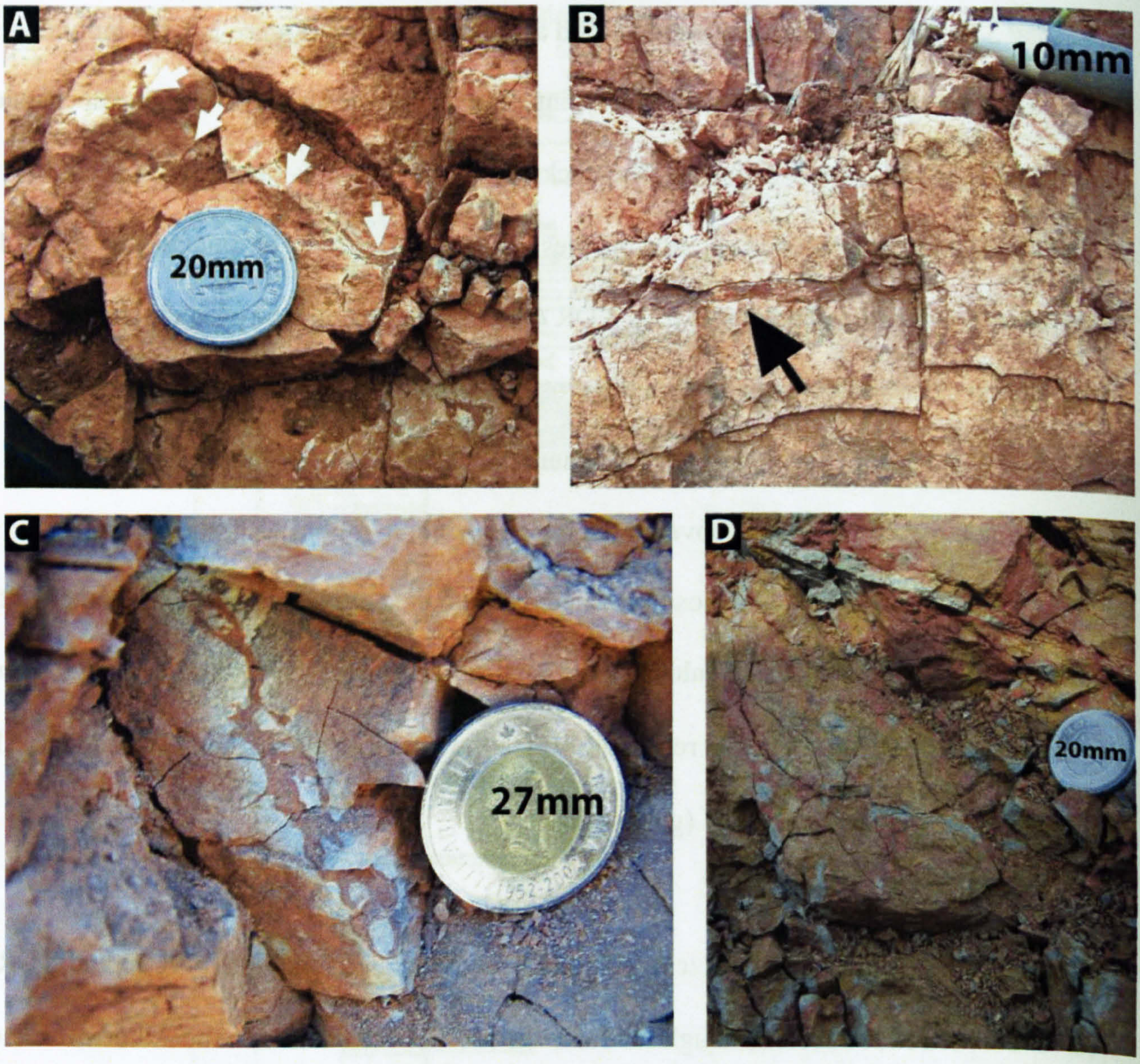


**Figure 3.5 Root traces in Russia. A) are branching and tapering rootlets from Boyevaya Gora. B) is a tap root at Sambullak (SAM 5a) . C) and D) show drab root haloes at Boyevaya Gora and Mescheryakovka.**

Most of the roots take the form of fibrous root systems (cf. Retallack 1997) which are mainly preserved as 20-50mm long traces. In those paleosols where the root networks are best preserved (KOR 4, KOR 11, KOR 17, KOR19, see Appendix 1 A1.1) it is possible to distinguish the nature of the rooting system. Those paleosols with a well-developed continuous calcrete layer (KOR 4 and KOR19) show a more tabular root system (Figure 3.5B) (cf. Retallack 1997), suggesting the calcrete layer is inhibiting water flow through the paleosol. In those horizons that have not developed a continuous calcrete layer (e.g. KOR 11, KOR 17 see Appendix A1.1) the roots have a more vertical orientation suggesting vertical

movement of water through the paleosol profile (Alonzo-Zarza 2003) and probably also sinker roots (Figure 3.5A) which would take advantage of deep groundwater during the dry season (Retallack 1997). Several horizons have roots showing drab-root halos (Figure 3.5C) (as defined by Retallack 2001a; Retallack 1997). These form ~1mm haloes around the root traces and are very pale blue (5B 8/2) to light bluish grey (5B 8/1). It is worth noting that in the Triassic at Boyevaya Gora there are no specific drab-root halos, although there is minor very light grey (N8) mottling in the sandstone above these horizons (Figure 3.5D).

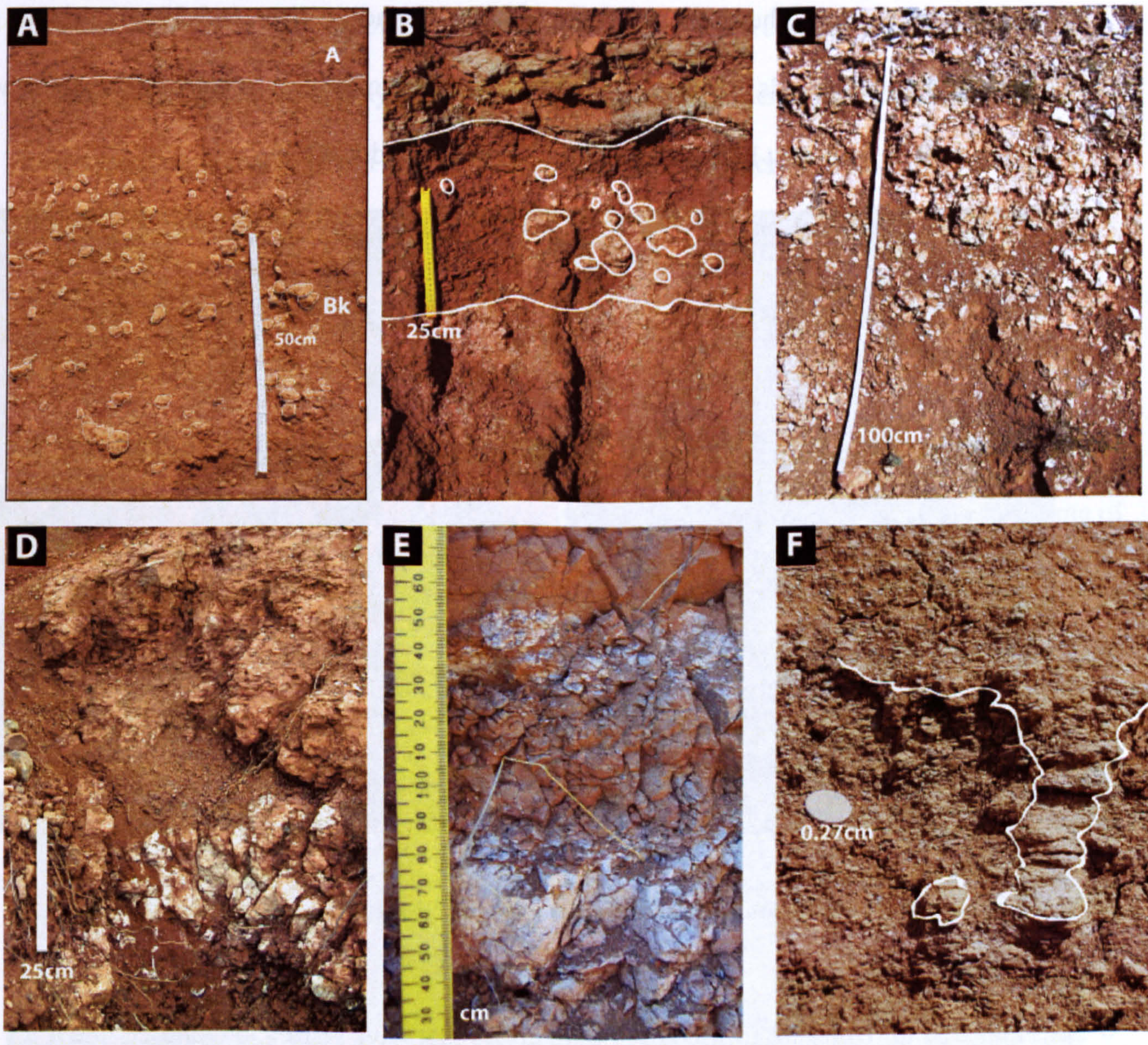


**Figure 3.6 Bk horizon development stages in Russia: (A) a stage II nodular horizon from Boyevaya Gora with A and Bk horizons marked (KOR 6). (B) Is a stage III horizon with possible mixed groundwater/pedogenic influences at Boyevaya Gora (KOR 23). (C) is a stage III horizon at Tuyembetka (TUY55) and (D) is a Stage IV horizon from Sambullak (SAM 7). (E) is a particularly well exposed Stage V calcrete with brecciated top (KOR4). F) is a groundwater calcrete from Petropavlovka (PET2).**

All paleosols at Boyevaya Gora have an evident Bk horizon with varying levels of maturity (see Table 2.2 for classification scheme). The maturity of Bk horizons range from nodules of 20-50mm in size (Stage II)(Figure 3.6A), through coalesced nodules forming a continuous carbonate layer (Stage III) )(Figure 3.6B) and the start of formation of a solid carbonate layer with nodules beneath (Stage IV) (Figure 3.6E), to thick indurated calcrete horizons (Stage V) (Figure 3.6D) (classification after Wright and Tucker 1991; Retallack 2001a; Alonso-Zarza 2003 see Chapter 2 Table 2.2). Of these the stage II horizons are most prevalent and seen throughout the section. The stage II nodules are found either in discrete 5-30cm horizons or dispersed 50-100cm bands and may or may not contain root traces. In some cases root traces are preserved as drab-root haloes (e.g. KOR 19 see appendix A1.1).

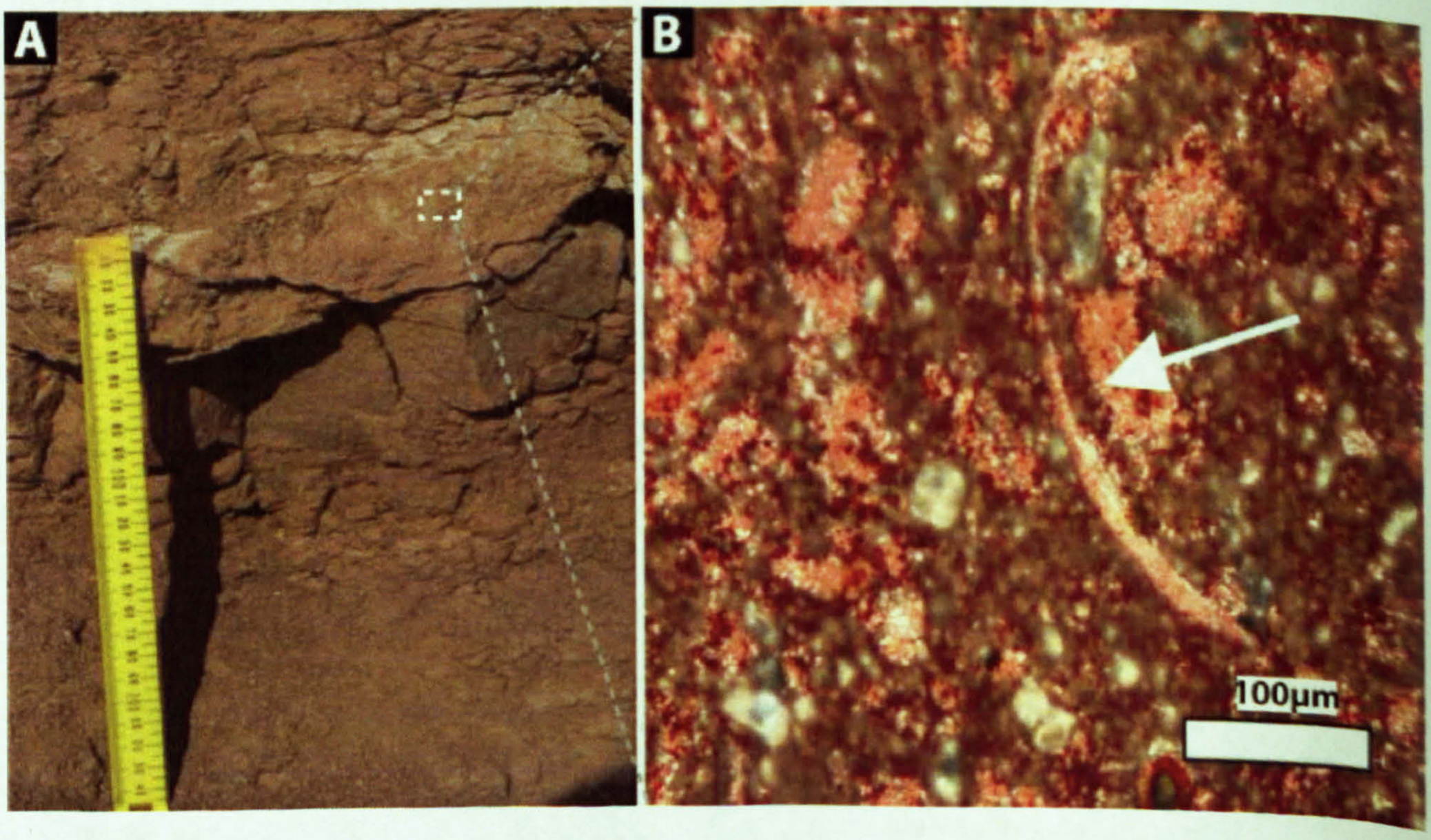


**Figure 3.7 Ostracod in KOR17 suggesting a lacustrine environment and the bed it originated from (scale in 25 cm) (A) shows the carbonate horizon when the thin section was taken from (B) shows the ostracod fossil arrowed.**

The stage III horizons are formed of nodule layers that have started to coalesce into a continuous calcrete horizon as a result of powdery calcite forming between the nodules (Wright and Tucker 1991). They form the second most prevalent stage of Bk horizon

development at Boyevaya Gora and are between 7-76cm thick, similar to the variations in thickness seen in the stage II nodules.

The stage IV horizons are defined by the occurrence of a laminated, solid calcrete top which is 8-16cm thick. Five of these maybe associated with ephemeral lakes (as described by Newell *et al.* 1999) and two of which (KOR 17 and KOR 25) have been found to contain ostracod fossils (Figure 3.7). They are also related to channel fills which have become calcified paleosols after the deposition of the channel fill (KOR 20) and contain desiccation cracks suggesting that the channel may have been waterlogged and then dried out (Figure 3.8A). These types of paleosol are not strictly speaking pedogenic calcretes, but instead are palustrine deposits (as described by Alonso-Zarza 2003). However, the thinness of these calcretes would suggest that they are related to ephemeral ponds, probably formed by sporadic intense rainfall (Gierlowski-Kordesch 1998). There are also examples of true pedogenic stage IV Bk horizons (as described by Alonso-Zarza 2003) for example KOR 3, KOR 8, KOR 11 and KOR 13 which all have rooted massive carbonate horizons and some of which show primary slickensides (KOR3) (Figure 3.8 B).

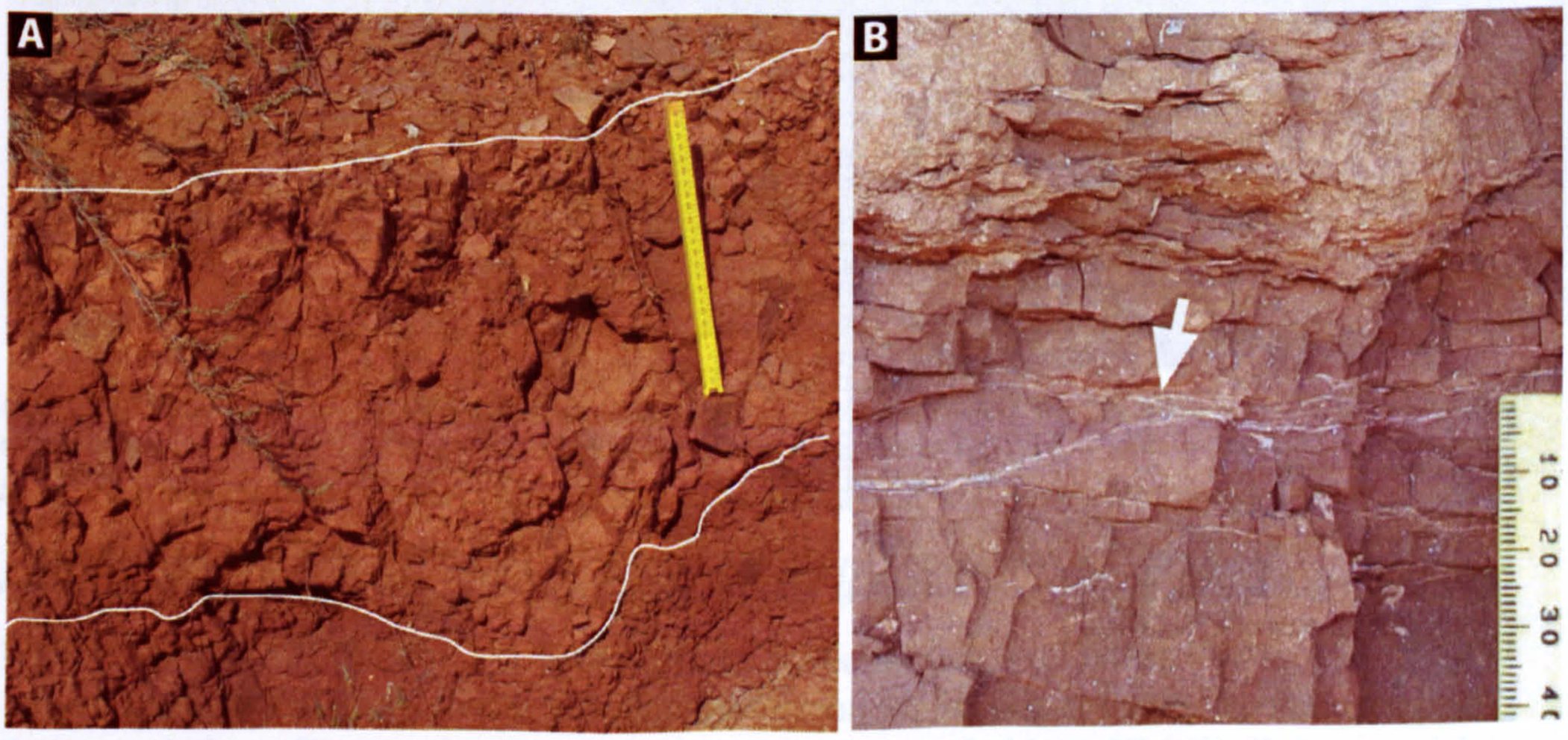


**Figure 3.8 Paleosol developed on minor fluvial channels and pedogenic slickensides A) Shows a minor channel fill the top of which has become a paleosol (scale = 25cm). B) Wedge shaped peds (outlined by later sparry calcite) interpreted as pedogenic slickensides (scale in cm).**

At Boyevaya Gora there are two Stage V horizons (KOR 4 and 19) of which one (KOR 4) is a spectacularly well-exposed example and comprises a 77cm thick, white (10R 7/4) calcrete unit which is predominantly massive although is cut by many iron-stained root traces (Figure 3.9). This is interpreted as a hardpan as described by Alonso-Zarza (2003). The top 5cm of the hardpan show minor brecciation with pisoliths of carbonate (Figure 3.6D) which were used to identify it as a stage V horizon (cf. Retallack 2001a). Above this there are lenses of reddened clay within the carbonate layers which are 16cm long and 8cm high and pinch in and out through the bed (Figure 3.9). These structures have been tentatively identified as shrink–swell structures (Dr N. Sheldon, *pers. comm.*) equivalent to the gilgai microtopography observed in modern Vertisols (Kovda and Wilding 2004).

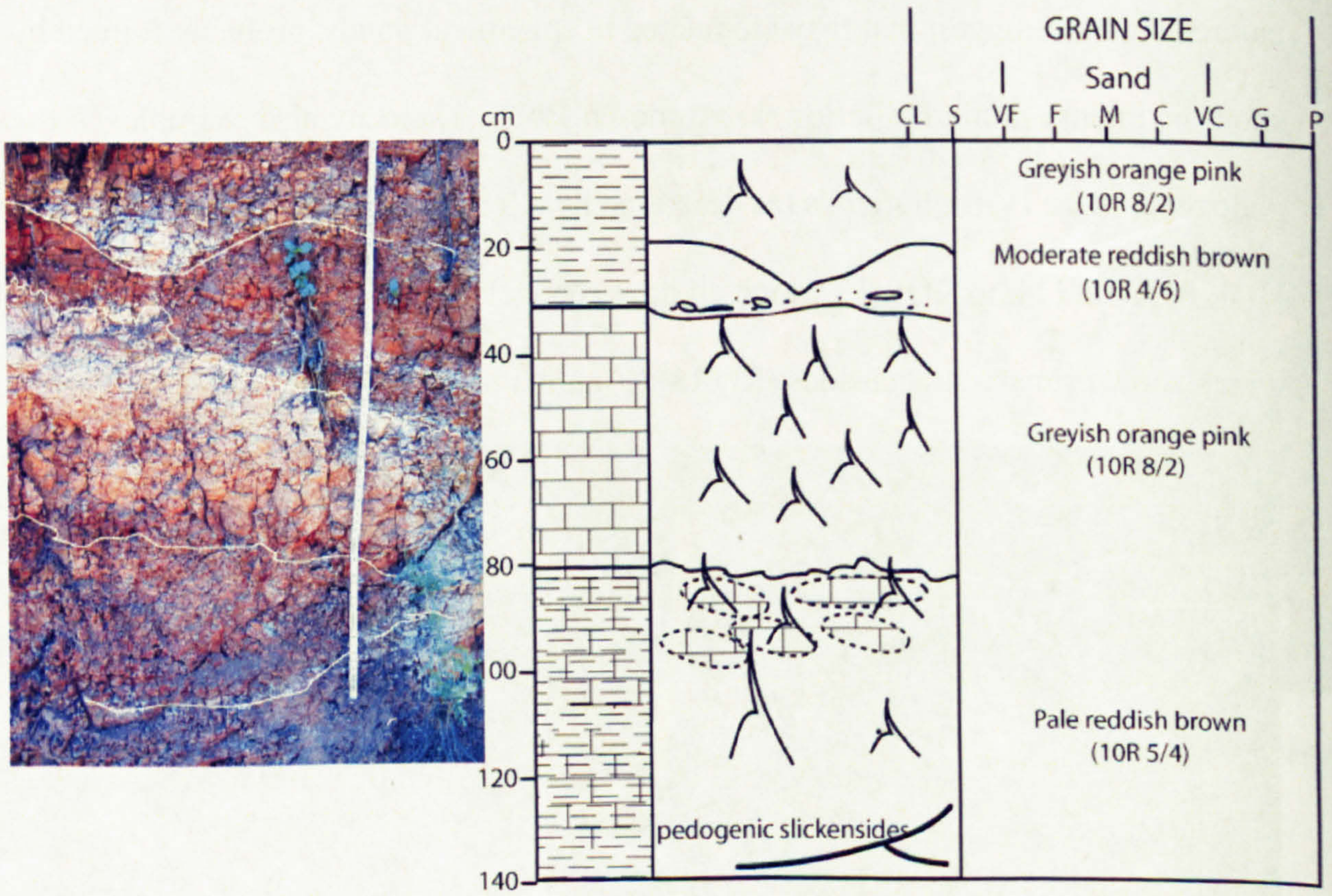


**Figure 3.9 The Stage Vat Boyevaya Gora (KOR4), exhibiting possible gilgai microtopography on the top surface and pedogenic slickenside's at base.**

The prevalence of stage II and III Bk horizons suggest that this was a relatively active floodplain as carbonate layers are thought to form at a relatively constant rate and more-developed Bk horizons take a longer time to develop and thus can be used to constrain periods

of non-deposition at the specific locality and constrain channel activity and flooding (Retallack 1997; Retallack 2001a). Retallack (1994, 2001) has suggested that it takes 10kyr to form a stage II calcic horizon and thus the Boyevaya Gora floodplain must have been relatively stable for at intervals of that duration at least.

Mottling and gleization is evident throughout the section, although it has different forms.). In many paleosols, (KOR2, KOR4, KOR6 KOR12, KOR14, KOR16, KOR18, KOR22, KOR28, KOR32) it takes the form minor mottles which are 1-2mm reduction spots (Figure 3.10C). These are thought to be caused by iron remobilisation within the paleosol or as reduction spots round degrading organic matter in the paleosol after burial during diagenesis (Retallack 2001a).

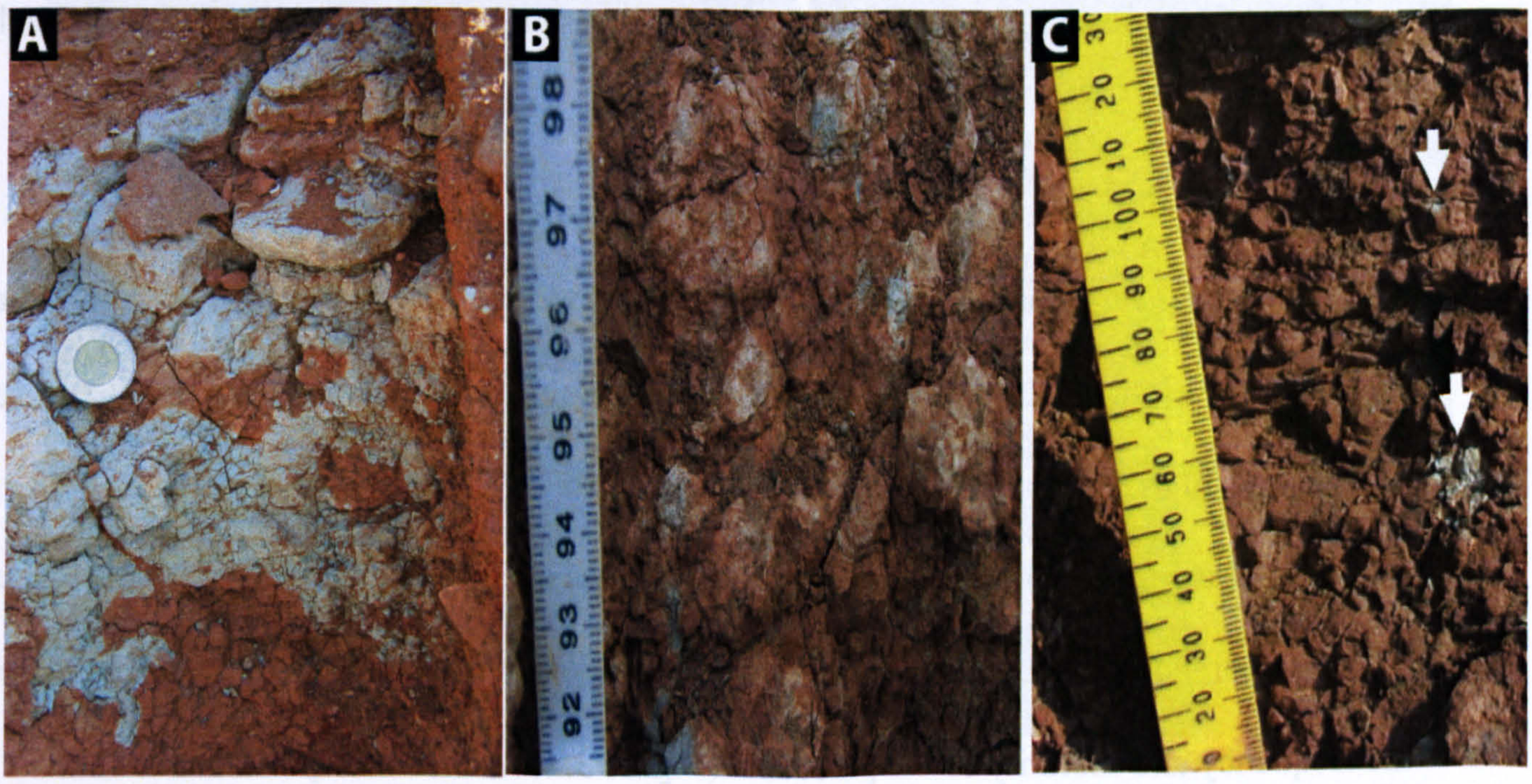


**Figure 3.10 Variations of gley and mottles. A) the strongly gleyed top of KOR 1 at Boyevaya Gora. B) the mottles surrounding nodules in KOR 21 at Boyevaya Gora. C) Mottles seen in KOR2 The coin in photo A) is 27mm in diameter. The scale in B) and C) is in cm.**

There are some paleosols which have distinct gleyed horizons (KOR1, KOR7, KOR10, KOR12, KOR15, and KOR28) ranging from 8-36cm thick, and normally associated with drab-root haloes. These primarily drab colours of very pale blue (5B 8/2), light greenish grey (5G 8/1), light grey (N7) and very light grey (N8). In the case of KOR1 this gley is quite

extensive and appears to be related to in filled desiccation cracks, although the gley continues down below these cracks for 14cm (Figure 3.10A). Several paleosols have overlying sandstones that are intensely gleyed (N8 and 5GY 8/1), contain drab-root haloes (see top of Figure 3.6B). KOR 15 and KOR 21 have nodules which themselves appear to be mottled (Figure 3.10B) possibly relating to drab-root haloes surrounding these nodules which were not visible in the field. This gley (opposed to the mottling) is associated with specific horizons, suggesting that its occurrence is related to pre-diagenetic processes. As such it probably represents the effects of periodic paleosol waterlogging as anaerobic microbes in poorly oxygenated water will reduce brown and red iron oxides and hydroxides from the ferric to ferrous states (Retallack 2001a). As these features are in the most part constrained to the upper horizons within the paleosol, it is plausible that they relate only to periodic waterlogging events, which is consistent with the presence of the ephemeral lakes (Newell *et al.* 1999).

There is vertical variation in the paleosol horizons at Boyevaya Gora. The paleosols at the bottom of the section are interbedded with numerous minor sand channels (Figure 3.4), some of which, as in the case of KOR 20, have undergone a level of paleosol development. Between 73 metres from the base of the section and the P/Tr boundary there is a change in both the sedimentation and paleosols: there is a lack of interbedded sands and an increase in the frequency and maturity of the paleosols (Figure 3.4). Also at this point there is the appearance of Vertisol-associated features (for example KOR4) suggesting periodic wetting and drying of the paleosol.

The paleosols of the earliest Triassic are significantly thinner than those of the Permian. The level of carbonate development is not greater than stage II and the nodules get no bigger than

30mm, with an average of 10mm. This is significantly smaller than the Permian average nodule size of 20-50mm. There is a shift in overall colour of the paleosol from brick red (10R), which dominates the Permian paleosols, to greyish yellow (5GY). Also, although the Triassic paleosols do show some evidence of root traces they are sparse and only preserved as drab root haloes (Figure 3.11A). Many of the overlying sandstone beds are gleyed, possibly suggesting they formed during flood events after which the water and sediment may have become anoxic (Figure 3.11B).

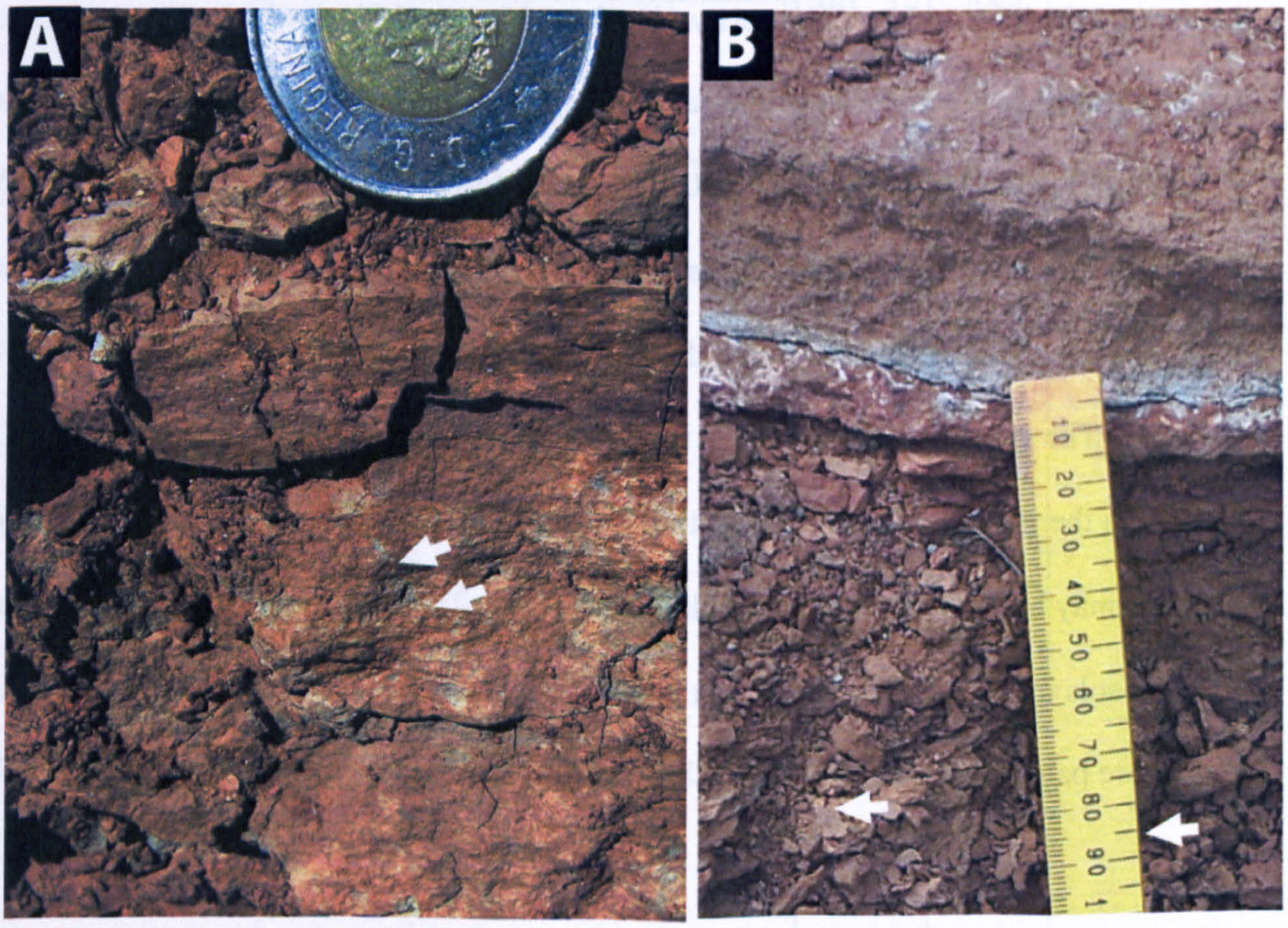


**Figure 3.11 Root traces in Triassic paleosols at Boyevaya Gora; KOR37 (A) and KOR36 (B). A shows a minor drab root halo (coin 27mm in diameter) and B shows the gleyed sandstone (just above top of ruler) overlying a paleosol (scale in cm).**

### *3.3.2 Sambullak*

The section at Sambullak represents over 130 metres of interbedded muds, sandy channels, paleosols and lacustrine limestones capped by thick multi-storey conglomerates. The section

below the multi-storey conglomerates is the lowest part of the Kulchumovskaya Svita, Vyatkian Gorizont, by vertebrate bones (Tverdokhlebov *et al.* 2005). The Permian age is supported by palaeomagnetic data (Taylor *et al.* 2009) which places the P/Tr Boundary at the base of the conglomerate.

There are a total of 30 paleosols exposed at Sambullak, many of which are compound horizons, which are especially prevalent at the base of the studied section (Figure 3.12, for individual paleosol descriptions see Appendix A1.2). As with the paleosols at Boyevaya Gora the vertical thickness of the paleosols varies from 35cm to 164cm which also appears to be partially linked to the maturity of the calcrete layers within the paleosol and thus their age (cf. Wright and Tucker 1991; Retallack 2001a; Alonso-Zarza 2003). However, SAM2, SAM6, SAM8, SAM7, SAM17 and SAM21 have all been eroded by overlying conglomerate and sand channels therefore the measured thickness may not be representative of their original thickness. The grain size of the rock is uniformly of clay grain size in the lower part of the section. In the top 40 metres of the section average paleosol grain size increases to silt grain size, this may be related to increased channel activity. There is also a minor colour change in the paleosols up section: the lower part is predominantly moderate red (5R 5/4), those in the middle are pale brown (5YR 5/2) and those at the top are moderate reddish brown (10R 6/6).

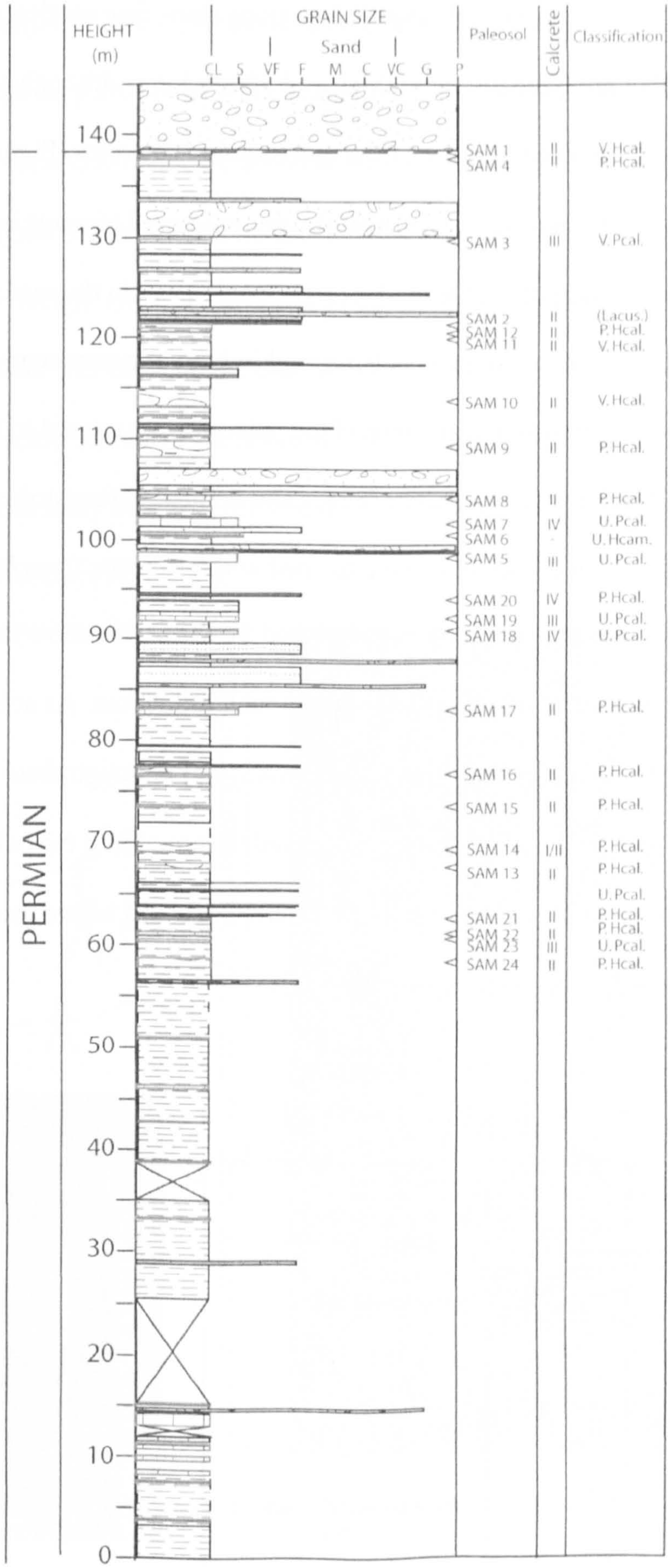


**Figure 3.12 The studied section at Sambullak. The arrows (<) mark the position of the palaeosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols and classification (see Table 2.2). P/Tr boundary is marked by the conglomerate at the top of the log (Sedimentological data for log from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

As at Boyevaya Gora, all the well-exposed sections show fine rootlets preserved as in fills of reddened clay that are typically 2mm thick and 30mm long, although some roots up to 300mm long are preserved in some of the more mature calcretes (Figure 3.5A). Similarly some of the Stage III calcretes (e.g. SAM 5) have preserved taproots which are thicker than the other rootlets (4mm) and have evident right-angles within the root structure (Figure 3.5B). This suggests that some of the paleosols formed in high or permanent water tables (Retallack 1997). There is also evidence that some of the paleosols are related to lacustrine deposits. For instance SAM 2 has evident limestone lenses and laminated limestones (25cm thick) (Figure 3.13) suggesting this paleosol may have formed with influence from lacustrine waters as described by Alonso-Zarza (2003). SAM 10 and SAM 19 also show similar features, although the rest of the other paleosols do not show any such influences. As at Boyevaya Gora some root traces are preserved as drab-root haloes (SAM 22) although these are rare (Figure 3.5C). Also, as at Boyevaya Gora, root traces are recorded throughout the paleosol apart from five horizons (SAM 1, SAM 8, SAM 12, SAM 21 and SAM 22) where root traces are only observed in the A horizon (see Appendix A1.2).

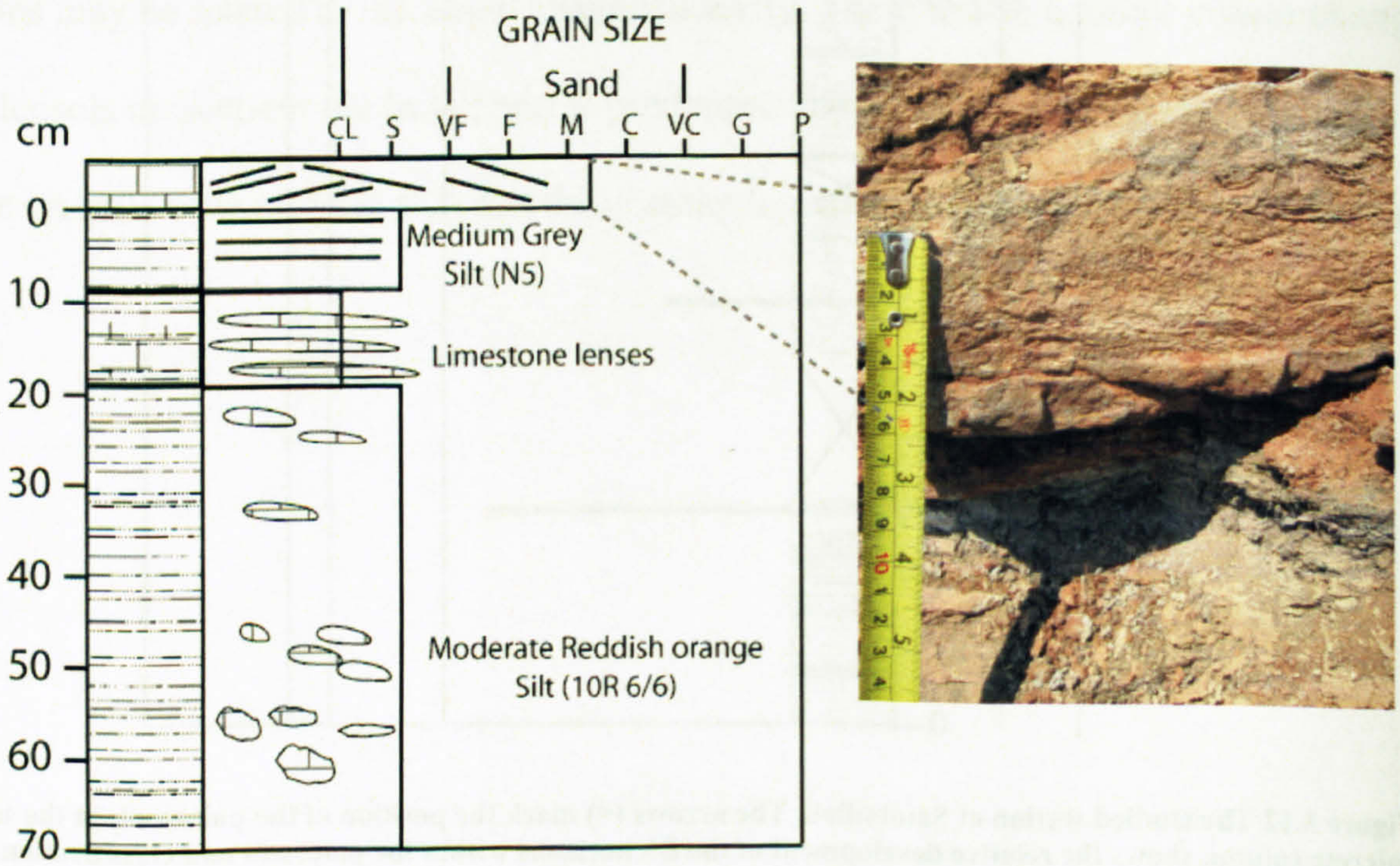


**Figure 3.13 Palustrine associated paleosol (SAM2) with associated limestone lenses.**

At Sambullak the majority of the paleosols have a developed Bk horizon, which range from 6-80cm thick, although they are not as well developed as the paleosols seen at Boyevaya Gora. There is one horizon (SAM6) which has no Bk horizon and a light coloured, but non calcified surface horizon (Figure 3.14). The Bk horizons that are present are mostly stage II horizons (classification after Wright and Tucker 1991; Retallack 2001a; Alonso-Zarza 2003). Possibly, the basin at Sambullak was more active than at Boyevaya Gora and the paleosols did not have as much time to develop extensive Bk horizons (cf. Retallack 1997; 2001a). The stage II horizons are predominantly 50-25cm thick and have a similar morphology to the dispersed nodular bands seen at Boyevaya Gora.

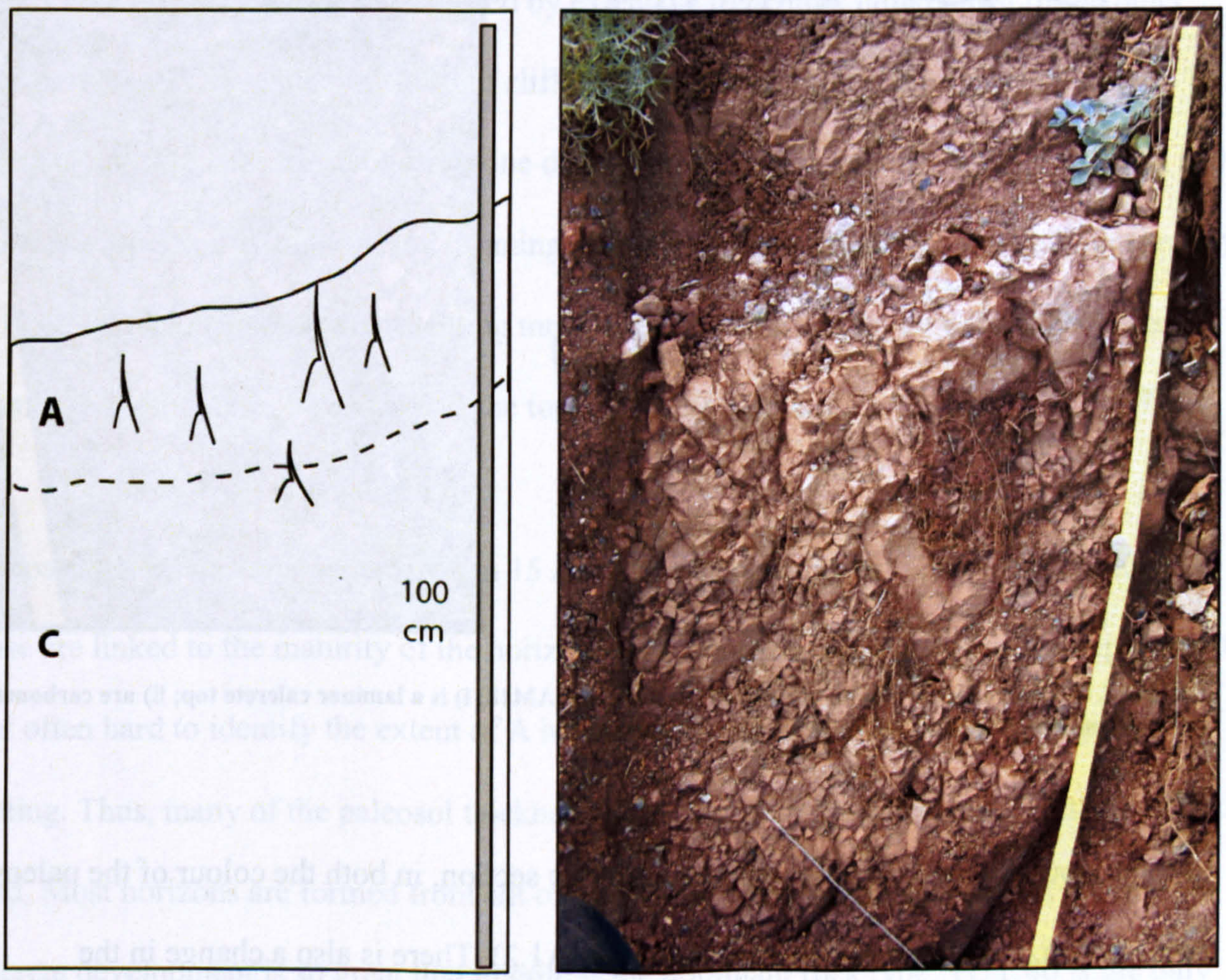


**Figure 3.14 A poorly developed paleosol (SAM 6) with light coloured A horizon and no Bk development (the scale is a metre in length).**

The stage III horizons are similar to those at Boyevaya Gora and range from 53-27cm in thickness. Some paleosols, such as SAM 5a, contain preserved tabular root systems (Figure 3.5A), suggesting that they formed in an area with a high water table (Retallack 1997). There

are two horizons (SAM 7 and SAM18) which have more developed Bk horizons. Both of these horizons were poorly exposed, but there was some evidence of laminar calcrete tops (of 10 and 17cm respectively, Figure 3.15) which would classify them at stage IV in Retallack's (2001) classification scheme or stage V as described by Alonso-Zarza (2003). However, SAM7 and SAM18 are both less developed as the Stage V Bk horizons at Boyevaya Gora.

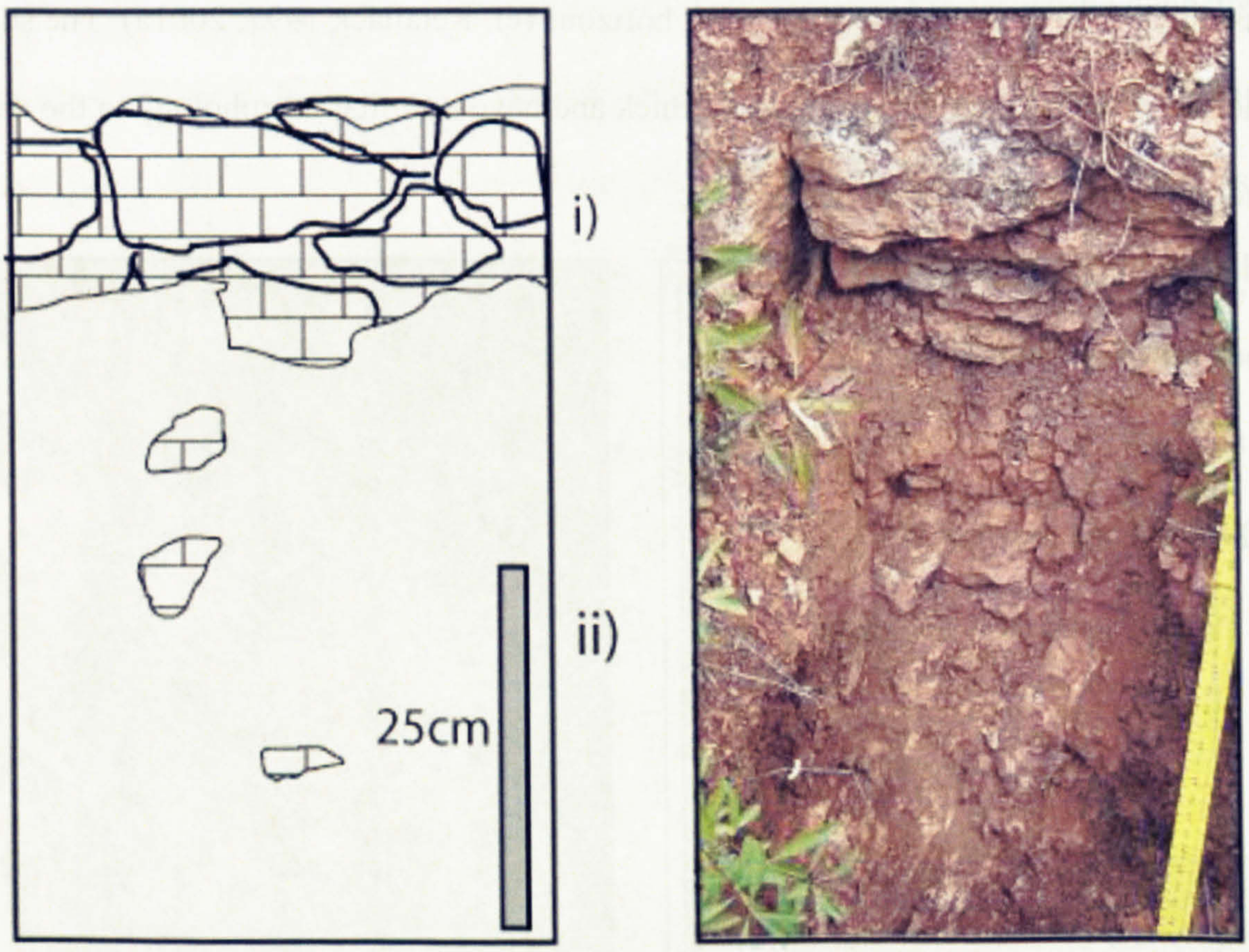


**Figure 3.15 A stage IV carbonate horizon at Sambullak (SAM18) i) is a laminar calcrete top; ii) are carbonate nodules below. Ruler at side of trench = 25cm.**

As previously stated there is some variation up section, in both the colour of the paleosols and the grain size of the sediment (see Appendix A1.2). There is also a change in the palaeoenvironment up section. The lower and mid parts of the section show evidence for minor temporary lacustrine influence, whereas two of the paleosols at the top of the section (SAM 1 and 3) below the start of the thick multi-storey have evidence of slickensides (Figure 3.8B) which implies drying out of the environment (cf. Kovda and Wilding 2004). There is

little variation in the development in the Bk horizons through the section, suggesting that this section had more active channels than seen at Boyevaya Gora and thus did not allow the paleosols as much time to develop (cf. Retallack 2001a).

### *3.3.3 Tuyembetka*

Seventy one paleosols were identified at Tuyembetka in a section which is 111 metres thick, more than in any other section studied (Figure 3.16, for individual paleosol descriptions see Appendix A1.3). Unfortunately the exposure at Tuyembetka is relatively poor as the section occurs on a hillside, which was exposed by extensive trenching, unlike most of the other Russian sections which are exposed in cliffs and steam-cut gullies. So, for many of the paleosols, it is impossible to observe fine details and features recorded in other sections and many are obscured by modern soil-forming processes. The section is comprised of primarily of Permian rocks probably representing most of the Lopingian (Taylor *et al.* 2009). The P/Tr boundary is thought to lie just above the top of the exposed section (Taylor *et al.* 2009).

The paleosol thicknesses vary between 15 and 130cm thick and, as with the other sections, these are linked to the maturity of the horizons (see Appendix A1.2). Due to the exposure, it was often hard to identify the extent of A horizons as they were often obscured by modern rooting. Thus, many of the paleosol thicknesses may actually have been underestimated in the field. Most horizons are formed from silt or clay grade sediment. In some cases the level of calcrete development is so great that micrite is the dominant rock type. TUY 40 is the only horizon that is predominantly of a fine-sand grain size and may relate to a paleosol forming in a disused minor channel.

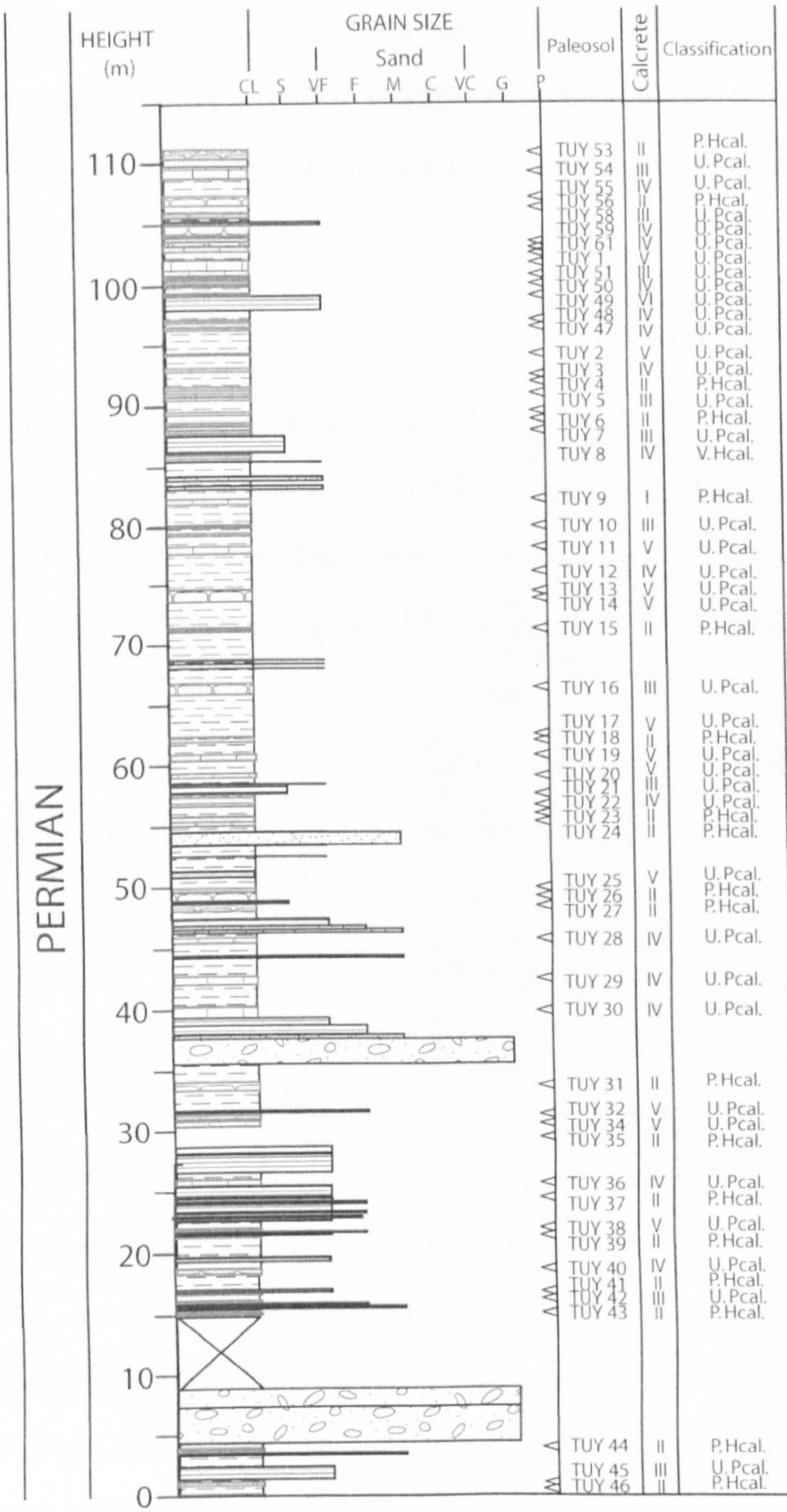


**Figure 3.16 The studied section at Tuyembetka. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols and classification (see Table 2.2). Note the relatively large number of paleosols per metre compared with other sections and the relative maturity of the carbonate within them (Sedimentological log data from unpublished field date by Dr A. Newell and Dr R. Twitchett).**

As with the other sections, root traces were observed throughout the section. They were especially evident in the well-exposed examples of Stage V and VI horizons where they are preserved as iron-stained root traces. However, in some of lesser developed calcrete paleosols it is also possible to observe root traces in the A horizons (examples TUY 6, TUY9, TUY10, TUY26, TUY46, TUY56). These often take the form of deep vertical root traces (Figure 3.17) related to vertical movement of water through the paleosol profile (Alonzo-Zarza 2003) suggesting a prevalent dry season (Retallack 1997).

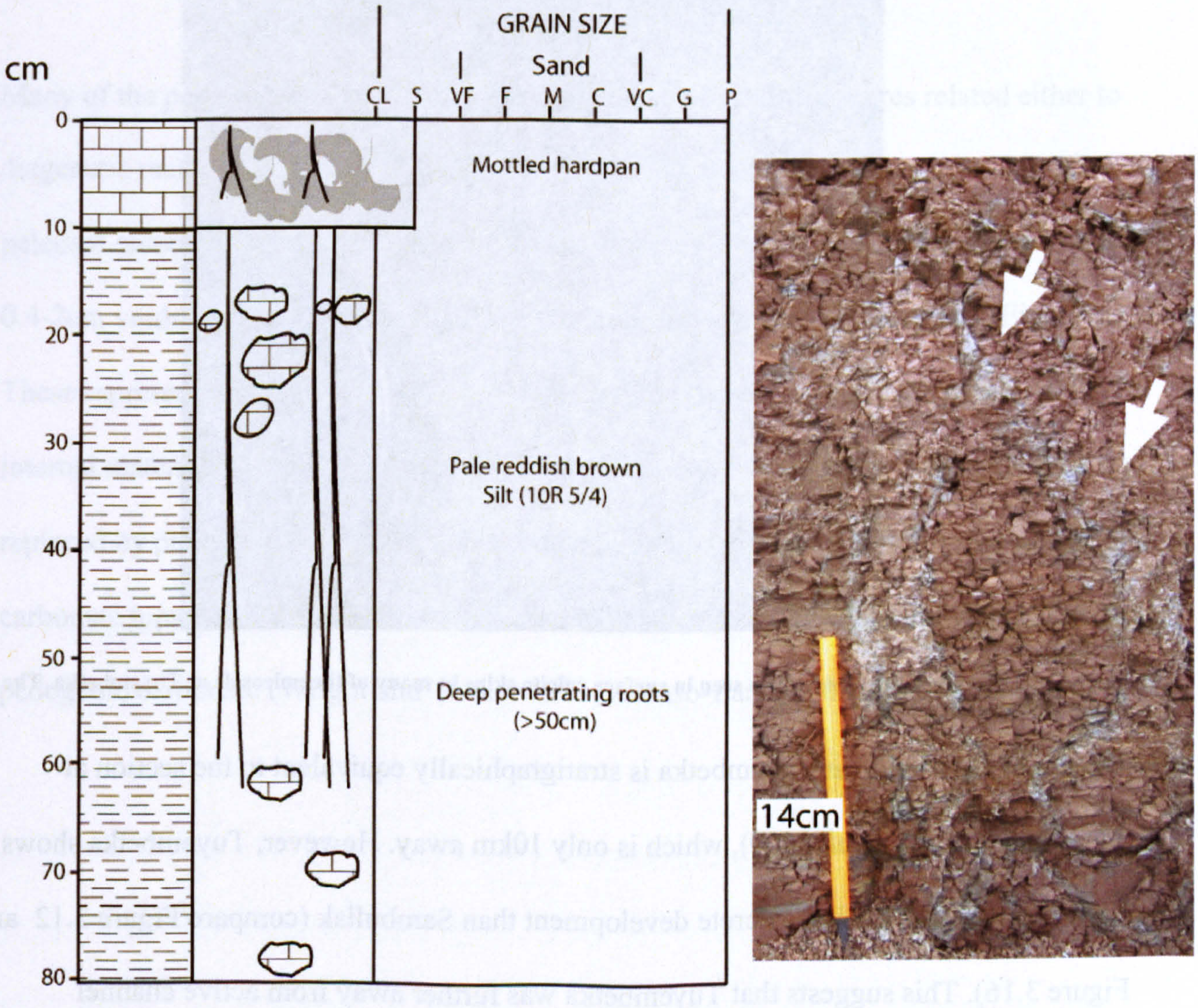


**Figure 3.17 Deep root traces at Tuyembetka (TUY46) which penetrate over 50cm. Deep penetrating root traces arrowed.**

The most evident feature of the paleosols at Tuyembetka is the level of calcrete development. Unlike the previous sections the average stage of Bk horizon development is stage IV. There is evidence of paleosols with stage VI Bk horizons (TUY 49 and 25) as described by

Retallack (2001). Both these horizons are relatively thin (53cm and 62cm respectively), although both show brecciated calcrete hardpans. There is also evidence in some of the calcrete hardpans of surface 'skins' (1-2mm thick) calcite with a characteristic 'knobbly' texture (Figure 3.18) possibly relating to repeated stages of recrystallisation. Even the stage II and III Bk horizons are more extensive and more indurated than those seen at any for the other sections in Russia (Figure 3.6C).

**Figure 3.18 'Knobbly' surface texture seen in surface calcite skins in many of the paleosols at Tuyembetka. The coin is 20mm in diameter.**

The top of the section at Tuyembetka is stratigraphically equivalent to the section at Sambullak (Taylor *et al.* 2009), which is only 10km away. However, Tuyembetka shows significantly more mature calcrete development than Sambullak (compare Figure 3.12 and Figure 3.16). This suggests that Tuyembetka was further away from active channel development, allowing more developed paleosols to form which were less likely to have been affected by groundwater originating from fluvial channels (Williams and Krause 1998). As these more mature paleosols take longer to form (Wright and Tucker 1991; Retallack 2001a; Alonzo-Zarza 2003).

The colour variation at Tuyembetka is also markedly different. Many of the paleosols are significantly redder than those elsewhere in Russia, and have chromae of 5R 8/2 – 5R 4/2 possibly relating to lack of moisture and organic matter relative to the other paleosols. Vertical variation seen at Tuyembetka is less evident than the other sections elsewhere in the basin. There is a decrease in the maturity of the calcretes in the lower parts of the section although this is not as marked as in other sections (Figure 3.16).

Many of the paleosols at Tuyembetka show evidence of calcitic features related either to diagenetic recrystallisation or to possible modern calcite formation (Figure 3.19A). The paleosol horizons with stage IV and above Bk horizons contain calcite-fills which manifest as 0.4-2cm voids that have been in filled by later euhedral sparry calcite crystals (Figure 3.19B). These represent original holes in the calcretes formed by roots or burrows of which the internal material has been removed by later diagenetic groundwater or diagenetic fluid and replaced by precipitated calcite crystals. Some paleosols (such as TUY 30) show diffuse carbonate tops and abrupt bases indicative of calcrete formed from groundwater rather than pedogenic carbonate (Wright and Tucker 1991; Alonso-Zarza 2003; Quast *et al.* 2006).

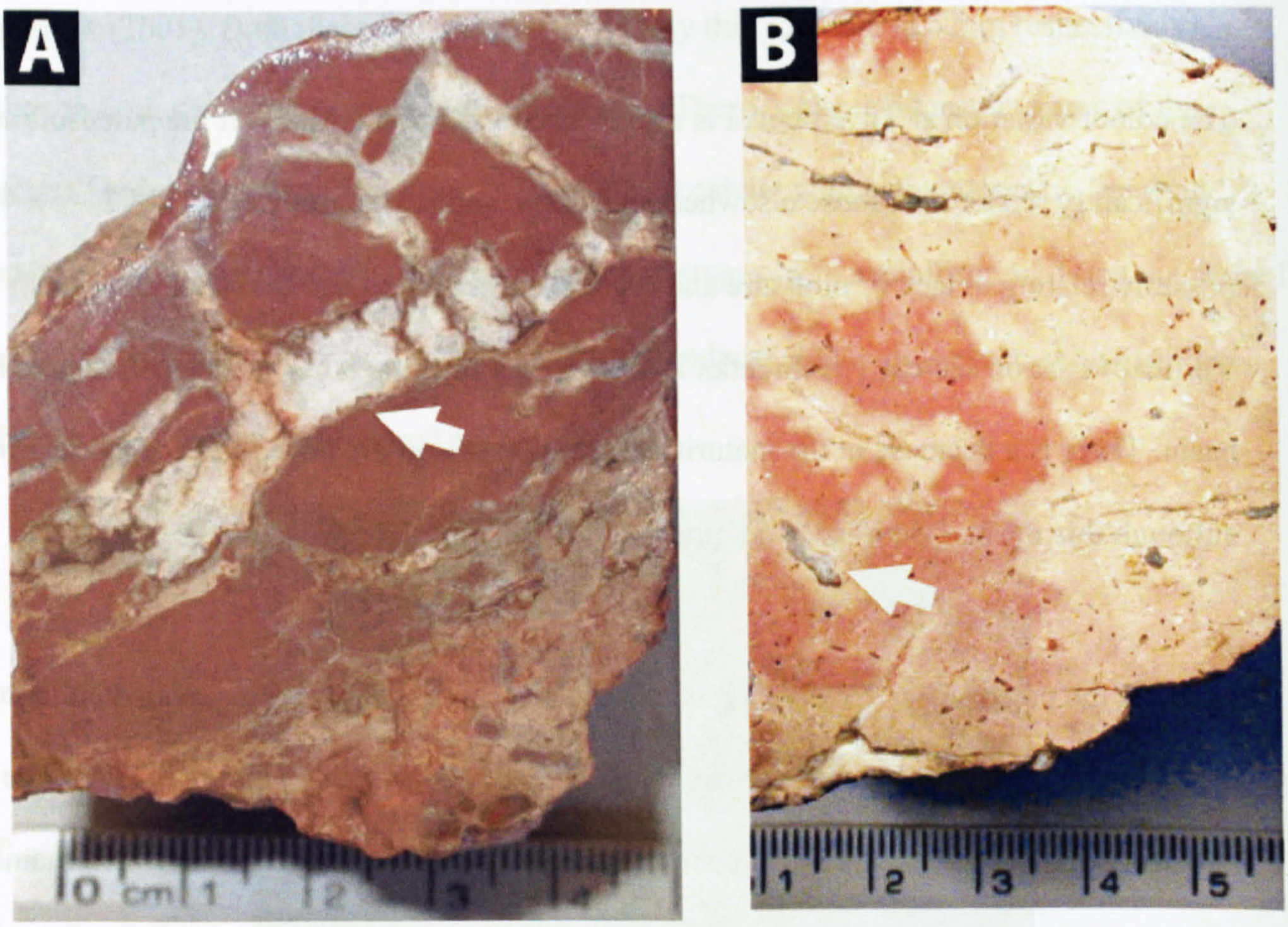


**Figure 3.19 Large cracks (A) and voids (B) in filled with sparry calcite seen at Tuyembetka. These exist in other sections but only at Tuyembetka are they cm in scale. Scale in both photos in centimetres.**

### *3.3.4 Vozdvizhenka*

Vozdvizhenka is a shorter section than those thus far described (33m in thickness) (Figure 3.20, for individual paleosol descriptions see Appendix A1.4). In total 17 paleosols were identified at Vozdvizhenka. The section at Vozdvizhenka is thought to cross the P/Tr boundary although its exact position is still debated (Taylor *et al.* 2009). The most prominent feature of the paleosols at Vozdvizhenka is the substrate from which they formed. Unlike almost all the other Russian sections, which are primarily formed of siltstones and claystones, the paleosols at Vozdvizhenka are formed from fine to very fine sandstone and unconsolidated siltstones.

All the paleosols at Vozdvizhenka have Bk horizons. However, unlike Tuyembetka or Boyevaya Gora, there is only one example of a paleosol containing a Bk horizon developed above stage II, and that is only stage III (Figure 3.20). Many of these nodules are either very large (5-6cm) or almost blocky in shape (Figure 3.21), suggesting they may be formed by groundwater rather than pedogenic meteoric water (Khadkikar *et al.* 2000; Alonzo-Zarza 2003). This is supported by the presence of mottling and the relative coarseness of the sediment which would have allowed increased groundwater flow.

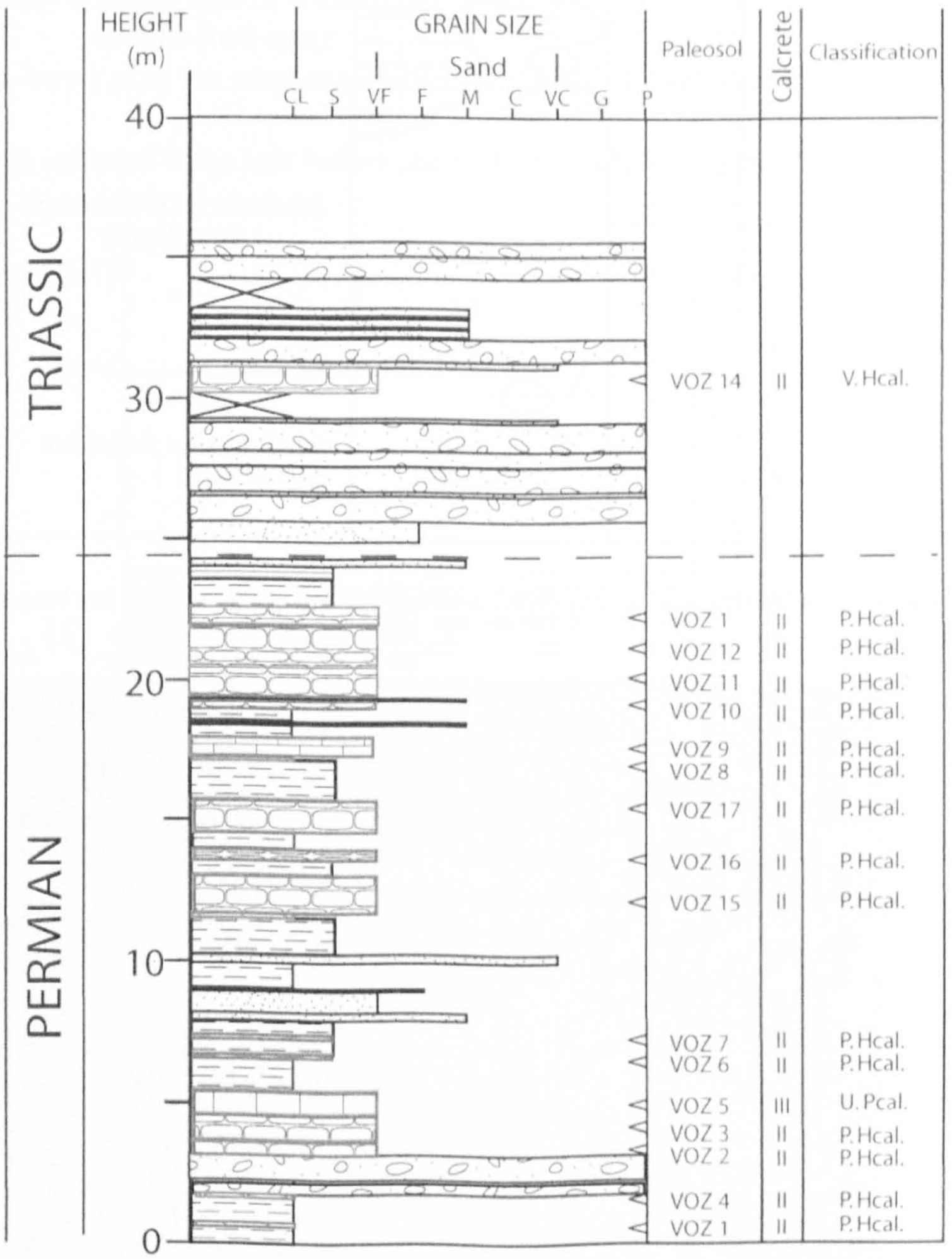


**Figure 3.20 The studied section at Vozdvizhenka. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols and classification (see Table2.2). P/Tr boundary based on magnetostratigraphy and sedimentology but due to poor magnetic recorded position of boundary is not precise (see Taylor *et al.* 2009). (Sedimentological data from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

There is, however, also evidence further up the section, 20cm below the P/Tr boundary, for pedogenic slickensides suggesting that there were periods when these paleosols must have periodically dried out. This paleosol (VOZ 14) also is capped by 3cm thick gravel beds (Figure 3.22) within which all clasts are well rounded and the lack of sorting would suggest a flash flood event (Leeder 1999).

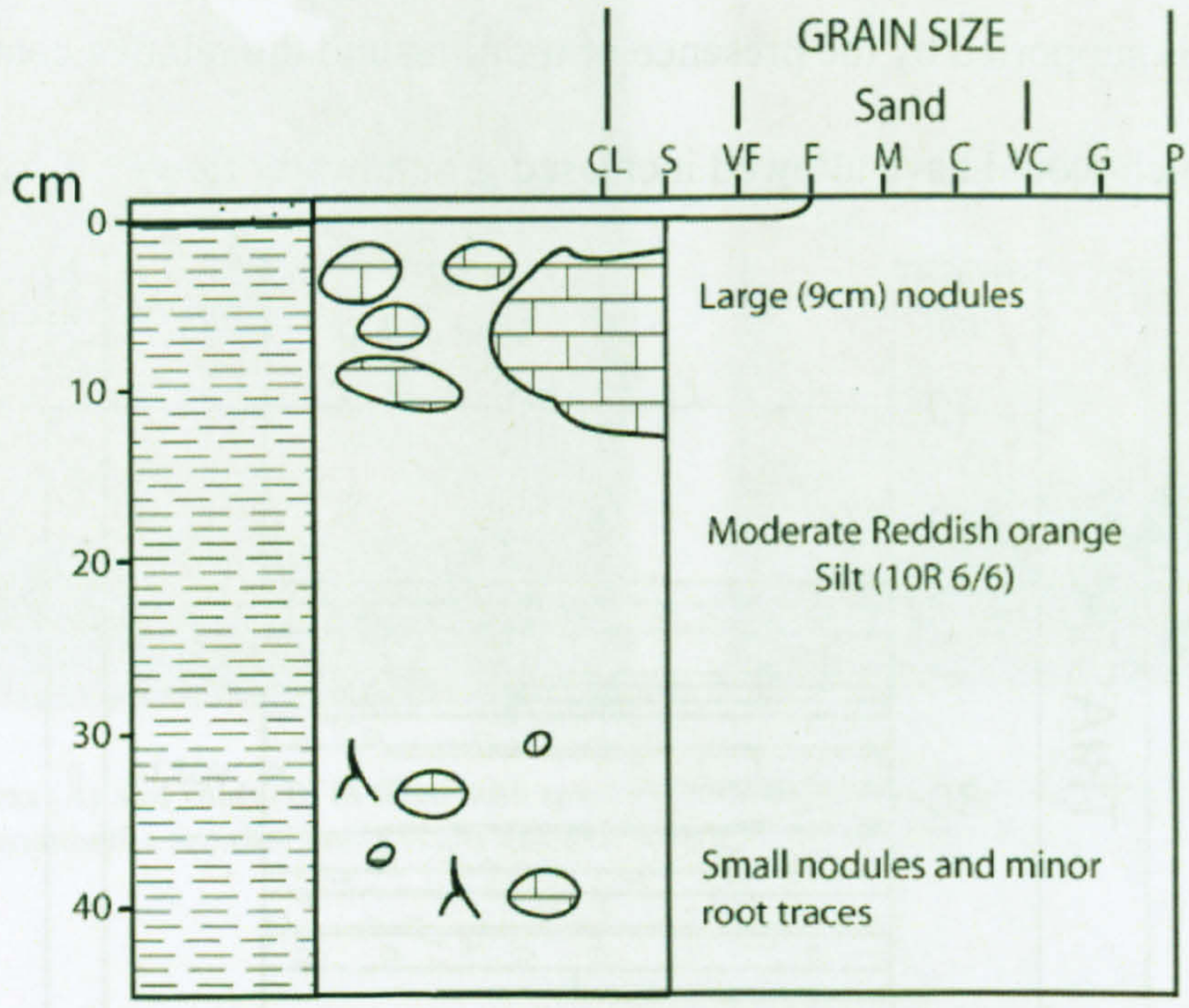


**Figure 3.21 Paleosol VOZ9 with large blocky (9cm) nodules. The top of this horizon has been eroded by the overlying sandstone bed.**

**Figure 3.22 Paleosol VOZ14 at Vozdvizhenka capped by 3cm gravel. Scale in cm.**

### *3.3.5 Krasnogor*

Krasnogor is 20km further south than the sections of Sambullak, Tuyembetka and Vozdvizhenka (Figure 3.2). The P/Tr boundary is thought to be at the base the coarse facies (Figure 3.23), however, the Lower Triassic sandstones at Krasnogor have yielded *Benthosuchus* fossils which has been assigned to the Staritskaya Svita (Tverdokhlebov *et al.* 2002), which may suggest that first Gorizont of the Triassic is missing (Figure 3.2) (Taylor *et al.* 2009). This being said the magnetostratigraphy yields a well defined Reverse-Normal change which is inferred to be just below the P/Tr boundary (Figure 3.3).

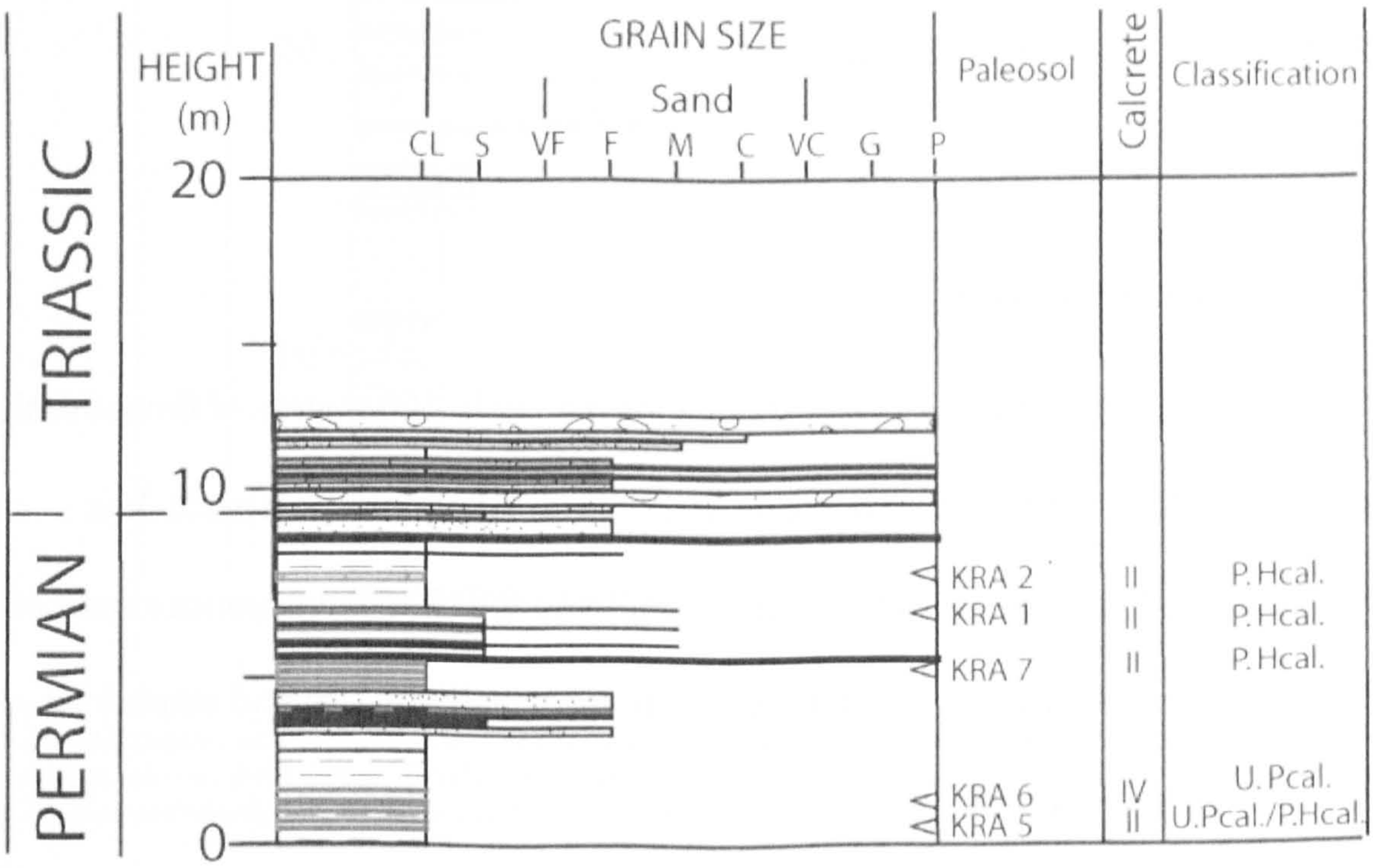


**Figure 3.23 The studied section at Krasnagor. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the development of the Bk horizons within the paleosols and classification (see Table 2.2). (Sedimentological data from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

Krasnagor shows many similar pedogenic features to the paleosols further north in the basin. In a section 21m thick a total of 6 paleosol horizons where identified (Figure 3.23) and, like at Vozdvizhenka, the Krasnagor horizons all show a developed calcitic Bk horizon (Figure 3.23), for individual paleosol descriptions see Appendix A1.5). Although the majority of the

paleosols also have stage II Bk horizons, there is one horizon at Krasnagor that shows stage IV development (KRA 6). This paleosol is only 36cm thick but shows a calcrete laminar top with some evidence of brecciation.

Like Vozdvizhenka the paleosol substrate is markedly coarser than the rest of the sections. It is composed predominantly of very fine to fine sandstone, and it also shows large nodules (>6cm), intense gleys and blocky continuous sheets of nodules suggesting a predominantly groundwater source in the formation of the carbonate (cf. Khadkikar *et al.* 2000; Alonzo-Zarza 2003). However, many of the nodule horizons have preserved (5-2mm in width) root traces implying that at least at some points the water table must have been below the level the of Bk horizon (cf. Alonzo-Zarza 2003).

### *3.3.6 Petropavlovka*

The section at Petropavlovka consists of approximately 100 metres of fluvial sandstones and mudstones along with channel deposits and occasional nodular paleosols. It is stratigraphically part of the Petropavlovskaya Svita which is the uppermost part of the Lower Triassic (Figure 3.3) and is constrained biostratigraphally by fish and amphibian remains (Tverdokhlebov *et al.* 2002).

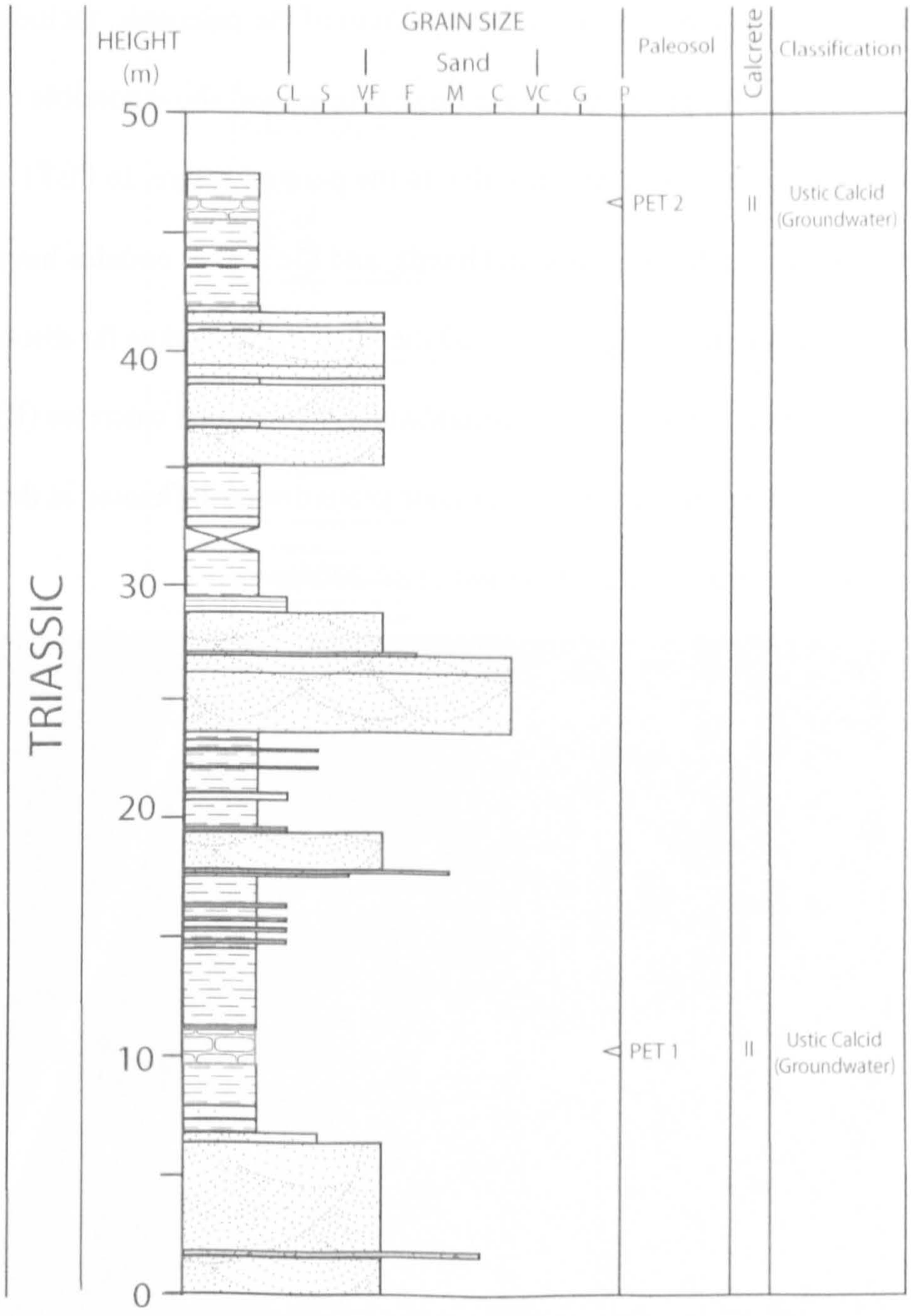


**Figure 3.24 The section at Petropavlovka. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols and classification (see table2.2). (Sedimentological data from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

The section is poorly exposed in a set of stream-cut gullies in the steppe and only yielded two identifiable paleosols (Figure 3.24, for individual paleosol descriptions see Appendix A1.6). All show green gleyed areas of up to 5cm (chromata 5G 8/1), which contrasts strongly with the moderate reddish orange (10R6/6) and light red (5R6/6) of the remaining paleosols (Figure 3.25 ). These gleys are concentrated in the top 10cm of the horizons although there are also mottled areas in the Bk horizons.

There is minor evidence of rooting in the top 25cm of the paleosols, including drab-root haloes. Also some of the Bk horizons are stage II level and show possible evidence of rooting, although identification is problematical due to the poor exposure. In PET1 in the lower part of the Bk horizon the nodules form distinct bands, and the higher nodules have gradational boundaries unlike the sharp edges observed the other sections thus far discussed (Figure 3.6 F). This is thought to be indicative of groundwater precipitated calcretes (Khadkikar *et al.* 2000). The excessive gleys also imply a major groundwater influence in the formation of the Bk horizons. (Khadkikar *et al* 2000; Quast *et al.* 2006).

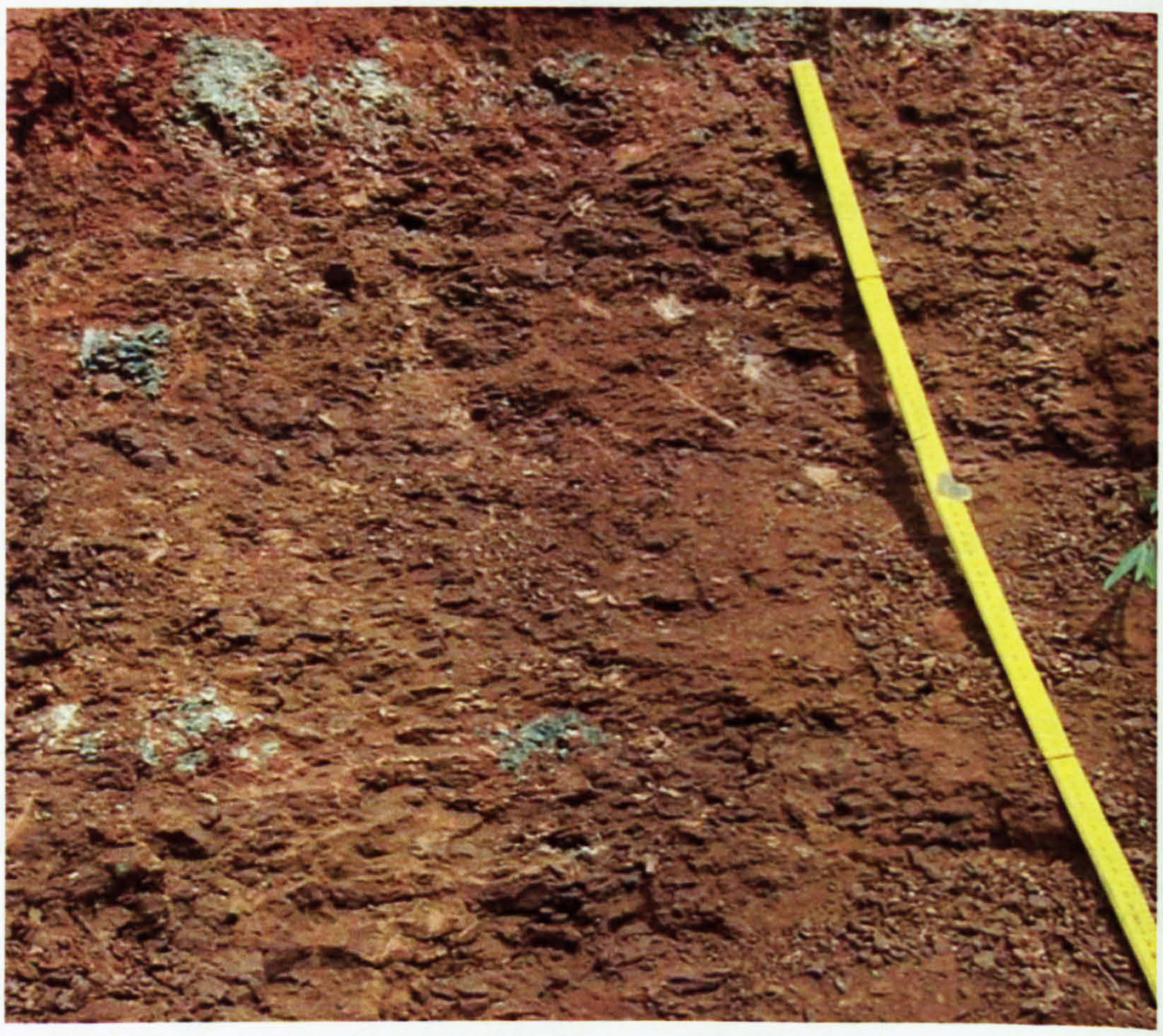

**Figure 3.25 (5cm) mottles areas in the paleosols at Petropavlovka. Scale is 1metre in length.**

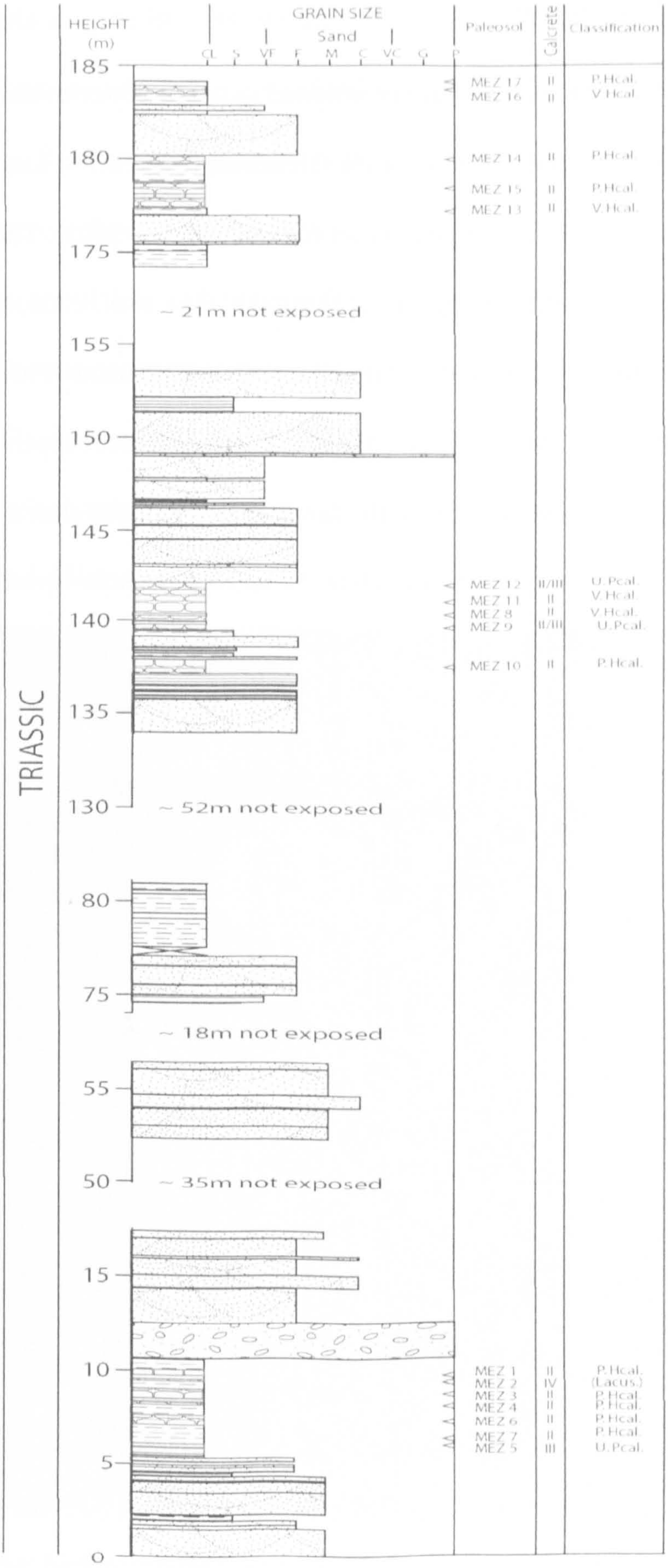


**Figure 3.26 The studied section at Mescheryakovka. The arrows (<) mark the position of the paleosols in the section. The calcrete column shows the relative development of the Bk horizons within the paleosols and classification (see Table2.2). (Sedimentological data from unpublished field data by Dr A. Newell and Dr R. Twitchett).**

### 3.3.7 Mescheryakovka

Mescheryakovka (184 metres thick) is assigned to the Petropavlovskaya Svita, Yarenskian Gorizont which is equivalent to top of the Olenekian (Figure 3.1) based on the occurrence of *Capitosauridae* and *Procolophoniae* (Tverdokhlebov *et al.* 2002). The section comprises of stacked sequences of tributary channels (Tverdokhlebov *et al.* 2002; Dr A. Newell and Dr R. Twitchett unpublished field data) and nodular paleosol horizons. There are 18 paleosol horizons (Figure 3.26, for individual paleosol descriptions see Appendix A1.7) which can be divided into two different pedotypes: the lower paleosols have similar affinities with paleosols from the Triassic of Boyevaya Gora, while the upper paleosols especially MES 16, have a morphology which is very different to anything else recorded in the Russian sections studied herein.

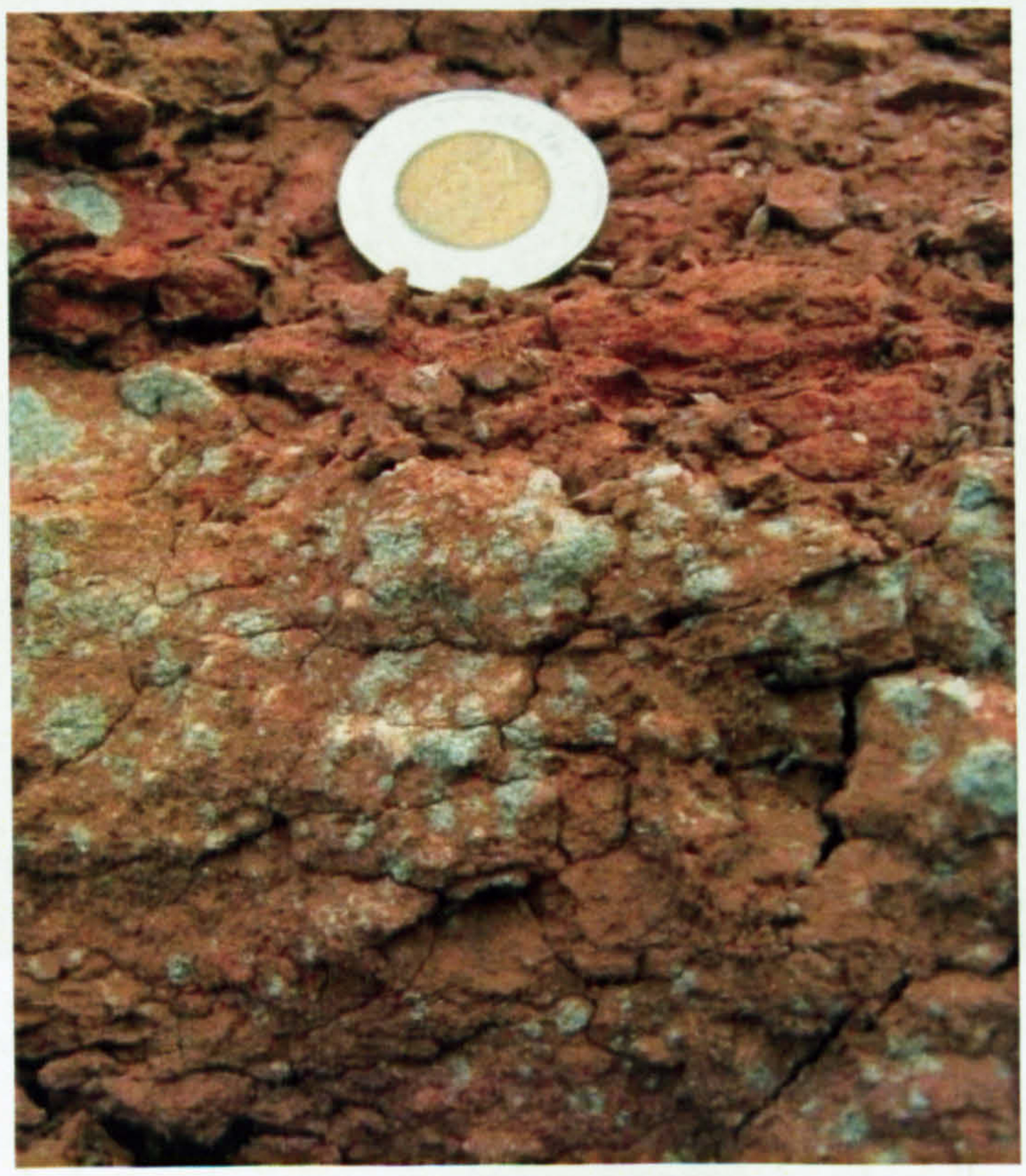

**Figure 3.27 'Speckled' gley in the A horizon of MES8. Coin 27mm in diameter.**

The lower paleosols (MES1, MES2, MES3, MES4, MES5, MES6, MES7, MES8 MES9, MES10, MES11, and MES12) are part of a stacked sequence made of siltstone. There is evidence for sparse root structures, although these only occur in the A horizons and never

penetrate the Bk horizons. The Bk horizons are only developed as far as stage II with relatively small (1-2cm) nodules and are confined to bands which are 10-40cm thick. Most of the A horizons have a light greenish grey gley (5G 8/1), while the lower horizons within the paleosol are a moderate yellowish brown (10YR 5/4) (Figure 3.27). In these lower paleosols there are some examples of deep (36cm) calcified rootlets (MES 8). From their irregular tubular shape and tapering appearance they have been tentatively identified as thick roots (after Retallack 1997). This is supported by the presence of calcite in these features which would suggest a rhizoconcretion, although an infilled crack could also act as a site for calcrete precipitation (Figure 3.28).


**Figure 3.28 Tubular rhizoconcretion from Mescheryakovka. Coin is 27mm in diameter.**

The upper paleosols at Mescheryakovka (MES14, MES15, MES16 and MES17) are quite different from anything else recorded in this study. The most striking feature is the change in colour: Rather than being shades of brick-red (10YR 5/4), like the rest of the Russian

paleosols, the colour of these paleosols is predominantly pale greenish yellow (10Y 7/2) and the A horizons are dominated by drab-root haloes of light red (5R6/6). The top 16cm of the paleosols have a gley of light bluish grey (5B 7/1) and contains possible desiccation cracks (Figure 3.29). The rooting in these horizons is dense (compared to previous paleosols) and extends from the paleosol surface down into the Bk horizon. The root traces are 10-15mm wide and show branching structures (Figure 3.29). They are preserved as drab haloes, suggesting waterlogging of the paleosol or a reducing environment allowing anaerobic bacteria to break down organic matter (Retallack 2001a).

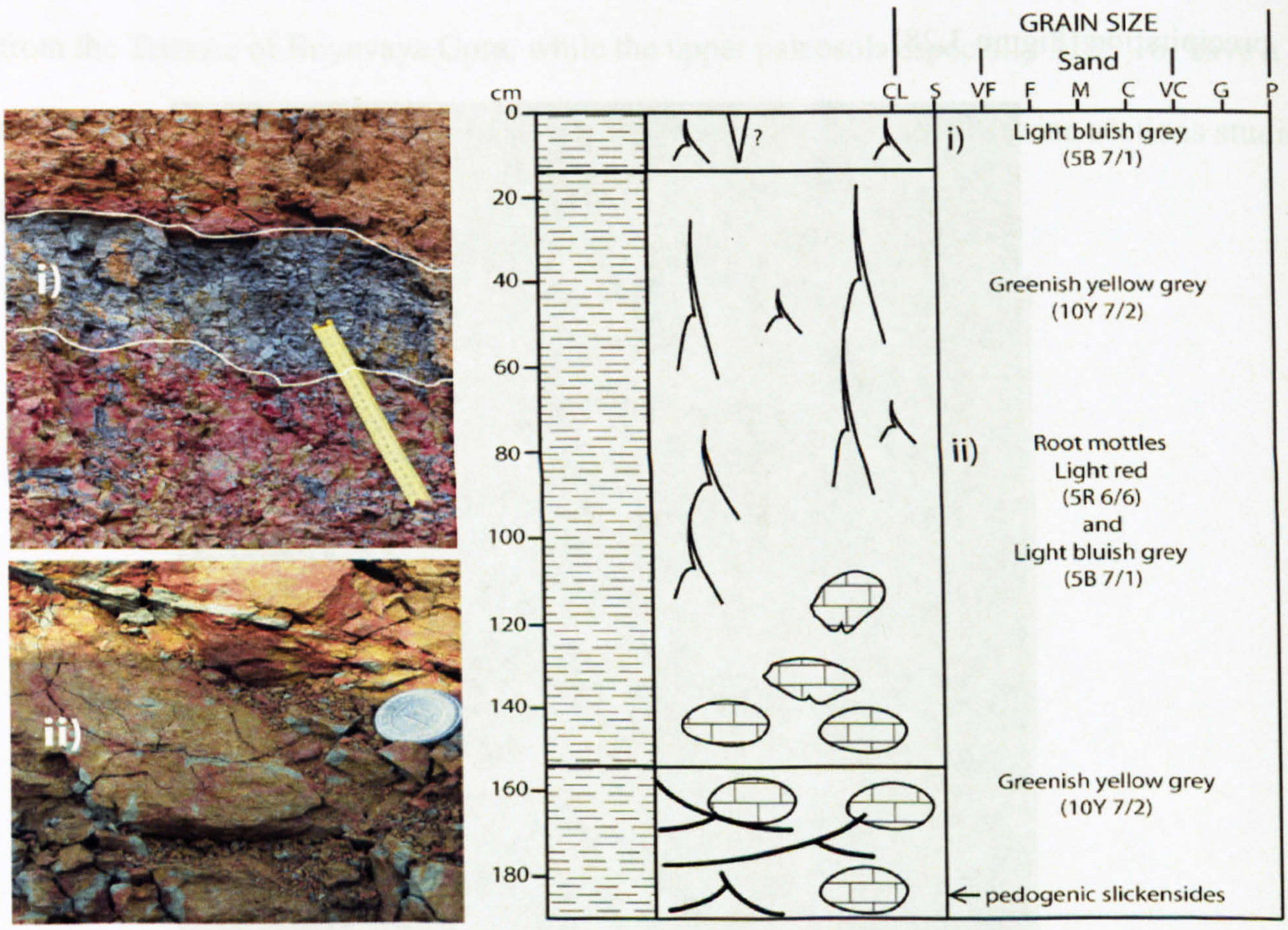


**Figure 3.29 Gleyed paleosol at the top of Mescheryakovka (MES16) showing deep rooting structures and extreme gleys. The numerals i) an ii) represent where in the log those photos were taken from (the scale in i) = 25cm and the coin in ii) is 20mm in size).**

Such gleys are commonly associated with swamp and fen facies (Retallack 1997). However, the Bk horizons directly below these gleyed horizons, contains evident pedogenic slickensides, which instead implies a periodic wetting and drying of the paleosol (cf. Kovda and Wilding 2004). The calcrete contained within the Bk horizon is of Stage II development

and is not concentrated within layers, nor does it show any other features associated with groundwater calcretes (cf. Khadkikar *et al* 2000; Quast *et al.*2006).

This apparent contradiction of associated gley and slickensides suggests that this is a pseudo-gley as described by Wright and Allen (1989). These form when the paleosols which are periodically, rather than permanently, waterlogged (Wright and Allen 1989). This would explain the juxtaposition of waterlogged features such as the gley, and features related to aridity (the developed Bk horizon and slickensides). It seems plausible that these paleosols formed in an arid environment allowing the formation of the deep root structure, slickensides and carbonate, and then the water table rose, or there was a period of intense rainfall which periodically flooded the paleosol creating anoxic conditions. Similar features have been recorded in the Plio-Pleistocene of Spain (Stokes and Mather 2000). Equally such features may be caused by reduction of iron hydroxides and oxides by anaerobic bacteria consuming organic matter while the paleosol is below the permanent water table (Retallack 2005a). These burial gleys can form in paleosols with no evidence of waterlogging and relate to the diagenetic process rather soil forming processes (Retallack 2005a). The reason for there limited occurrence within the upper paleosols at Mescheryakovka may be an increase in organic matter in these paleosols.

## 3.4 Discussion

### *3.4.1 Classification*

Classification of paleosols, as described in Chapter 2, can be a controversial process. Based on the simplified identification key of Retallack (1993) used in the field (Chapter 2, Figure 2.1) the paleosols in Russia are classified as either Vertisols based on the presence of

slickensides; Aridisols based on the presence of a Bk horizon which is less than 1metre from the surface; Alfisols for those paleosols with a Bk horizon deeper than 1m or Inceptisols based on the lack of a Bk horizon and the presence of a cambic epipedon.

There are other features seen in the Russian paleosols that can be positively identified as belonging to certain modern soil types and thus can also be used in classification. Several of the carbonate nodules show a ped nucleus, a feature unique to Vertisols, with a primarily spherical morphology, and have sharp boundaries with the surrounding sediment suggesting a pedogenic source (Khadkikar *et al* 2000). Also KOR 4 (Figure 3.9) has features that can be interpreted as being gilgai microtopography which is found in modern Vertisols (Kovda and Wilding 2004, Dr Nathan Sheldon, *pers. comm.*). Several paleosols (SAM 1, 3, KOR 4) have evidence of slickensides (Figure 3.8B) and mud cracks (SAM 10, 20, KOR1,11, 26) which are related to primary shrinking and swelling of the paleosol as it is wetted in the rainy season and subsequently dries out. These factors have been attributed to Vertisols (Khadkikar *et al.* 2000).

Cleveland *et al.* (2008), however, suggest that terms such as Vertisol should not be used as the USDA Soil Taxonomy (Soil Survey Staff, 1999) defines these as containing seasonally opening cracks and although wedge-shaped slickensides (see Figure 3.8B) are interpreted to be seasonally active, this is still an interpretation and cannot be tested. In their classification, Cleveland *et al.* (2008) suggest that paleosols showing these features as defined are being 'Vertic' and the rest of their name is derived from other characteristics (Table 3.1). Although they concede that if these paleosols could have been observed while they were still active soils they would be defined as being a 'Vertisols'. It is possible to use the parameters used by Cleveland *et al.* (2008) to classify many of the paleosols seen in Russia (Table 3.1) and to

build on the system they use to classify paleosols seen in Russia that are not seen in New Mexico. For instance KOR 4 (Figure 3.9) could be classified as being a 'Vertic Petrocalcid' based on having both Vertisol features and a petrocalcitic horizon. A petrocalcitic horizon is a subsurface soil horizon cemented firmly with calcium carbonate (Soil Survey Staff, 1999) and thus is synonymous to a Bk horizon of stage IV and greater levels of development (see Chapter 2). Equally SAM 6 (Figure 3.14) would be defined as being a Ustic Haplocambid as it has a light-coloured, but non-calcified surface horizon (ochric epipedon) and darker sub-horizon with minor mottles (cambic horizon) (Soil Survey Staff, 1999)(Figure 3.14). This paleosol also lacked any evidence of a Bk horizon and contained evidence of fine (<2mm) root traces.

| Soil order | Suborder | Classification | Diagnostic features | Russian soils showing similar features |
|---|---|---|---|---|
| Aridisols | Calcids | Ustic Haplocalcids | 1) Calcic horizon with upper boundary within 100cm of soil surface<br>2) Do not have a petrocalcitic horizon within 150cm depth of the mineral soil surface<br>3) do not have intersecting pedogenic slickensides | e.g. KOR36, KOR2, KOR6, KOR15, |
| | | Vertic Haplocalcids | 1) Large 25cm thick layer of intersecting slickensides within 100cm of the mineral soil surface<br>2) have 30% of clay in all fine earth fraction<br>3) Calcic horizon with upper boundary within 100cm of soil surface | e.g. KOR 5, SAM1. |
| | | Ustic Petrocalcids | 1) have a calsic or petrocalcitic horizon within 100cm of soil surface<br>2) have petrocalcitic horizon within 150cm of base of section<br>3) do not have intersecting pedogenic slickensides | e.g. TUY47 TUY 2 |
| | Cambids | Ustic Haplocambids | 1)Have a subsurface cambic horizon within 100 cm of the mineral soil surface or its lower boundary at a depth of 25 cm<br>2) do not have a calcic or petrocalcic horizon unless its upper boundary is more than 100 cm below the mineral soil surface<br>3) do not have intersecting pedogenic slickensides | e.g. SAM6 |

**Table 3.1 Classification used by Cleveland *et al.* (2008) in the Late Triassic of New Mexico being a simplification of the USDA Soil Taxonomy system (Soil Survey Staff, 1999). Also a list of Russian examples which show the features used by Cleveland *et al.* (2008).**

However, the USDA Soil Taxonomy system (Soil Survey Staff, 1999) used by Cleveland *et al.* (2008) cannot be used to distinguish non lacustrine or groundwater paleosols from those with identifiable lacustrine and groundwater influenced paleosols such as those seen in some

of the Russian sections. This is because all these paleosols in Russia have a Bk horizon with a depth less than 1m and thus would be classified as Aridisols (after Retallack 1993) or Ustic Haplocalcids (after Cleveland *et al.* 2008). Differentiating of paleosols formed, or influenced by, lacustrine or groundwater processes is important when studying the geochemistry of carbonate material formed in these paleosols. This is because the isotopic composition in such paleosols is controlled by fractionated ground and lacustrine waters rather than meteoric waters (Cerling and Quade 1993; Alonso-Zarza 2003).

These paleosols can be identified in the field by being both rooted and having features that relate to a palustrine setting such as thin limestone beds containing ostracod fossils (KOR 17 and 25) and laminated limestone lenses (SAM 2) (see, Figure 3.7 and Figure 3.8). Equally paleosols dominated by groundwater processes can be identified by having nodules with diffuse boundaries that forming distinct bands (PET 1 and PET 2, Figure 3.6F), (Wright and Allen 1989; Khadkikar *et al.* 2000). Thus, new terms must be used to differentiate these paleosols.

Cleveland *et al.* (2008) suggests the presence of intense gleyed colours could be used to indicate waterlogging but some of the lacustrine associated paleosols (e.g. SAM2, Figure 3.13) have no evidence of gleyed colours.

| Classification after Retallack [a] | Classification using USDA horizons [b] | Diagnostic features | Examples |
|---|---|---|---|
| Inceptisols | Ustic Haplocambids | 1) Have some relict structures [a]<br>2) Does not have intersecting pedogenic slickensides [a+b]<br>3) Do not have a calcic or petrocalcic horizon [a+b]<br>4) Have a subsurface cambic horizon within 100 cm of the mineral soil surface or its lower boundary at a depth of 25 cm [b] | e.g. SAM6 |
| Vertisols | Vertic Haplocalcids | 1) Have no relict structures [a]<br>2) Large 25cm thick layer of intersecting slickensides within 100cm of the mineral soil surface [a+b]<br>3) Has have a calcic or petrocalcic horizon [a+b]<br>4) Calcic horizon with upper boundary within 100cm of soil surface [b]<br>5) have 30% of clay in all fine earth fraction | e.g. KOR5, SAM1 |
| Vertisols | Vertic Petrocalcids | 1) Have no relic structures [a]<br>2) Large 25cm thick layer of intersecting slickensides within 100cm of the mineral soil surface [a+b]<br>3) Have a calcic or petrocalcic horizon [a]<br>4) Calcic horizon with upper boundary within 100cm of soil surface [b]<br>5) have petrocalcic horizon within 150cm of base of section [b] | e.g. KOR4 |
| Aridisols | Ustic Petrocalcids | 1) Have no relict structures [a]<br>2) Does not have intersecting pedogenic slickensides within 100cm of the mineral soil surface or other shrink swelling structures [a+b]<br>3) Have a calcic or petrocalcic horizon [a]<br>3) Have a calsic or petrocalcic horizon within 100cm of soil surface [b]<br>4) Have petrocalcic horizon within 150cm of base of section [b] | e.g. TUY47 TUY2 |
| Aridisols | Petronodic Haplocalcids | 1) Have no relict structures [a]<br>2) Does not have intersecting pedogenic slickensides within 100cm of the mineral soil surface or other shrink swelling structures [a+b]<br>3) Have a calcic or petrocalcic horizon [a]<br>4) Calcic horizon with upper boundary within 100cm of soil surface [b]<br>5) Do not have a petrocalcic horizon within 150cm depth of the mineral soil surface [b]<br>6) One or more horizons, within 100 cm of the soil surface and with a combined thickness of 15 cm or more, that contain 20 percent or more (by volume) nodules or concretions [b] | e.g. KOR36, KOR2, KOR6, KOR15, |
| Aridisols/Alfisols | Ustic Calcids (Lacustrine) | 1) Have no relict structures [a]<br>2) Does not have intersecting pedogenic slickensides within 100cm of the mineral soil surface or other shrink swelling structures [a+b]<br>3) Have a calcic or petrocalcic horizon [a]<br>4) Calcic horizon with upper boundary within 100cm of soil surface [b]<br>5) Have petrocalcic horizon within 150cm of base of section [b]<br>6) Is associated with lacustrine limestone; contains ostracods or forms in channel fills [c] | e.g. KOR17, SAM2, |
| Aridisols | Ustic Calcids (Groundwater) | 1) Have no relict structures [a]<br>2) Does not have intersecting pedogenic slickensides within 100cm of the mineral soil surface or other shrink swelling structures [a+b]<br>3) Have a calcic or petrocalcic horizon [a]<br>4) Calcic horizon with upper boundary within 100cm of soil surface [b]<br>5) Have petrocalcic horizon within 150cm of base of section [b]<br>4) Carbonates which has diffuse boundaries and forms distinct lines [c] | e.g. PET 1, PET 2 |

**Table 3.2 Paleosol classification used in this study and the equivalent classifications based on the Retallack (1993) classification and Soil Staff Survey (1999).The diagnostic features are primarily based on the definitions in the USDA Soil Taxonomy system classifications but with additions to differentiate groundwater and lacustrine related paleosols. The bracketed terms refer terms not used in the USDA classification or where the one of the classification terms is inferred.**

**[a] After a literal interpretation of Figure 2.1 (Chapter 2) from Retallack (1993, 1997, 2001) [b]After Soil Staff Survey (1999) Cleveland *et al.* (2008). [c] criteria used to differentiate between lacustrine and groundwater carbonates (see text).**

Therefore in an attempt to encapsulate all this detail an abridged version of USDA Soil Taxonomy system as adapted by Cleveland *et al.* (2008) was used. For those paleosol types which are not adequately described by this method, as discussed above, modifiers were used. Lacustrine and groundwater derived carbonates have been divided for the reasons given above and are identified by placing "(lacustrine)" or "(groundwater)" after the USDA taxonomic name.

Finally it is possible that some of these paleosols may represent soil types which no longer have any direct modern analogue. For instance modern Mollisols are classified primarily on the presence of a mollic epipedon, which is a dark (organic-rich), well-structured surface horizon (Soil Survey Staff 1999; 2006; Retallack 2001a). This is directly related to an extensive and dense root network of grasses (Retallack 2001a). However, grasslands did not evolve until the middle Tertiary and it has been suggested that previously forests may have graded out into scrub and then to true desert vegetation (Retallack 2001a). Some of the palcosols (e.g. KOR6) in the Russian sections have features similar to those seen in Mollisols; for instance many of the lack any shrink–swell structures which would classify them as Vertisols and evidence of water saturation within 100cm of the palaeosurface (cf. Soil Survey Staff 1999). Therefore it may be possible that some of the paleosols represent a soil type that has become 'extinct' which, in the modern world, have been replaced by Mollisols.

### *3.4.2 Palaeoenvironmental interpretation*

Palcosols are an extremely valuable tool for understanding palaeoenvironmental conditions. Using the environmental classification of Retallack (1994), the presence of such features as relatively abundant rooting traces of between 2-6mm wide, some of which are deeply penetrating, and a developed Bk horizon, would indicate that most of these Russian paleosols

formed in a brakeland, wooded grassland or desert shrubland environment. The extremely well developed Bk horizons in many Permian paleosols, some of which are shallow (e.g. KOR4) may point to desert shrubland as being the best modern analogue (cf. Retallack 1994). The Triassic paleosols, especially those of the Olenekian (Petropavlovka and Mescheryakovka) may represent dry woodlands, based on the presence of deeply penetrating roots and deep Bk horizons (cf. Retallack 1994) although this assumes modern environmental analogues are valid when applied to the Permian–Triassic periods.

The palaeoenvironment inferred from the paleosols agrees with previous interpretations which have concluded that in the Late Tatarian (Kulchumovskaya Gorizont) the palaeoenvironment of the South Urals shifted from lacustrine to meandering rivers. The over-bank deposits of this time are thought to have been dry, semi-arid steppe-land which was not flooded for thousands of years (Newell *et al.* 1999; Tverdokhlebov *et al.* 2005). A low-shrub Tatarian flora was thought to have made up the ground cover, which in some areas was dominated by herbaceous lycopods and horsetails and in others by conifers and gymnosperm flora (Tverdokhlebov *et al.* 2005; Dr. M. Stephenson, *pers. comm.*).

| Section | Level of Calcrete development | | | | | | Average depth to Bk horizon (cm) |
|---|---|---|---|---|---|---|---|
| | None | II | III | IV | V | VI | |
| Boyevaya Gora | _ | 20 | 9 | 9 | 2 | _ | 22 |
| Krasnogor | _ | 11 | 3 | 1 | _ | _ | 24 |
| Sambullak | 1 | 22 | 6 | 2 | - | | 37 |
| Tuyembetka | - | 20 | 13 | 17 | 14 | 1 | 38 |
| Vozdvizhenka | _ | 14 | 3 | _ | _ | _ | 45 |
| Mescheryakovka . | _ | 13 | 3 | 1 | _ | _ | 51 |
| Petropavlovka | _ | 2 | _ | _ | _ | _ | 37 |

**Table 3.3 Summary of the numbers of different levels of Bk development in the South Urals, Russia. See Appendix 1 for more detailed descriptions.**

The variation in type and features of paleosols between sections gives a more detailed insight into the differences in palaeogeography across the basin in the Permian. As the level of calcrete development can be used as a proxy for time (Retallack 1994; Retallack 2001a), sections containing more mature paleosols were further away from areas of active channel development. At Sambullak and Krasnagor there are considerably fewer mature paleosols (greater than stage II development) than at Tuyembetka (Table 3.3) despite their relative geographical closeness (Figure 3.2). This suggests that Sambullak and Krasnogor were closer to the active river system, while Tuyembetka represents a part of the basin further away from the rivers, possibly on a palaeohigh. As such it was only affected by the most dramatic flood events and was drier, with time to form more mature calcrete profiles.

The uppermost Lower Triassic (Petropavlovskaya) is thought to be more arid than the Permian in the South Urals (Tverdokhlebov *et al.* 2002). This is confirmed by the evidence from Petropavlovka as the only carbonate material found formed by groundwater, rather than meteoric, based on the irregular nature of the nodules (Khadkikar *et al* 2000; Quast *et al.* 2006 see Figure 3.6F). The presence of only groundwater-related carbonate at this section may suggest a depressed water table, indicating more arid conditions (cf. Alonso-Zarza 2003). Mescheryakovka also shows evidence of deep rooting, slickensides, and carbonate related to arid environments (cf. Wright and Allen 1989;, Figure 3.29). However, Mescheryakovka also record the deepest average depth to Bk horizon when compared to the Permian sections (Table 3.3) suggesting this section was wetter (cf. Retallack *et al.* 2003). One solution is that there was an increase in seasonality and intensity of rainfall rather than a wetter climate (cf. Wright and Allen 1989).

### *3.4.3 Changes across the P/Tr boundary*

The section at Boyevaya Gora has paleosols spanning the P/Tr boundary and records a distinct change in paleosol morphology between the last paleosols of the Permian and the first paleosols of the Triassic. Some of these changes are similar to changes reported from paleosols in both Antarctica and Karoo across the P/Tr boundary. The most striking similarity is the colour shift from a brick-red (10R) to a browner hue in the Triassic, seen in both Karoo (2.5.YR) (Retallack *et al.* 2003) and Russia (5GY) (Figure 3.30). Also, as in Antarctica and Texas (Retallack and Krull 1999; Krull and Retallack 2000; 2005c), the first paleosols of the Triassic are poorly developed and linked to an increase in coarse-grade sediments.

The Russian Late Permian paleosols have dispersed carbonate nodules, which in Karoo have been linked to the influence of monsoonal activity (Retallack *et al.* 2003; Retallack 2005b). However, unlike Karoo, the earliest Triassic carbonate nodules in Russia do not form deeper, well-focused zones; instead they become smaller and more ephemeral (Figure 3.30). This may suggest that, unlike Karoo, the Russia paleosols show an increase in rainfall earliest Triassic which causes a deepening of the Bk horizon (cf. Retallack 1994). The Triassic paleosols at Boyevaya Gora were, however, undoubtedly wetter than those of the Permian as roots are only poorly preserved as minor drab root haloes (Figure 3.11A) rather than as reddened clay in fills. This may be due to the Triassic paleosols being formed when the basin was more active and dominated by braided river channels increasing the amount of water present in the basin. This is supported by the fact that many of the Triassic paleosols are overlain by strongly gleyed sandstone beds (Figure 3.11 B), indicating flooding and waterlogging of the paleosols below.

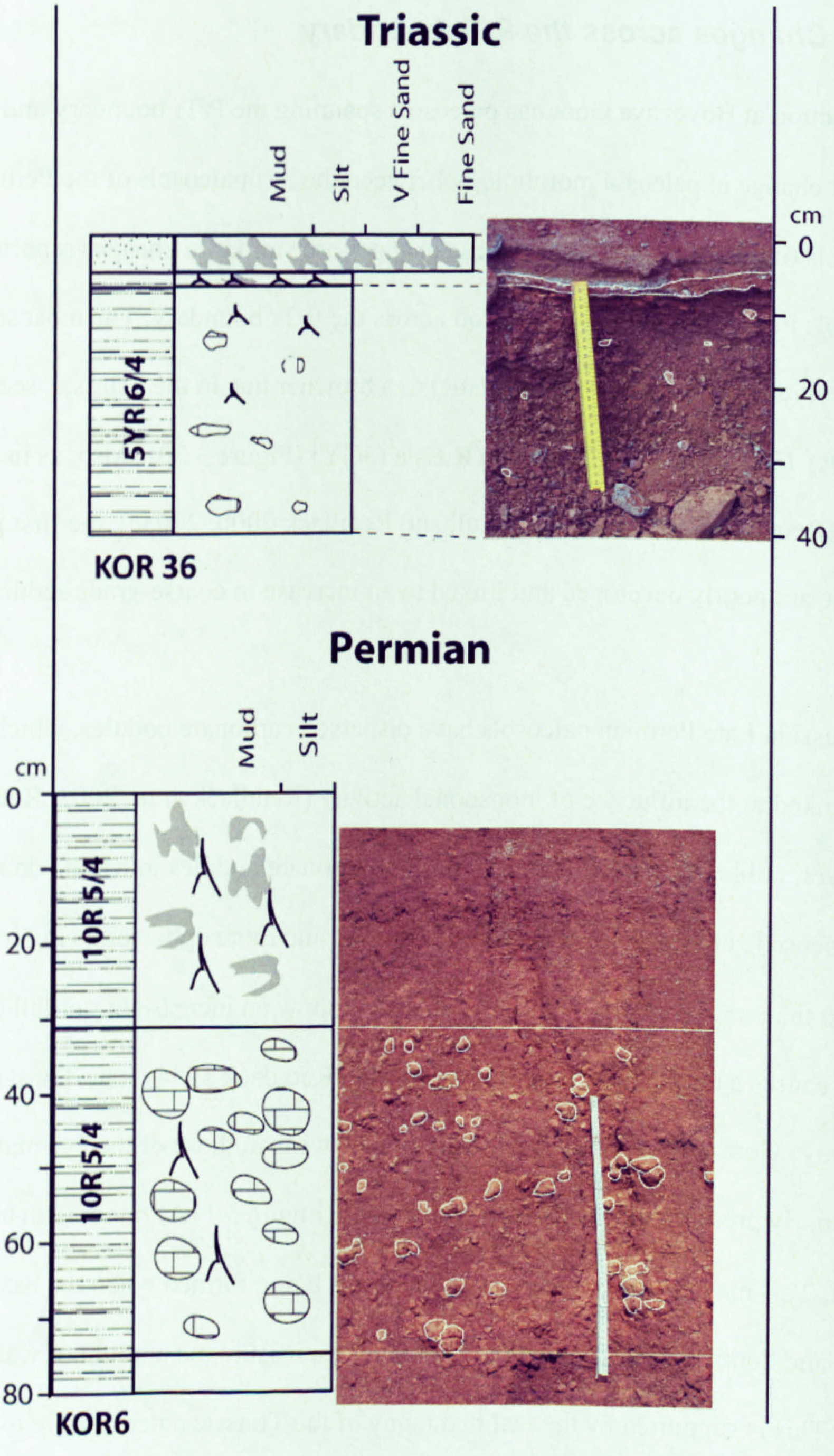


**Figure 3.30 Typical Stage II paleosols from the Permian and Triassic of Boyevaya Gora. Note the change in colour and thickness between the paleosols.**

In the interval just prior to the P/Tr boundary there is the appearance of pedogenic slickensides suggesting Vertisol forming conditions at Sambullak, Boyevaya Gora and

Krasnagor (see Figure 3.4, Figure 3.12, Figure 3.23). At Boyevaya Gora paleosols with Vertic features first appear ~210m before the boundary (Figure 3.4), while in the others these features first occurs 1-5metres before the P/Tr boundary. Vertisols are often interpreted as being associated with sub-humid climates (Khadkikar *et al.* 2000), although equally they may just suggest an increase in seasonality preceding the P/Tr boundary as the presence of pedogenic slickensides indicate repeated wetting and drying of the paleosol (Soil Staff Survey 1999; Khadkikar *et al.* 2000).

## 3.5 Summary

Overall the paleosol evidence from Russia suggests that the Permian represented a desert scrubland environment. In the Triassic this dry environment continued but the presence of possible depressed water suggest an increase in amount of waterlogging of the paleosols:

1. Similar to what is observed in Antarctica and the Karoo basin, there is a distinct change in paleosols across the P/Tr boundary itself from more stable, better-developed, paleosols to less-developed, less stable paleosols in the earliest Triassic. This change is related to a change in facies, from meandering fluvial systems to coarse conglomeratic fans;

2. Unlike the paleosols at Karoo, the earliest Triassic in Russia paleosols do not show a deep calcic horizon (although they are present at the top of the Early Triassic at Mescheryakovka) suggesting that the climate there was not an increase in rainfall just after the P/Tr boundary, as in Karoo;

3. Also in Russia Vertisols increase in the Latest Permian, suggesting that the palaeoclimate may have already started to change in the Southern Urals before the P/Tr boundary.

# Chapter 4. Isotopic and mineralogical variation in paleosols from the Southern Urals

## 4.1 Introduction

There have been many studies that have used the stable isotopic composition of pedogenic carbonate from throughout the Phanerozoic to investigate changes in atmospheric $CO_2$, temperature and atmospheric chemistry (Cerling 1991; Mora *et al* 1991; Liu *et al.* 1996; Cerling and Quade 1993; Ekart *et al* 1999; Ghosh *et al.* 2001; Robinson *et al.* 2002; Dworkin *et al.* 2005; Prochnow *et al.* 2006; Quast *et al.* 2006; Tarbor *et al.* 2007). This is because pedogenic carbonate is formed in equilibrium with meteoric water at atmospheric temperatures and $pCO_2$ values, and thus is directly affected by changes in atmospheric chemistry (Cerling 1991; Mora *et al* 1991; Cerling and Quade 1993; Ekart *et al* 1999). However, all the authors listed above stress that efforts have to be made to discern between those isotopic values that reflect the primary pedogenic carbonate, and those that reflect later alteration, be it by groundwater fluids, diagenesis or even telogenesis, all of which can overprint the primary pedogenic values.

From the seven sections studied in the field (Chapter 3), the sections at Boyevaya Gora and Sambullak were chosen for rigorous isotopic study with the aim of recovering a palaeoclimatic signal. Preliminary investigation was carried out at Tuyembetka Krasnogor and Mescheryakovka. Boyevaya Gora and Sambullak were chosen for rigorous isotopic study because (1) they both represent the most extensive sections that either cross or come up to the P/Tr boundary, (2) the paleosols present did not exhibit strong groundwater morphologies, such as at Vozdvizhenka and Petropavlovka (see Chapter 3), and (3) they contain the highest proportion of stage II carbonate nodules, which have been identified as having the highest

potential to preserve palaeoclimatic data (Ekart *et al.* 1999; Alonso-Zarza 2003, Dworkin *et al.* 2005). In addition, preliminary assessments were made of paleosols at Tuyembetka to assess isotopic variation in drier sedimentary settings in the Permian, and at Krasnogor to look at variation across the basin. Also paleosols from Mescheryakovka to were analysed to gain insights into isotopic variation in the Olenekian.

## 4.2 Isotope results

At Boyevaya Gora micritic carbonate was analysed from a total of 37 paleosols (see Chapter 2), of which 33 were horizons from the Permian and 5 from the earliest Triassic (see Appendix A2.1). In addition; 47 paleosols from Sambullak, 19 at Tuyembetka and 8 at Krasnogor were analysed of which all were Permian. Figure 4.1(and Appendix A2.1) shows the unscreened isotopic results for the micritic carbonate analysed from the Permian sections. Also 8 paleosols from the Triassic section at Mescheryakovka were analysed (see Figure 4.2 and Appendix A2.1).

There are four excursion events identified in the isotopic results in the Permian (P1, P2, P3, P4,) and two in the Triassic (Tr1, Tr2) (Figure 4.1). P1, P2, P3 and Tr2 all occur in both the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values while P4 and Tr1 are only recorded in the $\delta^{18}O_{carb}$ values. P1 is only recorded at Boyevaya Gora, and represents an excursion of –9‰ in $\delta^{13}C_{carb}$ values and –4‰ in $\delta^{18}O_{carb}$ values. This excursion is constrained to the values within one paleosol (KOR35) (Appendix A2.1). P2 is also only recorded at Boyevaya Gora. The $\delta^{13}C_{carb}$ record has an excursion of –9‰ in a single paleosol horizon (KOR25) (Appendix A2.1) like P1. The $\delta^{18}O_{carb}$ shows the excursion starting slightly earlier in the three paleosols below (KOR26, KOR27 and KOR24; Appendix A2.1) and records an excursion of –8.00‰.

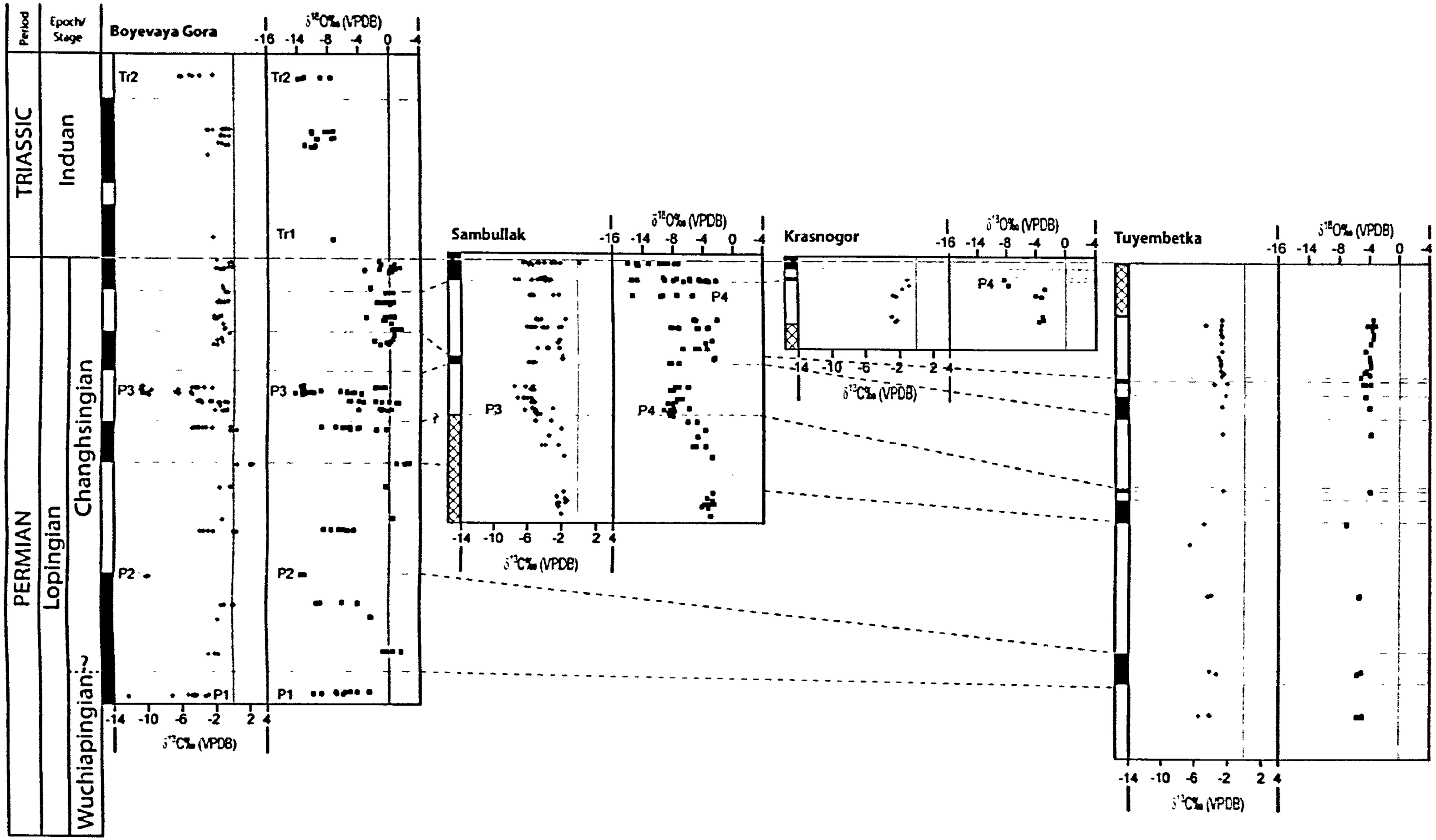


**Figure 4.1 Micritic carbonate values from the Late Permian and earliest Triassic sections from the Southern Urals of Russia correlated using magnetostratigraphic data (Taylor *et al.* 2009 see Chapter 3 for stratigraphic information). Sections arranged west to east. See Appendix A2.1 for raw data.**

P3 is recorded in both $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values and is present at Boyevaya Gora and, to a lesser extent at Sambullak. At Boyevaya Gora it is constrained by 2 paleosols (KOR22, KOR23, see Appendix A2.1) with values as low as $\delta^{13}C_{carb}$ –11.06‰ and $\delta^{18}O_{carb}$ –11.30‰. The paleosol that contains these negative values (KOR22) also contains nodules which have isotopic values as positive as $\delta^{13}C_{carb}$ –4.90‰ and $\delta^{18}O_{carb}$ –4.91‰ (Figure 4.1, Appendix A2.1). At Sambullak the excursion is less pronounced in terms of magnitude and is spread over 10 paleosols (SAM17, SAM13, SAM14, SAM21, SAM22, SAM23, SAM24a, SAM24b, SAM24c, SAM24d, SAM24e, 04.7.24.a; Appendix A2.1). The excursion is as negative as $\delta^{13}C_{carb}$ –7.39‰ and $\delta^{18}O_{carb}$ –9.49‰ and while the $\delta^{13}C_{carb}$ values become more positive after the event the $\delta^{18}O_{carb}$ values stay negative.

P4 is only recorded at Sambullak and Krasnogor and is only observed in the $\delta^{18}O_{carb}$ values (Figure 4.1). At Sambullak it is recorded in 4 horizons (SAM12, SAM2, SAM3, SAM4, SAM1; Appendix A2.1) up to the P/Tr boundary. Like P3 at Boyevaya Gora the excursion manifests itself as an increase in the range of isotopic values rather than a shift in the mean. $\delta^{18}O_{carb}$ values range from –14.15‰ (SAM1) to as positive as –7.50‰ in the same paleosol (see Appendix A2.1). At Krasnogor P4 is only observed in two paleosols (KRA 2 and KRA1; Appendix A2.1) and the lowest $\delta^{18}O_{carb}$ values are –8.37‰ (KRA 2) which youngest Permian soil.

Only Boyevaya Gora has paleosols in the Induan (Figure 4.1) and while $\delta^{13}C_{carb}$ values (–0.10‰ to –4.90‰ see Appendix A2.1) are similar to those in the Permian (Figure 1) the $\delta^{18}O_{carb}$ values become more negative (Tr1; Figure 4.1) and become as negative –11.44‰

(KOR36). The negative value in KOR36, at the very top of the section, is also matched by a –2‰ excursion in $\delta^{13}C_{carb}$ values (Tr2).

The section at Mescheryakovka is the only analysed section in the Olenekian. There are no obvious trends in the section in either $\delta^{13}C_{carb}$ or $\delta^{18}O_{carb}$ (Figure 4.2), although this may be due to the fact that only 8 paleosols from this section were analysed (Appendix A2.1). Compared with the Permian and Early Triassic values (Figure 4.1) the isotope values have a more negative range in values, with a range for −6.42‰ to −10.62‰ and −1.53‰ to −17.66‰ for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ respectively. These are the most negative micritic $\delta^{18}O_{carb}$ values of any section studied in Russia.

Before any detailed interpretation of the isotopic results can be carried out it is imperative to determine how much of the variation within the stable isotope signal is a result of later alteration and how much is related to the vadose pedogenic carbonate formed from meteoric water. Sources of alteration to the vadose pedogenic isotopic signature fall into three broad categories: (1) the effects of evaporation on the isotopic signal, (2) interactions with the phreatic groundwater table and surrounding rock, and (3) alterations caused during diagenesis. To assess the extent to which such factors may have affected the isotope signal a combination of petrographic, isotopic, X-ray diffraction (XRD) and scanning electron microscope techniques was used.

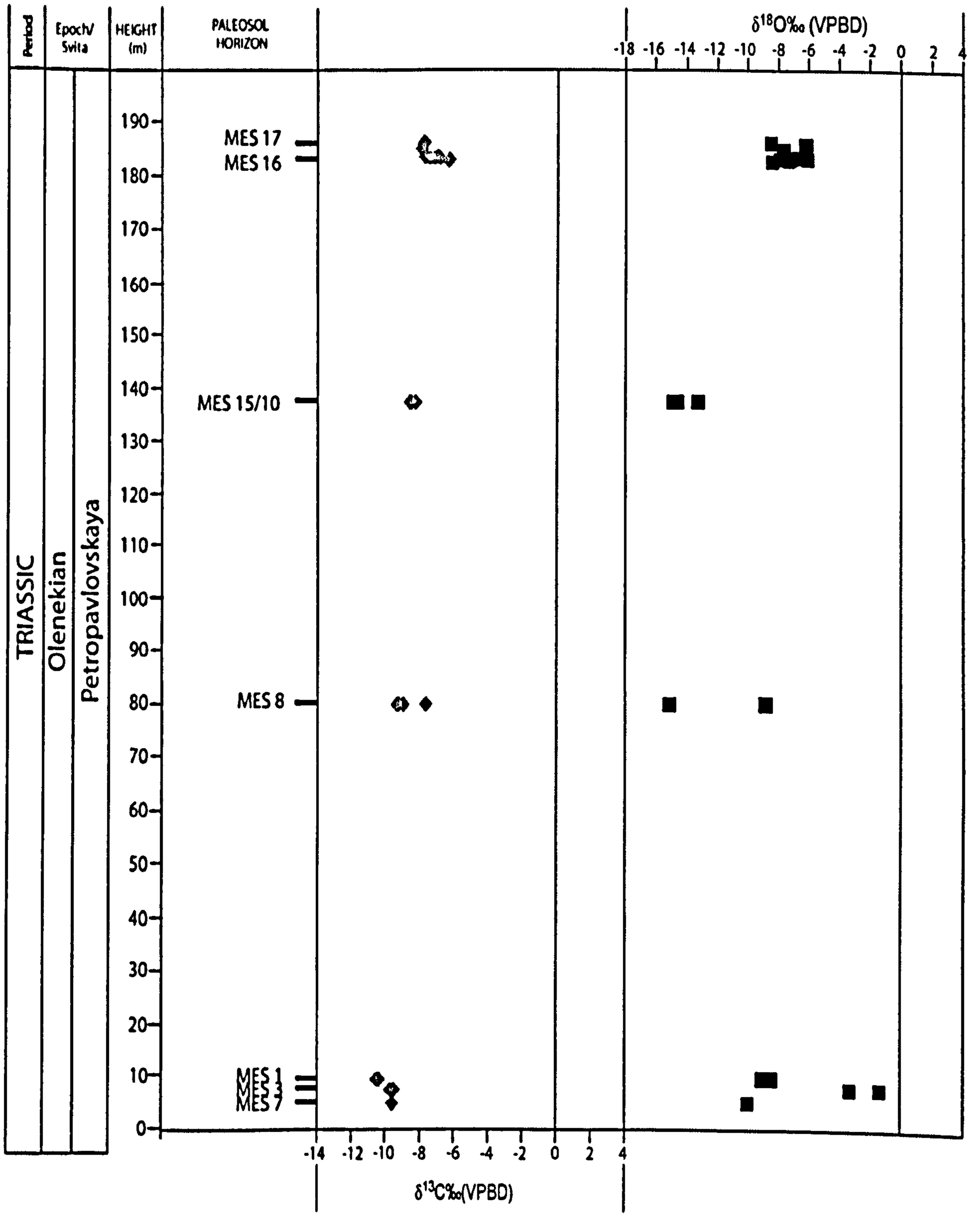


**Figure 4.2 Micritic carbonate values from Mescheryakovka in the Olenekian (see Chapter 3 for stratigraphic information). See Appendix A2.1 for unscreened data.**

## 4.3 Diagenesis and alteration of the isotope signal

Climate is only one of several factors that can affect the chemical characteristics of pedogenic calcretes. Other factors include the composition and texture of the parent material, landscape position, vegetation, latitudinal location, and the duration of soil development (Mack and

James 1994). All of these factors, especially the maturity of a soil and local influence of groundwater, have the effect of fractionating the isotopic signal such that the carbonate no longer represents equilibrium with vadose meteoric water (Quast *et al.* 2006). It has also been noted that many paleosol calcretes from the Palaeozoic have been altered both physically and geochemically by diagenesis (Quast *et al.* 2006). This problem has been encountered in other paleosol studies across the P/Tr boundary (e.g. Macleod *et al.* 2000) and therefore it is important to quantify the role of diagenesis in influencing the isotopic signal observed in the Russian paleosols.

### *4.3.1 Stage of calcrete development*

Once a calcrete forms a solid layer its relative permeability decreases, this attenuated infiltration of meteoric water enhances the effect of evaporation (Liu *et al.* 1996; Ekart *et al.* 1999). As a result once the Bk horizon has become more mature than stage II the nodules are likely to become isotopically less negative as the light isotopes are selectively evaporated (Ekart *et al.* 1999). Equally any carbonate associated with palustrine or groundwater paleosols may be more likely to reflect the local evolved groundwater, or local lacustrine bodies which also have different isotopic compositions due to enhanced evaporation (Wright and Tucker 1991) and the effects of the breakdown of organic matter (Tabor *et al.* 2007).

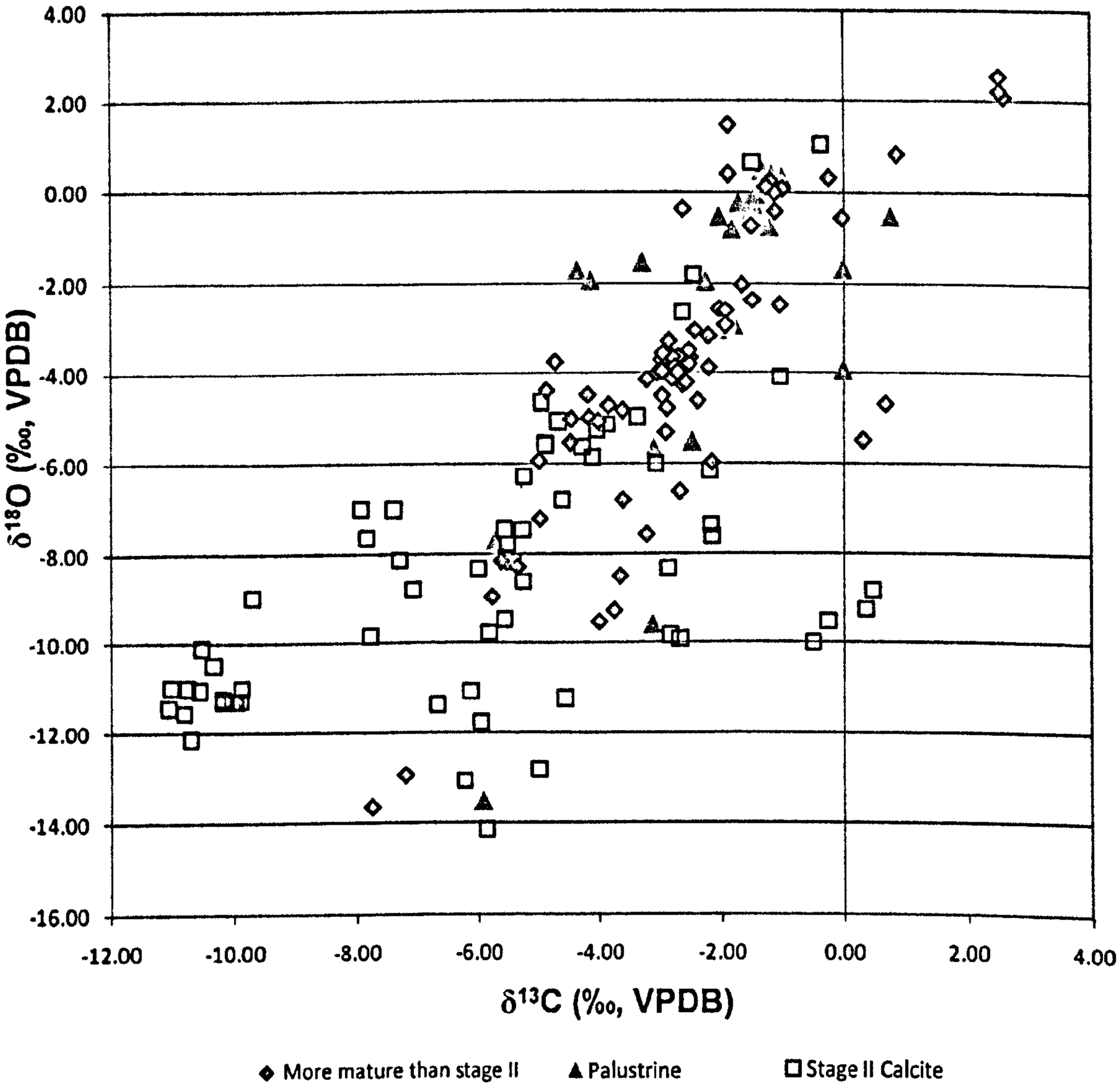


**Figure 4.3 Cross plot of those micritic carbonate values from palustrine and mature micrite compared against micritic pedogenic values from stage II and I calcretes (see Table 1 and Appendix A2.1).**

When the more mature calcretes are compared to the stage II nodules it is possible to see that the more mature calcretes are shifted towards the more positive end of the range of the values from the Stage II nodules (Figure 4.3) suggesting some influence of evaporation. However, the significant overlap suggests that evaporation may have only partially overprinted the more mature calcretes and the palustrine calcretes are also only partially affected by fractionated lacustrine waters. This is also true of the isotopic results from calcretes associated with palustrine paleosols (see Chapter 3). There is a positive covariance between $\delta^{13}C$ and $\delta^{18}O$ values. This has been observed in vadose pedogenic carbonates by other authors (Cerling 1991; Ghosh *et al.* 2001; Quast *et al.* 2001; Robinson *et al.* 2002) as well as in modern systems (Alonso-Zarza 2003).

### 4.3.2 Macromorphology

*Pedogenic nodules*

Throughout all the sections in Russia the micromorphologies of the pedogenic stage II nodules are remarkably similar. Those that are not associated with groundwater-influenced paleosols (see Chapter 3) all have a rounded to subrounded morphology and have sharp boundaries with the surrounding matrix suggesting a pedogenic origin (Wright and Tucker 1991; Alonso-Zarza 2003; Khadkikar *et al.* 2000). Many appear to have formed around a core of less consolidated soil matter (Figure 4.4A) which is a typical feature of pedogenic Vertisol nodules where a ped is used as a centre for nucleation (Khadkikar *et al* 2000). Nodules are primarily only cemented by cryptocrystalline carbonate and are very powdery, suggesting that they have not undergone much compaction or diagenesis since they formed (Figure 4.4B).

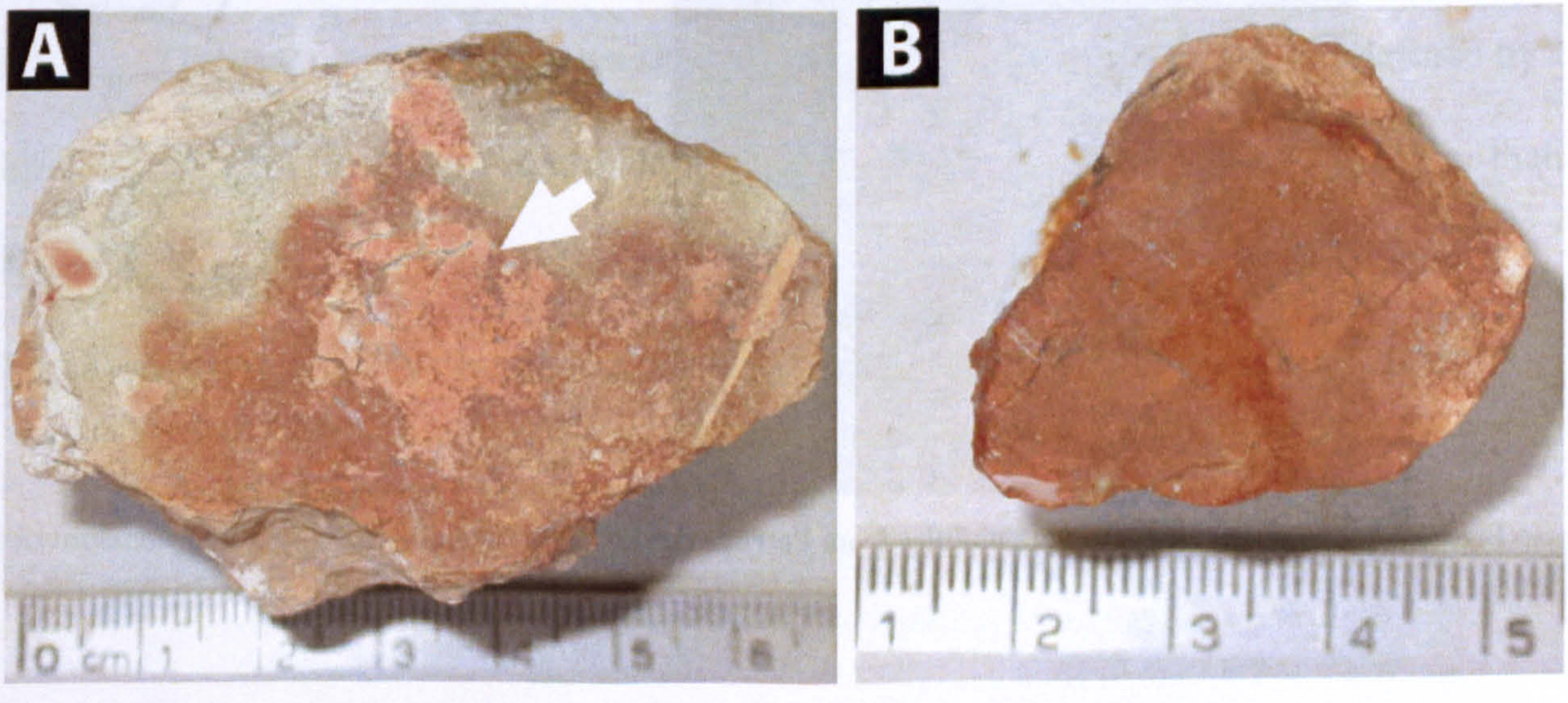


**Figure 4.4 Internal macromorphology of pedogenic nodules. A) Appears to have formed around a core which has subsequently become compacted. B) Shows the typical poorly cemented nature of the majority of the nodules found in Russia. Scale in centimetres.**

*Groundwater nodules*

Those carbonate nodules associated purely groundwater are easily distinguished from those formed from meteoric waters. The groundwater carbonates all show diffuse margins with the

surrounding sediment, rather than the smooth (Figure 4.5), sharp contacts of in pedogenic nodules (Khadkikar *et al*. 2000, Alonso-Zarza 2003). Both of these morphologies have been observed at Petropavlovka (Chapter 3), and include features such as nodules 1-4cm in width aligned in a continuous sheet that are indicative of vadose groundwater-formed calcretes (Khadkikar *et al*. 2000). These nodules are thought to record the groundwater isotopic values which may be highly fractionated from the atmospheric values caused by lack of recharge from the atmospheric system (Alonso-Zarza 2003) and thus must be discounted from any palaeoclimate analysis. Nodules with similar morphologies have been identified at Boyevaya Gora (i.e. KOR33, see Appendix A1.1)

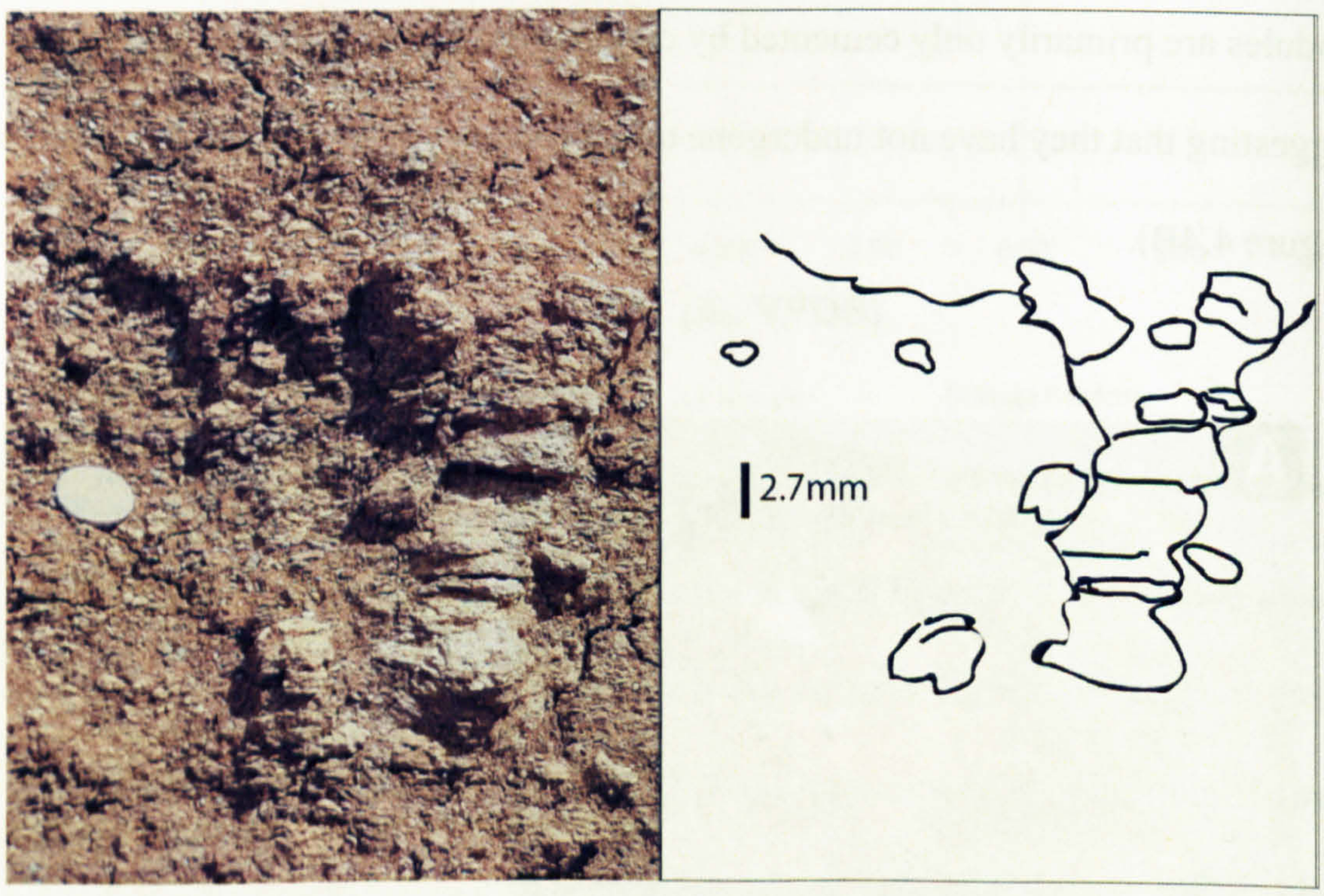


**Figure 4.5 Groundwater carbonate nodules from Petropavlovka. Note the indistinct edges and non-spherical nature.**

### *4.3.3 Micromorphology*

One of the simplest ways to determine if the carbonate material has been altered by later recrystallisation and diagenesis is by petrographic screening of samples. Dworkin *et al.* (2005) suggest that the textures that are useful for indicating un-recrystallised pedogenic carbonates are: 1) anhedral grains of calcite in the micrite to microspar grain size, 2) crystic –

plasmic fabric (primarily fibrous and circumgranular textures), and 3) rhombic calcite crystals.

The nodular calcretes from Russia principally show features associated with primary pedogenic formation. 70% of the nodules are made of muddy crypto- to microcrystalline masses (the microcrystalline crystals being between 5 and16μm). Many nodules show a characteristic clotted texture of cryptocrystalline concretions surrounded by a coarser microcrystalline matrix (Figure 4.6A). This texture is commonly associated with vadose environments where nodules grow and coalesce (Wright and Tucker 1991; Quast *et al.* 2006). There are dark areas of mottled clays and iron oxides that are often found in the slides and these mask the optical properties of the calcite. There is also evidence for floating grains of very fine quartz which are not in contact with any other surrounding quartz grains (Figure 4.6 B). These represent clastic grains that have been displaced by the growth of carbonate and are also associated with the vadose zone carbonate formation (Khadkikar *et al.* 2000; Quast *et al.* 2006). All of the pedogenic carbonates show alpha calcrete micromophology as defined by Wright and Tucker (1991), and so are likely to be formed to pedogenic processes rather than biological processes. Similar micromorphologies have been seen in modern pedogenic nodules from grassland soils in the Kursk region of Russia (cf. Mikhailova *et al.* 2006).

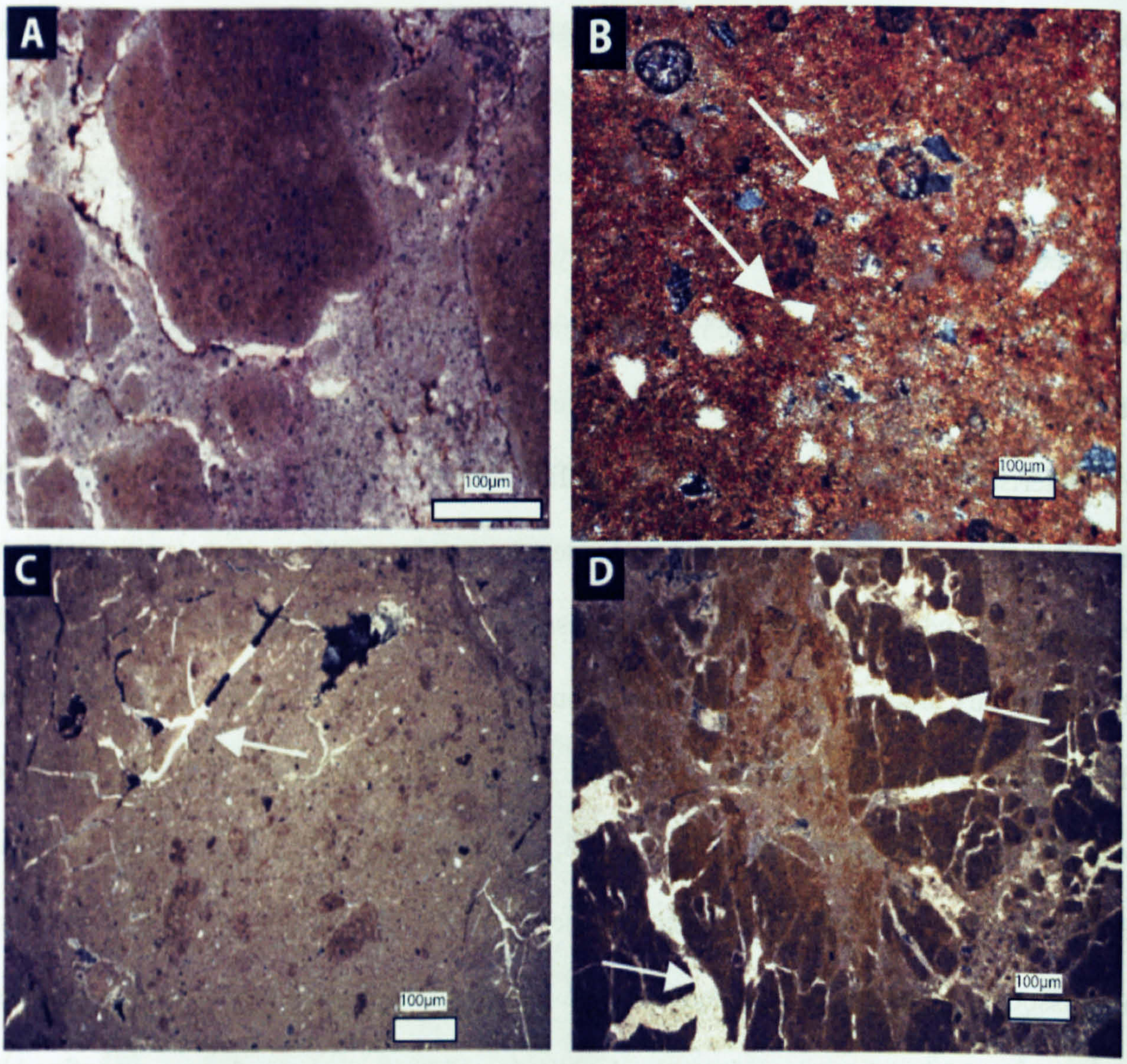


**Figure 4.6 Photomicrographs of typical textures seen in the carbonate nodules. A) Shows a clotted texture seen in the micro and cryptocrystalline carbonates (KOR2). B) Floating grains of quartz (arrowed) in a carbonate matrix (KOR12). C) Anhedral to euhedral sinuous veins of calcite (KOR2). D) These veins cross cut earlier pedogenic structure (KOR1).**

Sinuous veins of anhedral to euhedral calcite are found randomly cutting across most of the nodules. The veins are filled with different levels of crystal growth. Some are formed of single crystals which span the width of the vein; others are formed of smaller stubby crystals (Figure 4.6 C and D). The elongated crystals are 5-15µm in width and generally 150-50µm in length. The vein crystals have distinct boundaries from the surrounding micro- and cryptocrystalline groundmass, suggesting two distinct phases of crystallisation (Figure 4.6A and D). These veins are also seen to grow around patches of crypto- and microcrystalline micrite (Figure 4.6A), again suggesting that they postdate the formation of the micritic

component. The sinuous vein structures are most likely to be an infill of cavities created by shrinking and swelling of voids or by rootlet action (Wright and Tucker 1991; Khadkikar *et al.* 2000; Quast *et al.* 2006).

Nodules KOR2.4 and SAM2.2 show poikilotopic morphology (Friedman 1965; Quast *et al.* 2006, see Appendix A2.1), that is to say they formed as cement filling spaces between clastic grains (Figure 4.7A). This morphology is confined to the nodules formed in a fine or very fine sand substrate. They may represent nodules precipitated from phreatic water rather than meteoric (Quast *et al.* 2006), although it is highly plausible that in a soil where a calcrete hardpan had not yet developed which would, isolate the soil water from the meteoric system, that these two waters would have very similar chemistries.

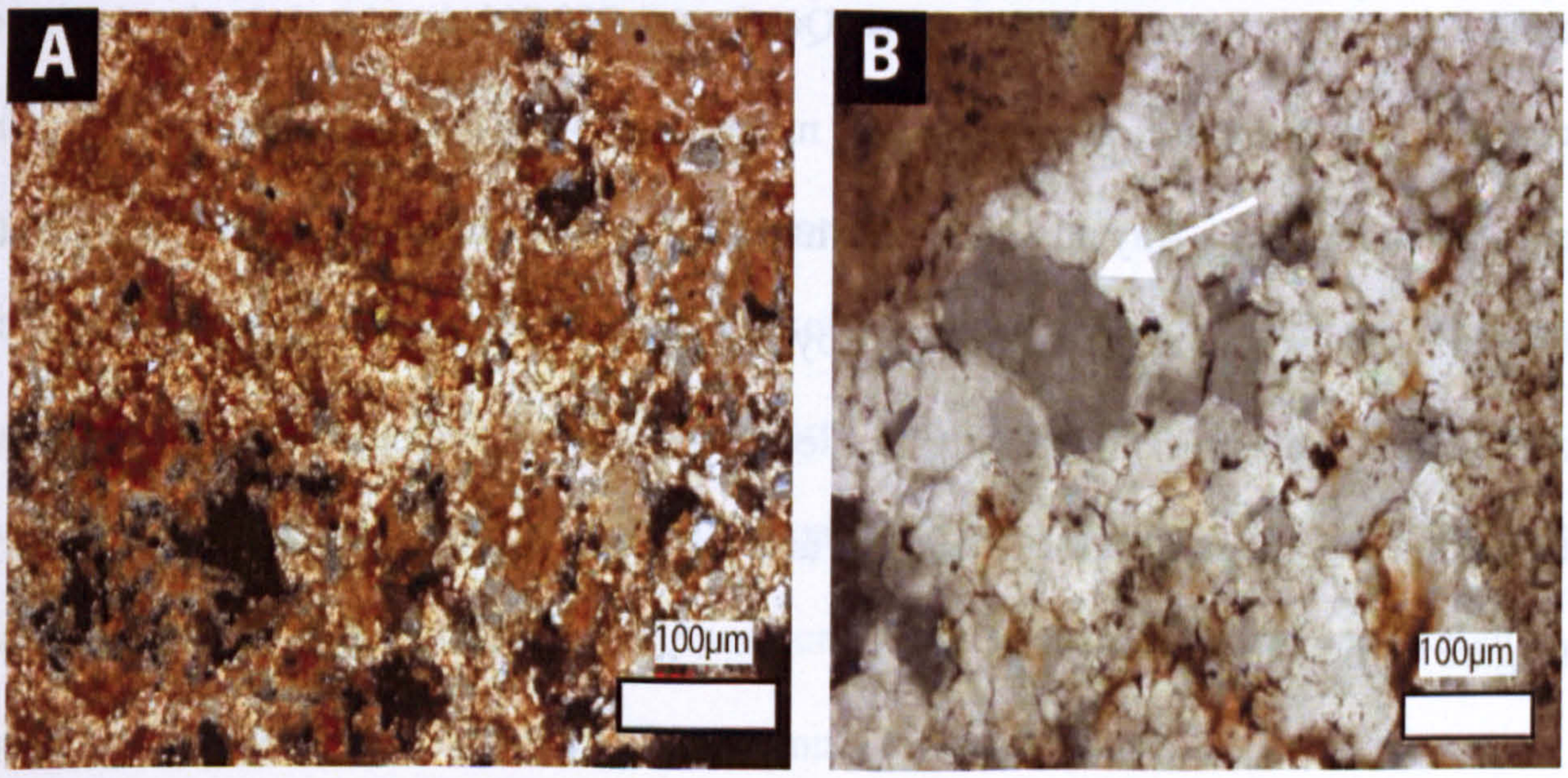


**Figure 4.7 Diagenetic textures A) Poikilotopic morphology related to groundwaters (SAM2.2). B) Concavo-convex crystal contacts suggesting neomorphism (KOR 21.9).**

There is evidence in some nodules (such as KOR21.9) of possible neomorphic features. Neomorphism and replacement within soil carbonate is common even when the soil is still part of the active vadose zone (Wright and Tucker 1991). However, it is also suggested to represent later diagenetic fabrics with characteristic concavo-convex crystal contacts (Figure

4.7B) which enclose smaller patches of crypto- and microcrystalline material (Quast *et al.* 2006). Diagenetic neomorphic features have been identified in only two horizons (SAM2 and KOR21) while the remaining horizons surrounding them show no such feature, which indicate that this texture may not be due to excessive burial but instead may be related to specific conditions within that nodule itself.

Petrographic analysis of the carbonate crystal structure can be used to divide all the calcrete samples analysed into crypto masses (Crp); cryptocrystalline masses containing sinuous veins (SpC); nodules where the calcite crystal size is above 20μm (MCr) and those nodules where the crystal size is above 20μm and contain sinuous veins (MCr/SpC) (Appendix A2.1).

As the sinuous veins are thought to represent a later phase digenetic or phreatic infill (Wright and Tucker 1991; Khadkikar *et al.* 2000; Quast *et al.* 2006) they were also sub-sampled to compare their isotopic composition to the micritic component of the nodule (see Chapter 2 and Appendix A2.1). Any nodules which have a calcite crystal size above 20μm are thought to be formed by groundwater rather than by pedogenic processes (Quast *et al.* 2006). Although the data from this study do not seem to support any significant difference between the crypto and microcrystalline carbonate and the calcite with a crystal size over 20μm (Figure 4.8).

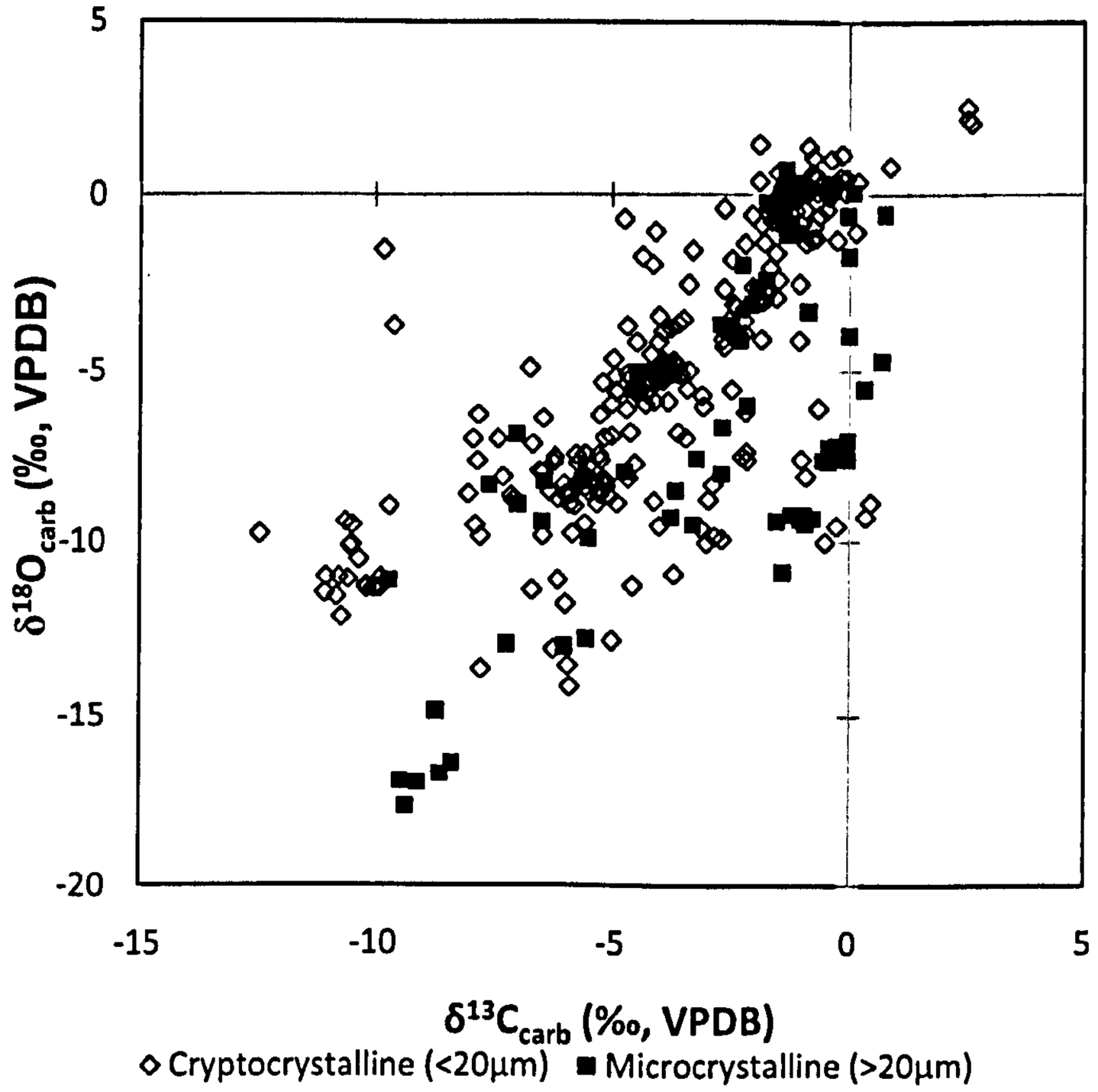


**Figure 4.8 Cross plot of those micritic carbonate values from microcrystalline calcite nodules (crystal size >20μm) compared against finer pedogenic calcite values (see Table 1 and Appendix A2.1).**

### *4.3.4 Isotopic composition of spar and micrite*

It has been proposed that, by comparing the isotopic values of the cryptocrystalline micritic component of a nodule, with that from the sparry vein-filling calcite, it is possible to discern whether the micritic component has been isotopically overprinted (Quast *et al.*2006). For each sample containing both a cryptocrystalline micritic and a sparry vein component, both components were analysed to allow comparison between the two.

There are examples of paleosols where the isotopic composition of every micritic part of the nodule is isotopically similar to the spar component from that nodule. At Boyevaya Gora KOR33, KOR2, KOR16, show this, also SAM14 and SAM13 at Sambullak; TUY27 at Tuyembetka; all bar KRA7e at Krasnogor and MES1, MES3 at Mescheryakovka (Figure 4.9 and see Appendix A2.2). These suggest that even though the micritic component may appear

petrographically unaltered, it has been influenced by the spar-forming event. Equally there are many paleosols that show good separation between the spar and micritic values (Figure 4.9 and see Appendix A2.2) suggesting that the micritic component of these nodules are unaltered. In most cases the spar values are isotopically more negative than those of the micrite (Figure 4.9 and see Appendix A2.2).

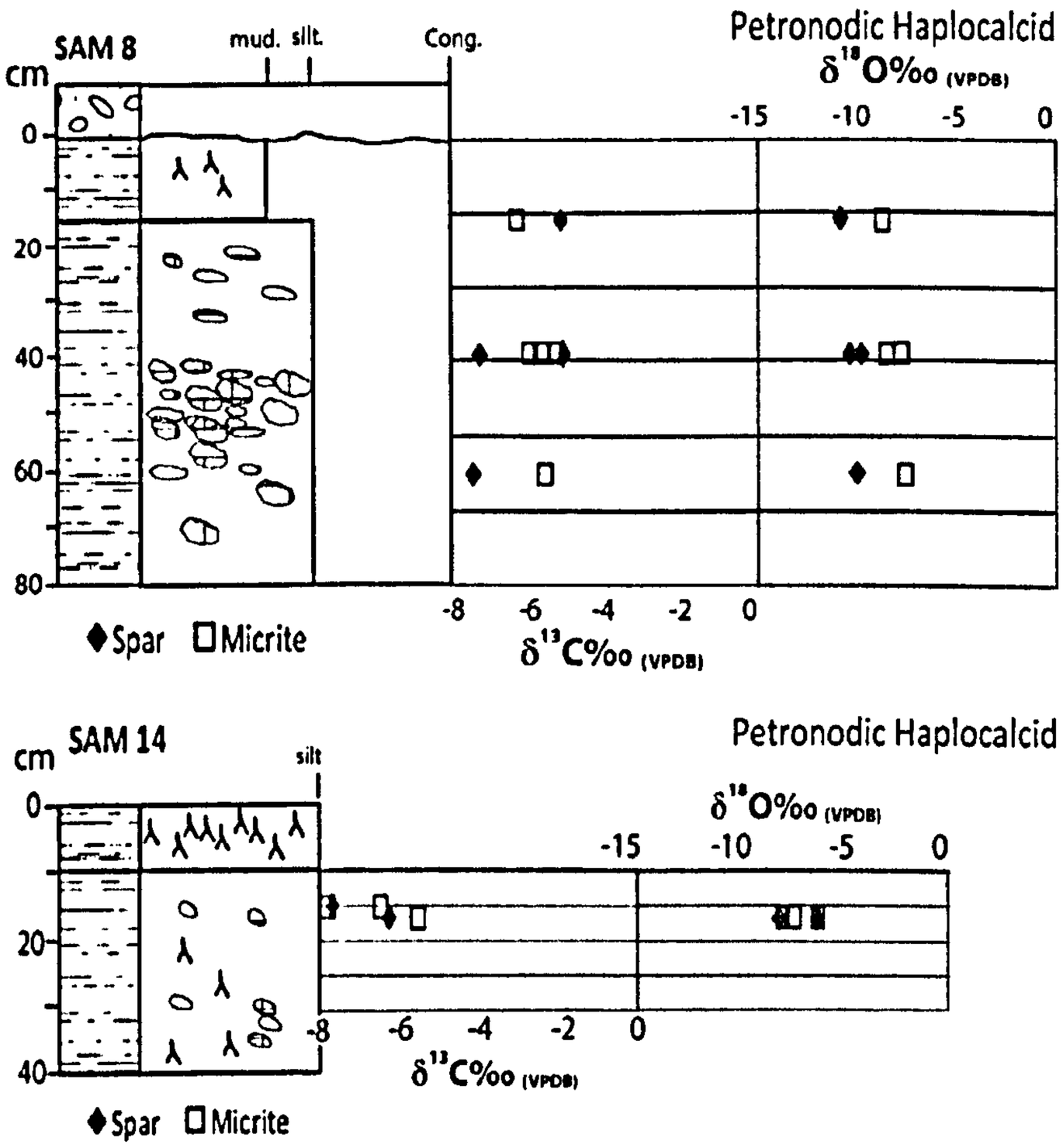


**Figure 4.9 Two isotopic depth plots of micritic (open square) and spar components (closed diamond). SAM14 shows strong overlap between the spar and micritic components suggesting the micritic values are altered. KOR6 shows strong separation suggesting the micrite is not affected by the spar forming event.**

To remove those nodules which the spar forming event had altered the micrite part of the nodule, all those nodules with spar and micritic values which were the same within 2 times experimental error (see Chapter 2) were deemed to be altered (cf. MacLeod *et al.* 2001; Quast *et al.* 2005; Dr Stephen Grimes *pers. comm.*) Those nodules that did not contain spar were compared against the average value of the other spar values from that horizon. This suggests that of the nodules at Boyevaya Gora 61 were affected by the later spar event; at Sambullak

42 were affected; at Tuyembetka 4 at Krasnogor all bar one; and at Mescheryakovka 14 were affected (see Appendix A2.2).

### *4.3.5 Variation with depth in paleosol*

The depth at which carbonate samples are taken from within a paleosol is often considered important, as only below a certain depth do the effects of evaporation not affect the soil water (Cerling 1991; Li *et al.*1996; Ekart *et al.* 1999). It is reported that in the first 30–50cm of a soil horizon the isotopic values are out of equilibrium with the atmosphere due to the effects of evaporation and plant respired $CO_2$ altering the soil water down to this point (Liu *et al.*1996; Dr Nathan Sheldon *pers. comm.* 2008). However, in stacked paleosol sequences, the actual depth from the palaeosurface may have been shortened (see Chapter 5) due to overprinting of older soils by newer soils (Kraus 1999). To rectify this issue all the horizons containing stage II nodular calcrete were sampled stratigraphically, thus allowing for a reconstruction of the stable isotope curves with depth. It is therefore possible to recognise if the isotopic values within a paleosol have reached equilibrium even if the top of the horizon is overprinted. It has been suggested that these fractionated top zones, can show an $\delta^{13}C$ enrichment of 2-3‰ and a $\delta^{18}O$ enrichment of 4-10‰ in modern soils (Pendall *et al.* 1994; Liu *et al.* 1996; Huang *et al.* 2005).

Twenty four paleosols at Boyevaya Gora contain stage II calcite and are exposed well enough to accurately sample stratigraphically within them. This is also true for 21 paleosols at Sambullak; 3 paleosols at Tuyembetka and 5 paleosols at Mescheryakovka and thus it was impossible to investigate how the isotope signal varies with depth within each paleosol (see Appendix A2.2).

There are four distinct trends seen within the depth plots. The first shows a positive shift in both the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values towards the top of the paleosol (Figure 4.10 A). Examples of this are KOR2, KOR6, KOR10, and KOR36 (see Appendix A2.2). The second type shows a positive correlation with depth (Figure 4.10B). The third type shows a lot of variability between the nodules but no trend through the section – these can be very thin nodule bands or thicker sections (Figure 4.10C). The final type shows little internal variation within the section (Figure 4.10D).

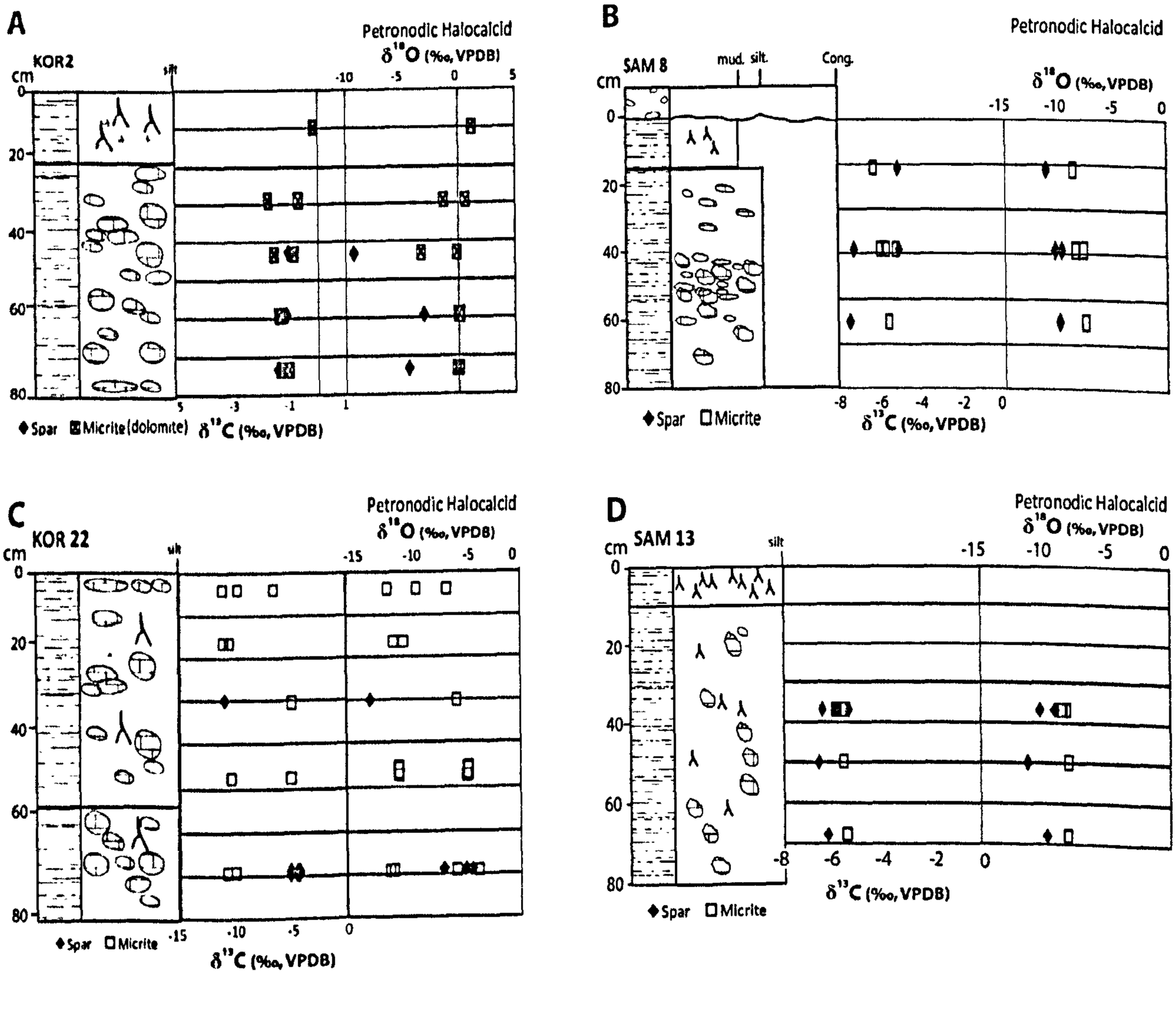


**Figure 4.10 Isotopic depth plots of micritic (open square) and spar components (closed diamond) within individual paleosol horizons, the crosses denote dolomitic micrite. A) Shows a positive shift towards the top of the profile in the micritic values. B) Shows a positive correlation down profile in the micritic values. C) Shows no overall trend but a lot of variation. D) shows no overall trend and a tight cluster of values.**

There are Russian paleosols (KOR2, KOR6, KOR10 and KOR36; see Appendix A2.2) that show positive values towards the top that become more negative and then stabilise with depth (Figure 4.10A; Appendix A2.2). This fits well with the diffusion-based model predicted by Cerling (1991) and observed by Liu *et al.* (1996). Most paleosols show little variation with depth which is interesting as these horizons often show a difference between the spar and micritic components (Figure 4.10 Table1) suggesting that they are probably not altered by diagenesis. Many of these paleosol horizons are overlain by sand channels (e.g. KOR10, KOR34 SAM8, SAM13 and SAM24, see Appendix A2.2) that may have eroded off the top part of the profile.

Trends with the opposite gradient to that observed in modern soils are harder to explain. For instance both the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values for SAM 8 show this pattern (Figure 4.10B). This horizon was eroded by conglomerate suggesting it became part of an active river system. In this case water from the active channel may have inundated the top of the paleosol and affected the geochemistry of the carbonate. There are other horizons, such as KOR22, which show a lot of internal variation (Figure 4.10C). It has been suggested that the fractionation model seen in modern soils is only found under relatively homogeneous climate condition (Pendall *et al.* 1994). Thus, those paleosols that show a large internal variation may have formed at times of climate change. This would also explain why those paleosols that show a negative excursion from the mean paleosol values in the section also have the greatest internal variation.

In summary, those nodules that show a fractionated (either positive or negatively) values at the top of the paleosol are probably out of equilibrium with the atmosphere and should not be used for palaeoclimate analysis. The paleosols that do not show a fractionated top are

assumed to have reached equilibrium and either the fractionated values were eroded or overprinted.

### *4.3.6 X-Ray diffraction results*

All the micritic samples that were selected for isotopic analysis were also analysed using X-Ray Diffraction (XRD) (Appendix A2.4). This revealed that the nodules were made of one of two main components. The first of these components was interpreted to be calcite by both manual and electronic identification. It had a maximum peak at 29.29 °2θ (± 0.11, 1σ std) with a d-spacing of 3.05Å. This is almost identical to the laboratory standard (3.03 Å) and to published values for calcite and calcium carbonate (3.04 Å and 3.02 Å respectively) (Joint Committee on Powder Diffraction Standards 1971). The other main component of the micritic material was found to be dolomite. This has a maximum peak at 30.64 °2θ (± 0.30, 1σ std) and a d-spacing of 2.91Å. This is more positive than the laboratory standard (2.88Å) but is close to the published values for ferroan dolomite (2.90Å) (Joint Committee on Powder Diffraction Standards 1971).

To test further where the dolomite occurred within the nodules, three nodules from different paleosols (KOR2.4, KOR10.8 and KOR21.10), which showed the strongest dolomite response (Appendix A2.4), were sub-sampled (Table 4.1). Different analyses were taken from shallow drill sites, deep drill sites, areas of less consolidation/possible alteration, from the edge of the nodule and from areas with high amounts of spar present. In all cases the main peak was of dolomite and the variation between the measurements was less than that between the peaks of calcite and dolomite.

There were some nodules that showed both a calcite and dolomite peak (e.g. KOR 2.4 and KOR21.10, Table 2). In all cases the calcite was the secondary peak, after dolomite and there

are no cases where there was a secondary dolomite peak associated with a primary calcitic one (Appendix 2.4). There is a suggestion that the calcite may be related to the spar component as in KOR21.10 a calcite secondary peak was found in those areas that contain large amounts of spar (Table 4.1, Appendix A2.3). Equally, when a nodule was disaggregated there was no calcite present in the finest fractions (below <10μm Figure 11) (method after Kraimer *et al.* 2005). This also suggests that the coarse crystals are dominantly calcite while the finer ones are dominantly dolomite in nodules that show both a dolomite and calcite XRD response.

| Sample | | Main component | Main Peak | 100% 2°θ | Secondary peak |
|---|---|---|---|---|---|
| **KOR 2.4** | Original | Dolomite | 580 | 30.7749 | Calcite III (29.4016) |
| | Shallow drill | Dolomite | 796 | 30.7089 | |
| | Deep drill | Dolomite | 298 | 30.8873 | Calcite III (29.5649) |
| | Edge of nodule | Dolomite | 891 | 30.7478 | Calcite III (29.3763) |
| | Repeat | Dolomite | 933 | 30.8295 | |
| **KOR 10.8** | Original | Dolomite | 874.84 | 30.6249 | Quartz High |
| | Shallow drill | Dolomite | 1027.87 | 30.6143 | Quartz |
| | Deep drill | Dolomite | 506 | 30.7588 | Quartz low |
| | Less consolidate | Dolomite | 626.26 | 30.5844 | Quartz |
| | Edge of nodule | Dolomite | 579.23 | 30.5719 | |
| **KOR21.10** | Original | Dolomite | 896 | 30.7348 | |
| | Shallow drill | Dolomite | 636.92 | 30.6562 | |
| | Edge of nodule B | Dolomite | 616.59 | 30.6596 | Quartz (50) |
| | High spar | Dolomite | 510.2 | 30.7603 | Calcite (100% 2°θ= 29.3826) |
| | Deep drill | Dolomite | 777.8 | 30.6271 | Quartz (31) |

**Table 4.1 Summary of multiple drill site XRD test. For further information see Appendix A2.3.**

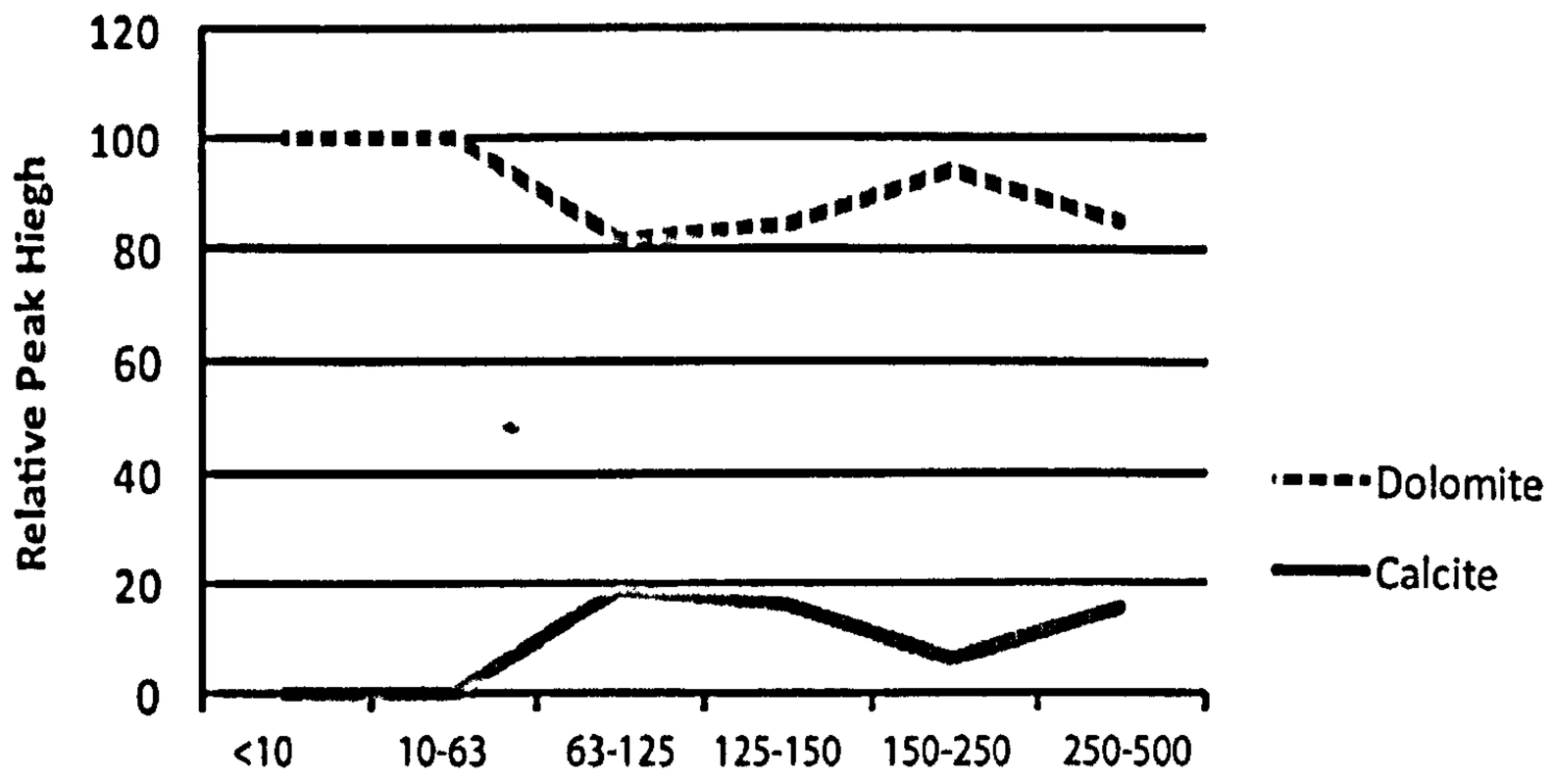


**Figure 4.11 The relative peak heights between the dolomite response and the calcite response for different grain sizes of a nodule. Note the increase of the dolomite response at the lowest sizes suggesting the dolomite makes up the cryptocrystalline carbonate.**

The presence of dolomite is also verified by the use of a dolomite-specific petrographic stain (Alkaline Alizian Red S). This stain selectively stains dolomite over calcite thus allowing identification of the part of the nodule fabric in which the dolomite is present. In the nodules containing dolomite it was the micro- and especially the cryptocrystalline parts of the fabric that took up most dolomite stain (Figure 4.12A). This suggests that the dolomite occurs in the primary pedogenic component of the nodule rather than as a result of a later recrystallisation event (cf. Quast *et al.* 2006). Those nodules which produced both a calcite and dolomite peak on the XRD were also stained with a calcite-specific stain (Alizian Red S). This showed that the calcite seems to be found in the sparry component of the nodule, suggesting a primary dolomite precipitation followed by calcitic phreatic water which filled in the veins forming the sparry crystals (Figure 4.12C).

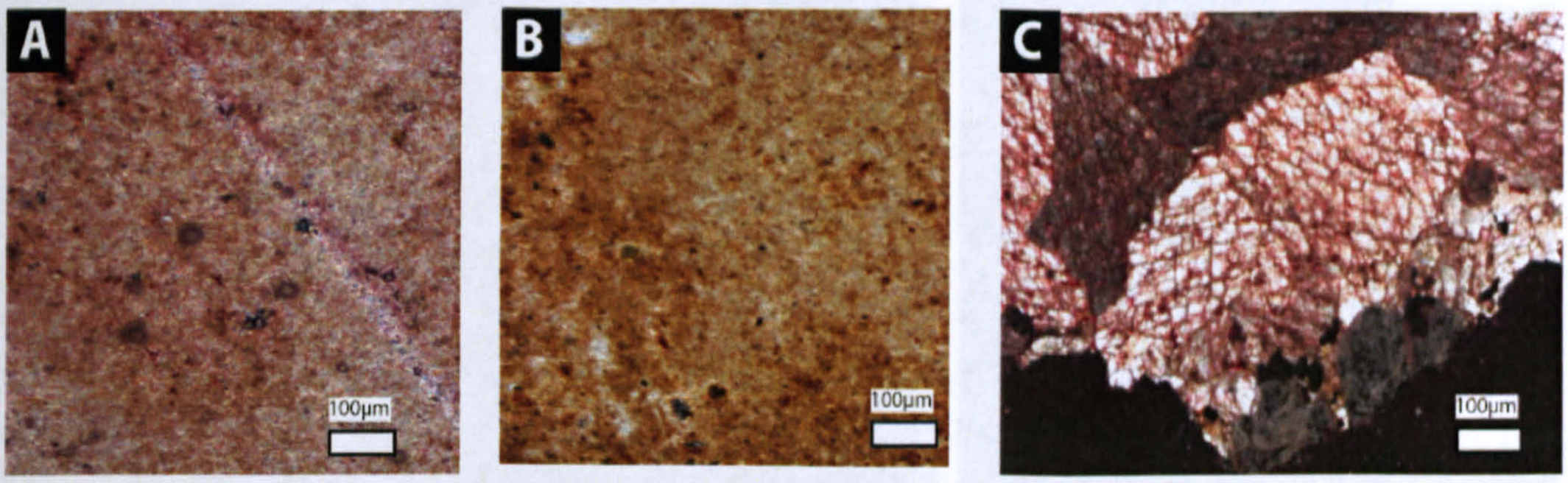


**Figure 4.12 Effects of the dolomite, and calcite specific stains. A) produced an XRD response of dolomite and reacted to the stain with the dolomite specific stain (Alkaline Alizian Red S while B) was identified as calcite did not. C) Shows the sinuous vein crystals reacting to the calcite specific stain (Alizian Red S) (KOR14.1).**

### *4.3.7 Scanning electron microscopy*

The presence of iron oxides masks the crypto- and microcrystalline morphology in many of the nodules seen through a petrographic microscope, which hinders accurate identification of the finest fraction of the nodules. To determine further whether the dolomite was formed as a primary feature or a replacement of earlier precursor calcites, nodule KOR 2.4 was analysed with a backscatter scanning electron microscope as this nodule had one of the strongest dolomitic XRD responses (Appendix A2.4). This analysis revealed that the areas that make up the densest parts of the clotted texture in the nodule are made entirely of dolomite rhombs of about 2-5µm in size (Figure 4.13). Elemental analysis of these areas showed prominent peaks in calcium, oxygen and magnesium. The sparry vein fill, by contrast, lacks a prominent magnesium peak confirming it is indeed calcite as the petrographic analysis suggests. It is also evident that the calcitic crystals are enveloping the dolomite rhombs, supporting the hypothesis that the dolomite preceded the calcite formation (Figure 4.13ii).

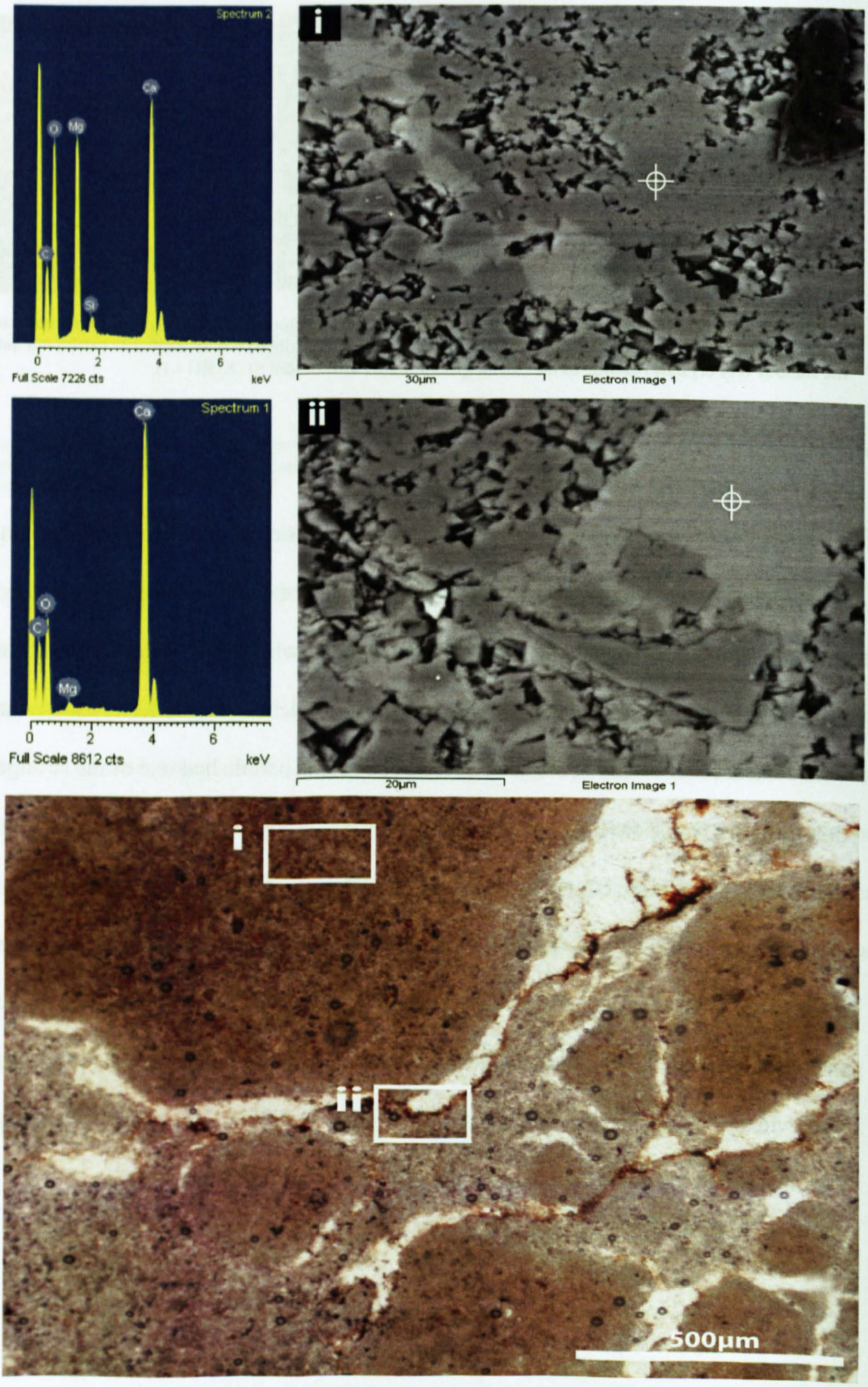


**Figure 4.13 SEM analysis of a nodule (from KOR 2.4) which produced a dolomitic response on XRD. i) is from the inside of a cryptocrystalline area, elemental analysis of which shows a high Mg peak (top left hand panel). ii) is from a sinuous vein and the elemental analysis does not show an Mg peak (middle left hand panel). The lower panel is a photomicrograph showing where the two SEM photos were taken from.**

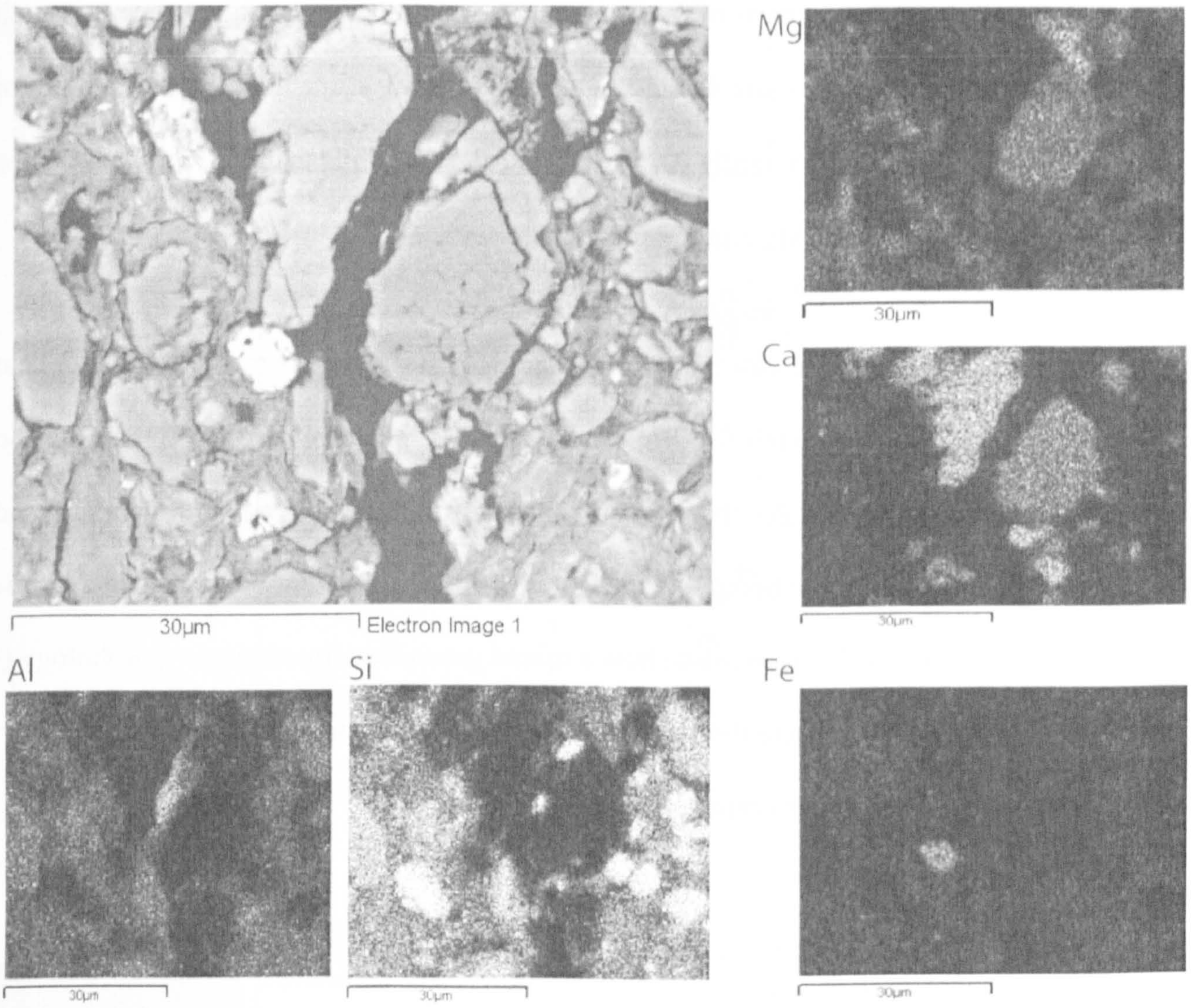


**Figure 4.14 Elemental mapping of a calcitic nodule (KOR 22.6). The top left hand image is the SEM image and the surrounding panels are the individual element maps.**

SEM analysis of a carbonate nodule which both XRD and staining techniques showed to be calcite (KOR 22.6) showed no evidence of dolomitic rhombs (Figure 4.14). Elemental mapping of the nodules reveals that the majority of the sample comprises areas of high silica content (interpreted as clays and quartz) surrounding areas of high calcium content (interpreted to be calcite) (Figure 4.14). Within the calcite areas there seems to be a variation in the amount of magnesium suggesting the presence of both high and low Mg calcite. However, the areas of clay also showed relatively high amounts of Mg (Figure 4.14 Mg). As this is only a semi-quantitative technique, this could be a result of different reflectance rates or interference from the clays. The Fe map attests to the presence of iron oxides which appear

to relate to the very bright parts of the images and slightly higher background values in the clay areas of the nodule (Figure 4.14 Fe). Other areas of the same nodule show submicron particles which are predominantly Al, Si, Mg and K, suggesting that they may also be areas of clays (Figure 4.14 Al, Si, Mg and K).

The carbonate found in the vast majority of paleosols in Russia is either dolomitic or calcitic. However, there is one exception at Boyevaya Gora. The paleosol horizon KOR 23 has both calcitic and dolomitic nodules (Figure 4.14). The distributions of the nodules are not random as the dolomitic part of the horizon is the lower part of the horizon while the upper part is calcitic. These are the horizons also show a mixed groundwater/pedogenic morphology (cf. Khadkikar *et al.* 2000) where the lower part of the section appears to be groundwater influenced and the upper is primarily pedogenic.

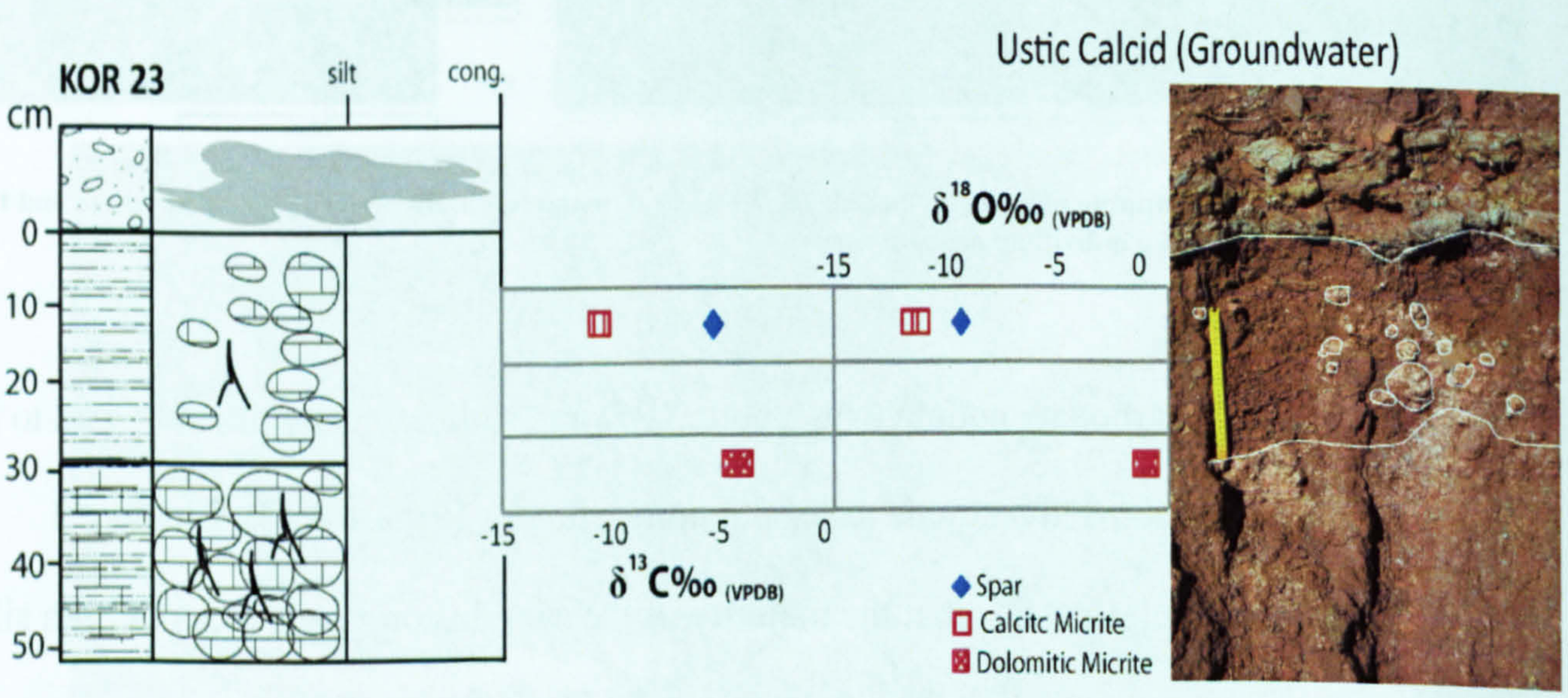


**Figure 4.15 Paleosol at Boyevaya Gora which contained both dolomitic (squares with crosses) and calcitic nodules (open squares). Note how the dolomite is restricted to the base of the nodular horizons.**

*XRD results compared with isotope results*

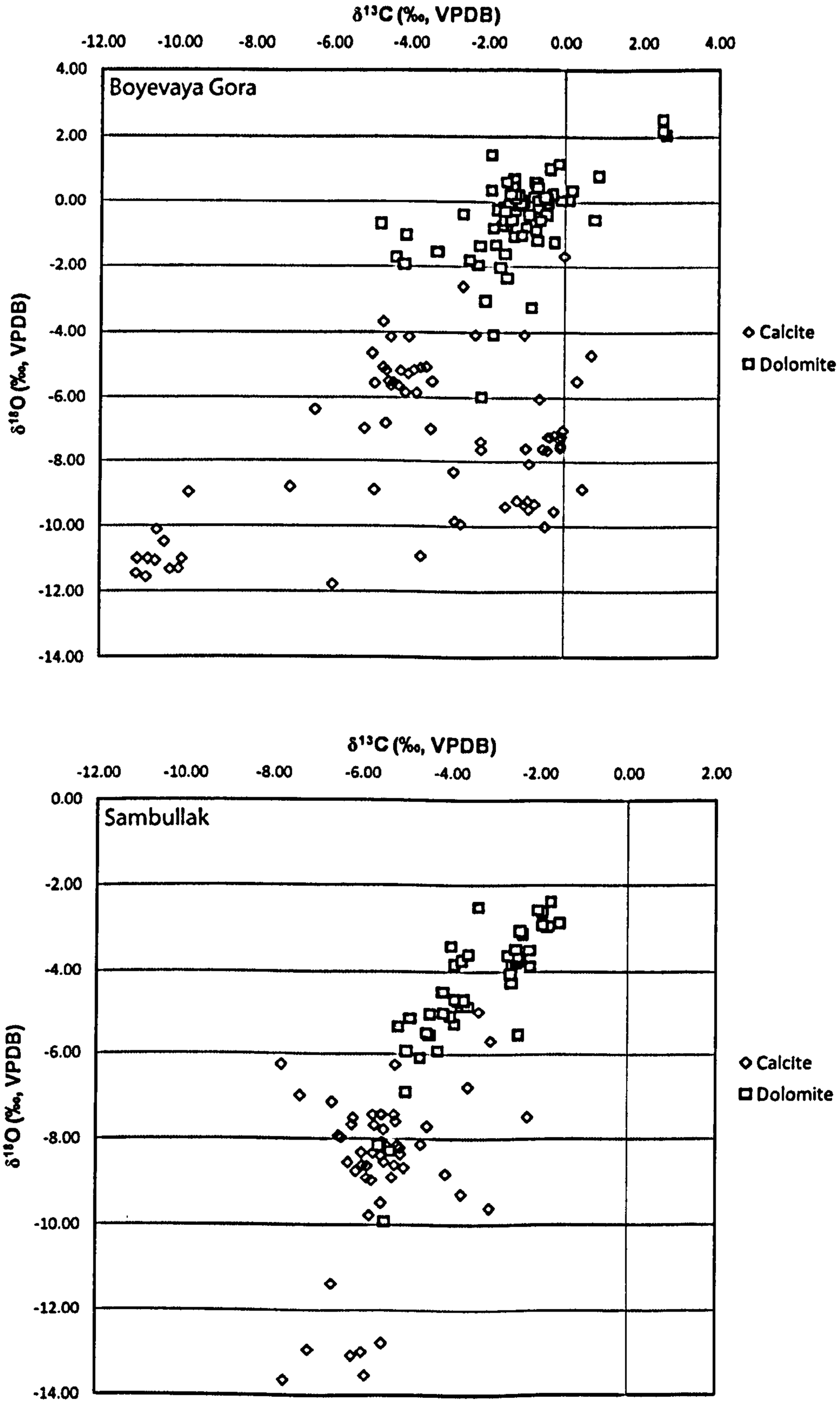


**Figure 4.16 $\delta^{13}C$ and $\delta^{18}O$ cross plots for Boyevaya Gora (top) and Sambullak (bottom). The open diamonds are those nodules of which the micritic component is calcite and the closed squares are dolomite.**

The XRD results show that the isotopically heavy values are primarily associated with the presence of dolomite while the lighter values are all related to calcite (Figure 4.16). In both localities there is an overlap between the dolocretes and calcretes suggesting possibly a similar origin for both the fluids that formed some of the dolomite and calcite. Also this overlap appears to be greater at Sambullak than at Boyevaya Gora.

## 4.4 Quantifying the effects of alteration on the isotope signature

As investigation into palaeoclimatic and palaeoatmospheric variation is the primary goal of this study it must be understood (a) how much of the isotope signature recorded at each section reflects the vadose pedogenic signal and (b) if any of the excursions identified in the primary data are the result of other influences or later alteration.

Table 4.1 shows the summary of the findings of Section 4.3 and the 4 criteria which will be used to assess the origins of the isotope results. These are:

(1) If the paleosol is associated with lacustrine units or the pedogenic carbonate shows ground water morphologies (section 4.3.2)

(2) If the calcrete is above or below stage II in development (section 4.3.1)

(3) Whether the micritic component was significantly different from the spar of the same nodule/horizon (Section 4.3.4)

(4) If the micritic component was dolomite or calcite (section 4.3.6 and 4.3.7)

(5) If the nodule was microcrystalline (greater than 20μm or not). (section 4.3.3)

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20μm |
|---|---|---|---|---|---|---|
| KOR 36 | KOR 36.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 36.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 36.3 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 36.4 | ✓ | ✓ | ✓ | ✓ | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| | KOR 36.5 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 36.6 | ✓ | ✓ | ✓ | ✓ | ✓ |
| KOR 33 | 04.8.2.f | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.2.f | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.2.f | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 33.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 33.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 33.3 | ✓ | ✓ | ×× | ✓ | ✓ |
| KOR 37 | KOR 37.1 | ✓ | ✓ | ? | ✓ | × |
| | KOR 37.2 | ✓ | ✓ | ? | ✓ | × |
| | KOR 37.3 | ✓ | ✓ | ? | ✓ | × |
| | KOR 37.4 | ✓ | ✓ | ? | ✓ | ✓ |
| | KOR 37.5 | ✓ | ✓ | ? | ✓ | ✓ |
| KOR 34 | KOR 34.1 | ✓ | ✓ | ×× | ✓ | × |
| | KOR 34.2 | ✓ | ✓ | ×× | ✓ | × |
| | KOR 34.3 | ✓ | ✓ | ×× | ✓ | × |
| | KOR 34.4 | ✓ | ✓ | × | ✓ | × |
| | KOR 34.5 | ✓ | ✓ | ×× | ✓ | × |
| | KOR 34.6 | ✓ | ✓ | ×× | ✓ | × |
| | KOR 34.7 | ✓ | ✓ | ✓✓ | ✓ | × |
| KOR 32 | 04.8.2.e | ✓ | ✓ | × | ✓ | × |
| | 04.8.2.e.i | ✓ | ✓ | ✓ | ✓ | × |
| | 04.8.2.e.ii | ✓ | ✓ | × | ✓ | × |
| | 04.8.2.e.iii | ✓ | ✓ | ✓ | ✓ | × |
| | 04.8.2.e.iv | ✓ | ✓ | ✓ | ✓ | × |
| | KOR 32.2 | ✓ | ✓ | ✓✓ | ✓ | × |
| | KOR 32.7 | ✓ | ✓ | ✓✓ | ✓ | × |
| | KOR 32.8 | ✓ | ✓ | ×× | ✓ | × |
| KOR 1a | 04.8.1.ac* | ✓ | ✓ | ✓ | × | ✓ |
| | 04.8.1.ac.I | ✓ | ✓ | ✓ | × | ✓ |
| | 04.8.1.ac.II | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 1.10 | ✓ | ✓ | ✓ | × | × |
| | KOR 1.7 | ✓ | ✓ | ×× | × | ✓ |
| | KOR 1.8 | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 1.9 | ✓ | ✓ | ✓✓ | × | ✓ |
| KOR 2 | KOR 2.1 | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 2.2 | ✓ | ✓ | × | × | ✓ |
| | KOR 2.3 | ✓ | ✓ | × | × | ✓ |
| | KOR 2.4 | ✓ | ✓ | ×× | × | × |
| | KOR 2.5 | ✓ | ✓ | × | × | ✓ |
| | KOR 2.6 | ✓ | ✓ | ×× | × | ✓ |
| | KOR 2.7 | ✓ | ✓ | × | × | ✓ |
| | KOR 2.8 | ✓ | ✓ | ×× | × | ✓ |
| | KOR 2.9 | ✓ | ✓ | × | × | ✓ |
| KOR 8 | 04.8.1.aa | ✓ | × | ? | | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| KOR 9 | KOR 9.1 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 9.2 | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 9.3 | ✓ | ✓ | ✓ | × | ✓ |
| KOR 4 | 04.8.1.w | ✓ | × | ? | × | ✓ |
| KOR 5 | 04.8.1.z | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 5.1 | ✓ | ✓ | ✓ | × | × |
| | KOR 5.2 | ✓ | ✓ | ×× | × | ✓ |
| | KOR 5.3 | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 5.4 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 5.5 | ✓ | ✓ | ✓✓ | × | ✓ |
| KOR 6 | KOR 6.2 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.3 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.4 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.5 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.6 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.7 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 6.8 | ✓ | ✓ | ✓✓ | × | ✓ |
| KOR 10 | 04.8.1.x | × | × | ✓ | × | × |
| | KOR 10.1 | × | × | ✓✓ | × | × |
| | KOR 10.11 | × | × | ×× | × | × |
| | KOR 10.12 | × | × | ×× | × | × |
| | KOR 10.2 | × | × | ×× | × | × |
| | KOR 10.3 | × | × | ✓✓ | × | × |
| | KOR 10.4 | × | × | ✓✓ | × | × |
| | KOR 10.5 | × | × | ✓✓ | × | ✓ |
| | KOR 10.6 | × | × | × | × | ✓ |
| | KOR 10.7 | × | × | ×× | × | × |
| | KOR 10.8 | × | × | ×× | × | ✓ |
| KOR 11 | 04.8.1.w | ✓ | × | ? | × | ✓ |
| KOR 12 | 04.8.1.v* | ✓ | ✓ | × | × | ✓ |
| | 04.8.1.v.I | ✓ | ✓ | × | × | ✓ |
| | 04.8.1.v.II | ✓ | ✓ | × | × | ✓ |
| | KOR 12.1 | ✓ | ✓ | × | × | ✓ |
| | KOR 12.3 | ✓ | ✓ | ×× | × | ✓ |
| KOR 13 | 04.8.1.u | ✓ | × | ? | × | ✓ |
| KOR 14 | 04.8.1.t | ✓ | × | ✓ | × | ✓ |
| | KOR 14.10 | ✓ | × | × | × | ✓ |
| | KOR 14.11 | ✓ | × | ✓ | × | ✓ |
| | KOR 14.14 | ✓ | × | ✓✓ | × | ✓ |
| | KOR 14.15 | ✓ | × | ✓✓ | × | ✓ |
| KOR 14a | KOR 14.8 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 14.9 | ✓ | ✓ | ✓ | × | ✓ |
| KOR 14b | 04.8.1.s | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 14.1 | ✓ | ✓ | ×× | × | ✓ |
| KOR 23 | 04.8.1.r* | × | ✓ | ✓ | × | × |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| | 04.8.1.r.I | × | ✓ | ✓ | × | ✓ |
| | 04.8.1.r.II | × | ✓ | ✓ | × | ✓ |
| | 04.8.1.r.III | × | ✓ | ✓ | × | ✓ |
| | KOR 23.1 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 23.2 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 23.3 | ✓ | ✓ | × | × | ✓ |
| | KOR 23.4 | ✓ | ✓ | ✓ | × | ✓ |
| KOR 22 | 04.8.1.q | ✓ | ✓ | × | ✓ | ✓ |
| | 04.8.1.q.I | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.1.q.II | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.1.q.III | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 22.1 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 22.10 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.11 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.12 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.13 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 22.14 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.2 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 22.4 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 22.5 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.6 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.7 | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 22.8 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| KOR 21a | 04.8.1.p | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 21.10 | ✓ | ✓ | ✓✓ | × | × |
| | KOR 21.4 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 21.5 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 21.6 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 21.7 | ✓ | ✓ | ✓✓ | ✓ | × |
| | KOR 21.8 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 21.9 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| KOR 21 | KOR 21.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 21.2 | ✓ | ✓ | ✓✓ | ✓ | × |
| | KOR 21.3 | ✓ | ✓ | ×× | ✓ | × |
| KOR 15 | 04.8.1.o | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 15.2 | ✓ | ✓ | ×× | × | × |
| | KOR 15.3 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 15.4 | ✓ | ✓ | ✓ | × | ✓ |
| | KOR 15.5 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 15.6 | ✓ | ✓ | ×× | × | ✓ |
| | KOR 15.7 | ✓ | ✓ | ✓✓ | × | ✓ |
| | KOR 15.8 | ✓ | ✓ | ×× | × | × |
| | KOR 15.9 | ✓ | ✓ | ✓✓ | × | ✓ |
| KOR 16 | 04.8.1.n* | ✓ | ✓ | ✓ | ✓ | ✓ |
| | KOR 16.10 | ✓ | ✓ | ×× | ✓ | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| | KOR 16.5 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 16.6 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 16.7 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 16.8 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 16.9 | ✓ | ✓ | × | ✓ | ✓ |
| KOR 16 a | KOR 16.1 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 16.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | KOR 16.3 | ✓ | ✓ | ✓✓ | ✓ | × |
| | KOR 16.4 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| KOR 17 | 04.8.1.m* | × | × | × | ✓ | × |
| | KOR 17.2 | × | × | × | ✓ | × |
| | KOR 17.3 | × | × | ✓✓ | × | × |
| KOR 18 | 04.8.1.l | ✓ | × | ? | × | ✓ |
| | 04.8.1.l.I | ✓ | × | ? | × | ✓ |
| | 04.8.1.l.II | ✓ | × | ? | × | ✓ |
| | 04.8.1.l.III | ✓ | × | ? | × | ✓ |
| KOR 19 | 04.8.1.k | ✓ | × | ? | | × |
| KOR 20 | 04.8.1.j | × | × | ? | | ✓ |
| KOR 24 | 04.8.1.l | ✓ | × | ? | × | × |
| | 04.8.1.l.I | ✓ | × | ? | ✓ | × |
| | 04.8.1.l.II | ✓ | × | ? | ✓ | × |
| | 04.8.1.l.III | ✓ | × | ? | ✓ | × |
| | KOR 24.5 | ✓ | × | ? | ✓ | × |
| | KOR 24.6 | ✓ | × | ? | ✓ | × |
| KOR 25 | KOR 25.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 25.3 | ✓ | ✓ | ✓ | | ✓ |
| | KOR 25.4 | ✓ | ✓ | ✓ | | ✓ |
| | KOR 25.5 | ✓ | ✓ | ✓ | ✓ | ✓ |
| KOR 26 | 04.8.1.g* | × | × | ? | ✓ | ✓ |
| KOR 27 | 04.8.1.f* | ✓ | ✓ | ? | ✓ | ✓ |
| | KOR 27.2 | ✓ | ✓ | ? | ✓ | ✓ |
| | KOR 27.4 | ✓ | ✓ | ? | ✓ | ✓ |
| KOR 28 | 04.8.1.e | ✓ | × | ? | × | ✓ |
| KOR 29 | 04.8.1.c | ✓ | × | ? | × | ✓ |
| | 04.8.1.c.I | ✓ | × | ? | × | ✓ |
| | 04.8.1.c.II | ✓ | × | ? | × | ✓ |
| | 04.8.1.c.III | ✓ | × | ? | × | ✓ |
| KOR 31 | 04.8.1.b* | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.1.b.I | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.8.1.b.II | ✓ | ✓ | × | ✓ | ✓ |
| | 04.8.1.b.III | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 31.1 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 31.2 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 31.5 | ✓ | ✓ | ×× | ✓ | ✓ |
| KOR 35 | 04.8.1.a | ✓ | ✓ | ✓ | ✓ | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| | KOR 35.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | KOR 35.3 | ✓ | ✓ | × | ✓ | ✓ |
| | KOR 35.5 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| SAM 1 | 04.7.24.u | ✓ | ✓ | × | ✓ | ✓ |
| | 04.7.24.u.I | ✓ | ✓ | ✓ | ✓ | ✓ |
| | 04.7.24.u.II | ✓ | ✓ | ✓ | ✓ | ✓ |
| | SAM 1.1 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 1.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 1.3 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 1.4 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 1.5 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| SAM 4 | 04.7.24.t | ✓ | ✓ | ? | ✓ | × |
| | 04.7.24.t.I | ✓ | ✓ | ? | ✓ | × |
| | 04.7.24.t.II | ✓ | ✓ | ? | ✓ | × |
| | 04.7.24.t.III | ✓ | ✓ | ? | ✓ | × |
| | SAM 4.3 | ✓ | ✓ | ? | ✓ | × |
| | SAM 4.4 | ✓ | ✓ | ? | ✓ | × |
| 2004 field season | 04.7.24.r | ✓ | × | ? | ? | ✓ |
| SAM 3 | 04.7.24.s | ✓ | × | ✓ | ✓ | × |
| | SAM 3.1 | ✓ | × | ✓ | ✓ | × |
| | SAM 3.2 | ✓ | × | ×× | ✓ | ✓ |
| | SAM 3.3 | ✓ | × | ✓ | × | ✓ |
| | SAM 3.4 | ✓ | × | ✓ | × | ✓ |
| | SAM 3.5 | ✓ | × | ✓ | × | ✓ |
| 2004 field season | 04.7.24.q | ✓ | × | ? | ✓ | ✓ |
| SAM 2 | SAM 2.1 | × | ✓ | ✓ | ✓ | ✓ |
| | SAM 2.2 | × | ✓ | ✓✓ | | ✓ |
| | SAM 2.3 | × | ✓ | ✓ | ✓ | ✓ |
| | 04.7.24.p | × | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 2.4 | × | ✓ | ✓✓ | ✓ | ✓ |
| SAM 12 | SAM 12.1 | ✓ | ✓ | ? | ✓ | ✓ |
| | SAM 12.2 | ✓ | ✓ | ? | × | × |
| SAM 10 | SAM 10.8 | ✓ | ✓ | × | × | ✓ |
| | SAM 10.9 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 10.7 | ✓ | ✓ | × | × | ✓ |
| | SAM 10.6 | ✓ | ✓ | ✓✓ | × | ✓ |
| SAM 10a | SAM 10.5 | ✓ | ✓ | ✓✓ | × | ✓ |
| | SAM 10.3 | ✓ | ✓ | ×× | × | ✓ |
| | SAM 10.4 | ✓ | ✓ | ✓ | × | ✓ |
| | SAM 10.2 | ✓ | ✓ | ✓✓ | × | ✓ |
| | SAM 10.1 | ✓ | ✓ | ✓✓ | × | ✓ |
| SAM 9 | 04.7.24.m | ✓ | ✓ | ✓ | × | × |
| | SAM 9.3 | ✓ | ✓ | ✓✓ | × | ✓ |
| | SAM 9.4 | ✓ | ✓ | × | × | ✓ |
| | SAM 9.2 | ✓ | ✓ | ×× | × | ✓ |
| SAM 8 | SAM 8.5 | ✓ | ✓ | ×× | ✓ | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| | 04.7.24.l | ✓ | ✓ | ✓ | × | ✓ |
| | SAM 8.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 8.3 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 8.4 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 8.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| SAM 5a | 04.7.24.k | ✓ | × | ? | × | × |
| | 04.7.24.k.I | ✓ | × | ? | × | × |
| | 04.7.24.k.II | ✓ | × | ? | × | × |
| | 04.7.24.k.III | ✓ | × | ? | × | × |
| SAM 20 | 04.7.24.j | ✓ | ✓ | ✓ | × | ✓ |
| | SAM 20.2 | ✓ | ✓ | ✓ | × | ✓ |
| | SAM 20.3 | ✓ | ✓ | × | × | ✓ |
| | SAM 20.4 | ✓ | ✓ | ×× | × | ✓ |
| | SAM 20.5 | ✓ | ✓ | ✓✓ | × | ✓ |
| SAM 19a | 04.7.24.i | ✓ | × | ? | × | ✓ |
| SAM 18 | 04.7.24.h | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.24.g | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.24.f | ✓ | × | ? | × | × |
| SAM 17 | SAM 17.1 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 17.2 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 17.3 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 17.4 | ✓ | ✓ | × | ✓ | ✓ |
| SAM 14 | SAM 14.1 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 14.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 14.3 | ✓ | ✓ | × | ✓ | ✓ |
| SAM 13 | SAM 13.3 | ✓ | ✓ | ×× | ✓ | × |
| | SAM 13.4 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 13.5 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 13.2 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 13.1 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| SAM 21 | SAM 21.1 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 21.2 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 21.3 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 21.4 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 21.5 | ✓ | ✓ | ✓ | ✓ | ✓ |
| SAM 22 | SAM 22.1 | ✓ | ✓ | ? | ✓ | ✓ |
| SAM 23 | SAM 23.2 | ✓ | × | ×× | × | ✓ |
| | SAM 23.3 | ✓ | × | ×× | × | ✓ |
| SAM 24a | SAM 24.1 | ✓ | ✓ | ×× | ✓ | ✓ |
| SAM 24b | SAM 24.3 | ✓ | ✓ | ? | ✓ | ✓ |
| | SAM 24.4 | ✓ | ✓ | ? | ✓ | ✓ |
| SAM 24c | SAM 24.5 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 24.6 | ✓ | ✓ | ×× | ✓ | ✓ |
| SAM 24d | SAM 24.8 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 24.9 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 24.10 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | SAM 24.11 | ✓ | ✓ | ×× | ✓ | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| SAM 24e | SAM 24.12 | ✓ | ✓ | × | ✓ | ✓ |
| | SAM 24.13 | ✓ | ✓ | ×× | ✓ | ✓ |
| | SAM 24.14 | ✓ | ✓ | × | ✓ | ✓ |
| 2004 field season | 04.7.24.d | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| 2004 field season | 04.7.24.d | ✓ | ✓ | ✓ | ✓ | ✓ |
| 2004 field season | 04.7.24.c | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.24.b | ✓ | × | ✓✓ | × | ✓ |
| 2004 field season | 04.7.24.a | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.24.a.I | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.24.a.II | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.23.o | ✓ | ✓ | ✓✓ | × | ✓ |
| 2004 field season | 04.7.23.n | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.23.l | ✓ | × | ? | × | × |
| 2004 field season | 04.7.23.k | × | × | ? | × | ✓ |
| 2004 field season | 04.7.23.j | ✓ | ✓ | ✓✓ | × | ✓ |
| 2004 field season | 04.7.23.h | ✓ | ✓ | ✓✓ | × | ✓ |
| 2004 field season | 04.7.23.I | ✓ | ✓ | ✓✓ | × | ✓ |
| 2004 field season | 04.7.23.i.I | ✓ | ✓ | × | × | ✓ |
| 2004 field season | 04.7.23.i.II | ✓ | ✓ | × | × | ✓ |
| 2004 field season | 04.7.23.g | ✓ | × | ? | × | ✓ |
| 2004 field season | 04.7.23.f | ✓ | × | ? | × | ✓ |
| TUY 53 | 04.7.26.b | ✓ | ✓ | ? | × | ✓ |
| TUY 54 | 04.7.26.d | ✓ | × | ? | × | ✓ |
| | 04.7.26.c | ✓ | × | ? | × | ✓ |
| | 04.7.26.c.I | ✓ | × | ? | × | ✓ |
| | 04.7.26.c.II | ✓ | × | ? | × | ✓ |
| TUY 55 | 04.7.26.f | ✓ | × | ? | × | ✓ |
| | 04.7.26.e | ✓ | × | ? | × | ✓ |
| TUY 56 | 04.7.26.g | ✓ | ✓ | ? | × | ✓ |
| TUY 57 | 04.7.26.h | ✓ | ✓ | ? | × | ✓ |
| TUY 58 | 0.4.7.26.i | ✓ | × | ? | × | ✓ |
| | 0.4.7.26.j | ✓ | × | ? | × | ✓ |
| TUY 59 | 0.4.7.26.k | ✓ | × | ? | × | ✓ |
| TUY 61 | 0.4.7.26.l | ✓ | × | ? | × | ✓ |
| TUY 1 | 0.4.7.26.o | ✓ | × | ? | × | ✓ |
| | 0.4.7.26.n | ✓ | × | ? | × | ✓ |
| | 0.4.7.26.m | ✓ | × | ? | × | ✓ |
| TUY 52 | 0.4.7.26.p | ✓ | × | ? | × | ✓ |
| TUY 56 | 0.4.7.26.q | ✓ | ✓ | ? | × | ✓ |
| | 04.7.26.q.I | ✓ | ✓ | ? | × | ✓ |
| | 04.7.26.q.II | ✓ | ✓ | ? | × | ✓ |
| | 04.7.26.q.III | ✓ | ✓ | ? | × | ✓ |
| TUY 49 | 0.4.7.26.r* | ✓ | × | ? | × | ✓ |
| TUY 2 | 0.4.7.26.s | ✓ | × | ? | × | ✓ |

| Paleosol | Nodules | Not Groundwt. or Lacus. | Stage II or I | Significant difference between Micrite spar[a] | Calcite | Crystal size <20µm |
|---|---|---|---|---|---|---|
| TUY 3 | 0.4.7.26.t | ✓ | × | ? | × | ✓ |
| TUY 54 | 04.7.26.u* | ✓ | × | ? | × | ✓ |
| TUY 23 | TUY 23.4 | ✓ | ✓ | ✓ | × | ✓ |
| | TUY 23.2 | ✓ | ✓ | ×× | × | ✓ |
| | TUY 23.3 | ✓ | ✓ | ✓✓ | × | ✓ |
| TUY 27 | TUY 27.3 | ✓ | ✓ | ×× | × | ✓ |
| | TUY 27.7 | ✓ | ✓ | ×× | × | ✓ |
| TUY 31 | TUY 31.3 | ✓ | ✓ | ✓✓ | × | ✓ |
| | TUY 31.4 | ✓ | ✓ | ×× | × | ✓ |
| TUY 38 | TUY 38.1 | ✓ | × | ✓✓ | × | ✓ |
| KRA 2 | KRA 2.2 | ✓ | ✓ | ×× | ✓ | × |
| KRA 1 | KRA 1.3 | ✓ | ✓ | ×× | ✓ | × |
| KRA 7a | KRA 7.12 | ✓ | ✓ | ×× | ✓ | × |
| KRA 7d | KRA 7.4 | ✓ | ✓ | ×× | ✓ | × |
| KRA 7e | KRA 7.3 | ✓ | ✓ | ? | ✓ | × |
| KRA 5a | KRA 5.4 | ✓ | × | ×× | ✓ | × |
| KRA 5c | KRA 5.11 | ✓ | ✓ | ×× | ✓ | × |
| KRA 5d | KRA 5.14 | ✓ | ✓ | ×× | × | × |
| MES 7 | MES 7.2 | ✓ | ✓ | ? | ✓ | × |
| MES 3 | MES 3.2 | ✓ | ✓ | × | ✓ | ✓ |
| | MES 3.3 | ✓ | ✓ | ×× | ✓ | ✓ |
| MES 1 | MES 1.2 | ✓ | ✓ | ×× | ✓ | ✓ |
| | MES 1.3 | ✓ | ✓ | × | ✓ | ✓ |
| | MES 1.4 | ✓ | ✓ | × | ✓ | ✓ |
| MES 8 | MES 8.4 | ✓ | ✓ | ✓✓ | ✓ | × |
| | MES 8.5 | ✓ | ✓ | ×× | ✓ | × |
| | MES 8.2 | ✓ | ✓ | ✓✓ | ✓ | ✓ |
| | MES 8.1 | ✓ | ✓ | ✓✓ | ✓ | × |
| MES 10 | MES 10.3 | ✓ | ✓ | ✓ | ✓ | × |
| | MES 10.4 | ✓ | ✓ | ✓✓ | ✓ | × |
| | MES 10.5 | ✓ | ✓ | ✓ | ✓ | × |
| MES 15 | MES 15.3 | ✓ | ✓ | ×× | ✓ | × |
| | MES 15.5 | ✓ | ✓ | ×× | ✓ | × |
| MES 16 | MES 16.3 | ? | ✓ | ×× | ✓ | × |
| | MES 16.4 | ? | ✓ | ×× | ✓ | × |
| | MES 16.5 | ? | ✓ | ×× | ✓ | × |
| | MES 16.6 | ? | ✓ | ✓✓ | ✓ | ✓ |
| | MES 16.1 | ? | ✓ | ✓✓ | ✓ | ✓ |
| | MES 16.2 | ? | ✓ | × | ✓ | ✓ |
| MES 17 | MES 17.10 | ? | ✓ | ×× | ✓ | ✓ |
| | MES 17.9 | ? | ✓ | ✓✓ | ✓ | ✓ |
| | MES 17.8 | ? | ✓ | ×× | ✓ | ✓ |

**Table 4.2 Summary of the screening results for all isotope results from Russia. Ticks refer to if the sample agrees with the statement in the column heading. In the significant difference between micrite and spar column two ticks is that the micrite from that nodule was significantly different from spar taken from the same nodule. One tick is that no spar was analysed from that nodule but the micrite was significantly different from the spar content of the nodules from the rest of the paleosol. One cross means the micritic values were the same as spar from the rest of the paleosol and two cross means the micritic component was the same as spar values from the same nodule .?refers to not enough data to make a classification (see Appendix A2.1 for values). [a]For explanations of significance see text (section 4.3.4).**

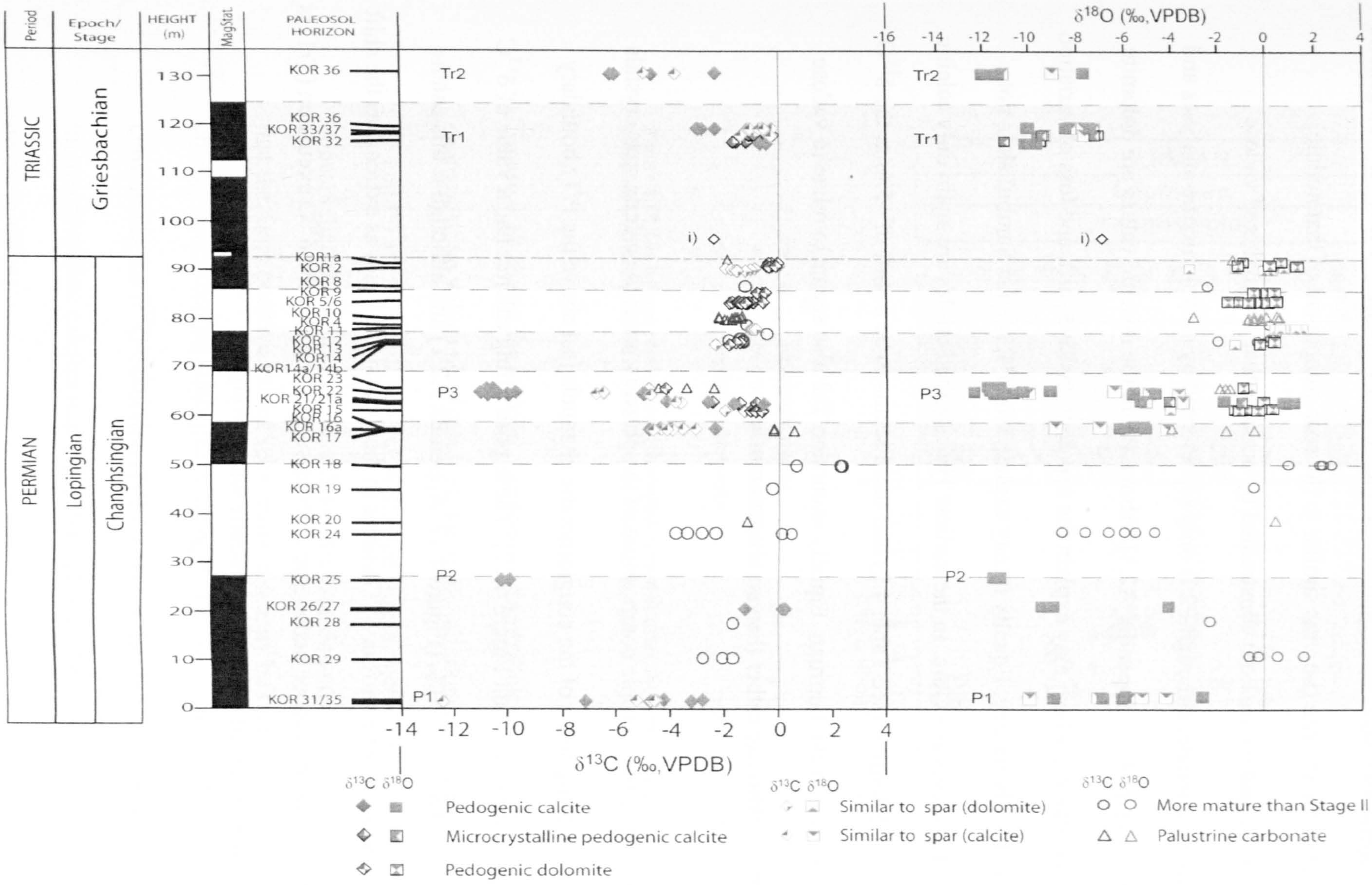


**Figure 4.17 The isotope results from Boyevaya Gora screened using the criteria in Table 4.1. For descriptions of the paleosols and stratigraphic information see Chapter 3. i) the isotopic value of pore filling calcite from sandstones just above the P/Tr boundary.**

Figure 4.17 shows the screened isotopic results from Boyevaya Gora. Using this screening it is now clear that magnitude excursion P1 is actually due to later diagenetic alteration of the micrite (i.e. it is similar to the spar component of that nodule). However, P2 and P3 are both constrained by nodules that are unaltered vadose pedogenic carbonate, although P2 is only represented by only 4 micritic analyses and one spar (Figure 4.17 Appendix A2.1). Above P3 all the micritic values are dolomite, rather than calcite, which may explain the apparent positive shift, and loss of variation up to the P/Tr boundary. Equally it may explain why P4, seen at Sambullak is not observed at Boyevaya Gora. In the earliest Triassic the nodules are again only calcitic rather than dolomitic (see Table 4.2) and there seems to be a shift of –5‰ in the $\delta^{18}O$ values relative to the Permian. Equally excursion Tr2 also seems to relate to vadose pedogenic carbonate rather than an alteration effect.

To investigate the isotopic composition of the phreatic water the calcite spar crystals found cementing some of the conglomeratic channels just above the P/Tr boundary were analysed (see (i) on Figure 4.17). These pore filling calcites had a value of $\delta^{13}C$ –2.21‰ and $\delta^{18}O$ –7.29‰ (Figure 4.17, Appendix A2.1) and although it this calcite does show a negative shift in $\delta^{18}O$ values in the Triassic, it is not as extreme as the shift in as the unaltered vadose pedogenic calcites suggesting that the $\delta^{18}O$ excursion (Tr1) is an atmospheric event rather than phreatic water overprint.

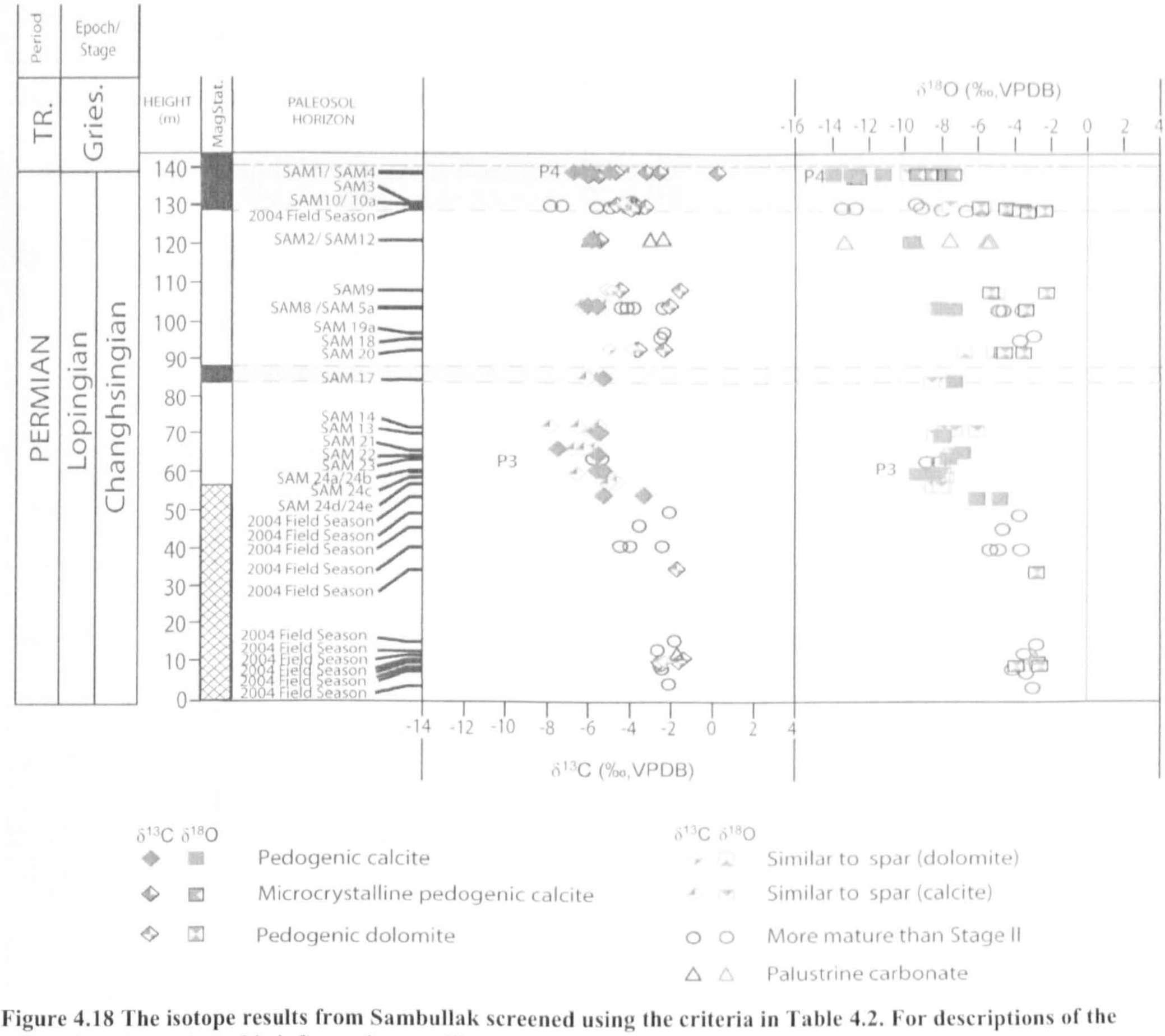


**Figure 4.18 The isotope results from Sambullak screened using the criteria in Table 4.2. For descriptions of the paleosols and stratigraphic information see Chapter 3.**

Figure 4.18 shows the isotopic variation at Sambullak. As with Boyevaya Gora the more positive values are a result of dolomite and more mature horizons. The excursions P3 and P4 are both still present in the vadose pedogenic micrite. Although below 50m it appears that all of the section is dolomitic (see Appendix A2.1) which would suggest that the more positive values seen below this may be related to this mineralogical change rather than an atmospheric change or an increase in paleosol maturity. When considering the $\delta^{18}O$ excursion (P4) it appears that the more positive values relate to the micro crystalline calcites and those that relate to the pedogenic calcite are the most negative values.

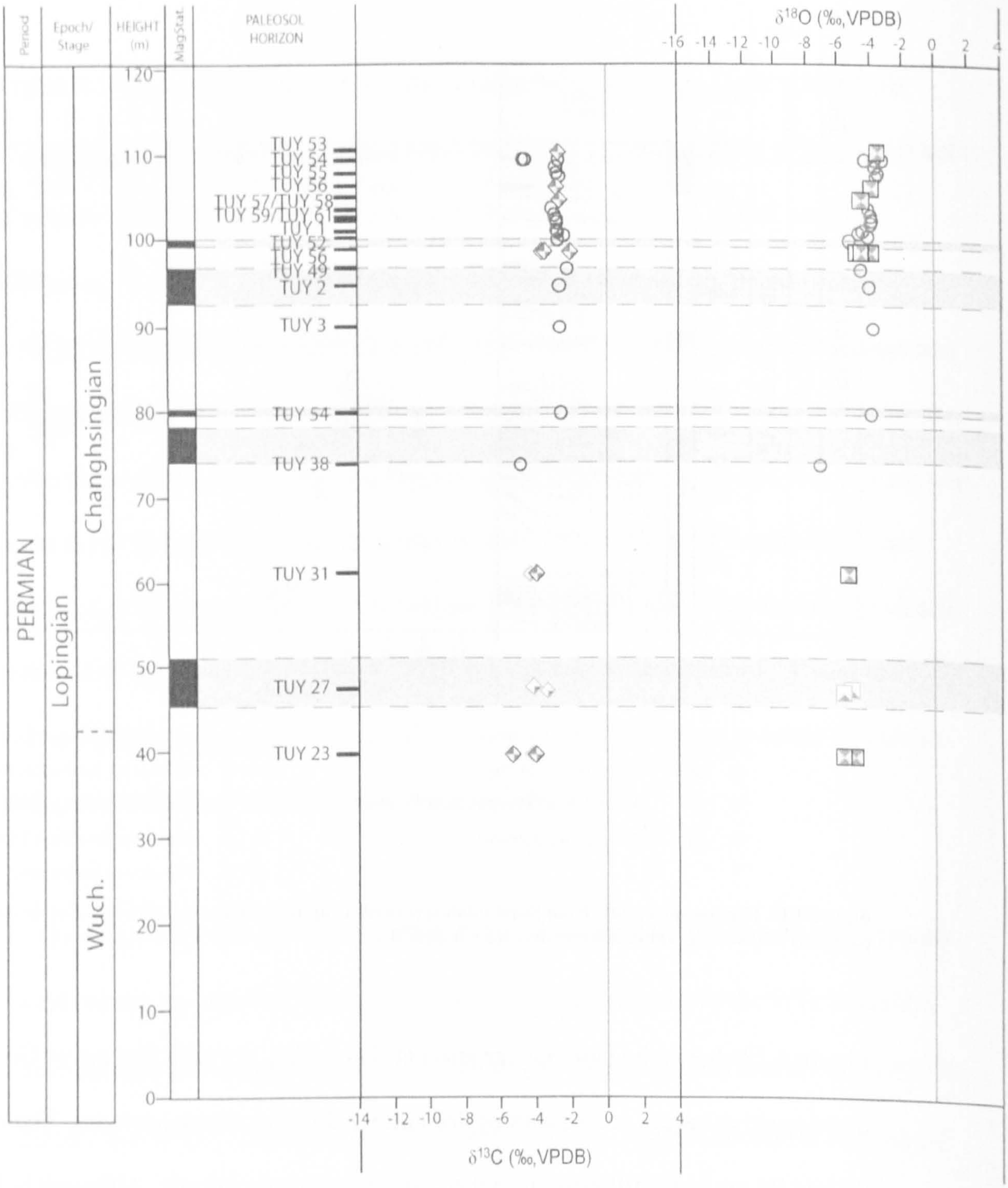


**Figure 4.19 The isotope results from Tuyembetka screened using the criteria in Table 4.2. For descriptions of the paleosols and stratigraphic information see Chapter 3.**

Tuyembetka has a restricted isotopic range compared with other sections and does not show any of the excursions seen in the other Permian sections (Figure 4.19). This is because the carbonate material from Tuyembetka is all dolomite rather than calcite (Appendix 2.1 and 2.4). As recorded in other sections, especially Boyevaya Gora (Figure 4.17), there is some isotopic variation within the dolomite which may follow the

isotopic trends seen in the calcite material, but the amount of variation is significantly reduced. This may explain why even though it overlaps with the sections at Boyevaya Gora, Sambullak, and Krasnogor it does not show any of the variation seen on those curves.

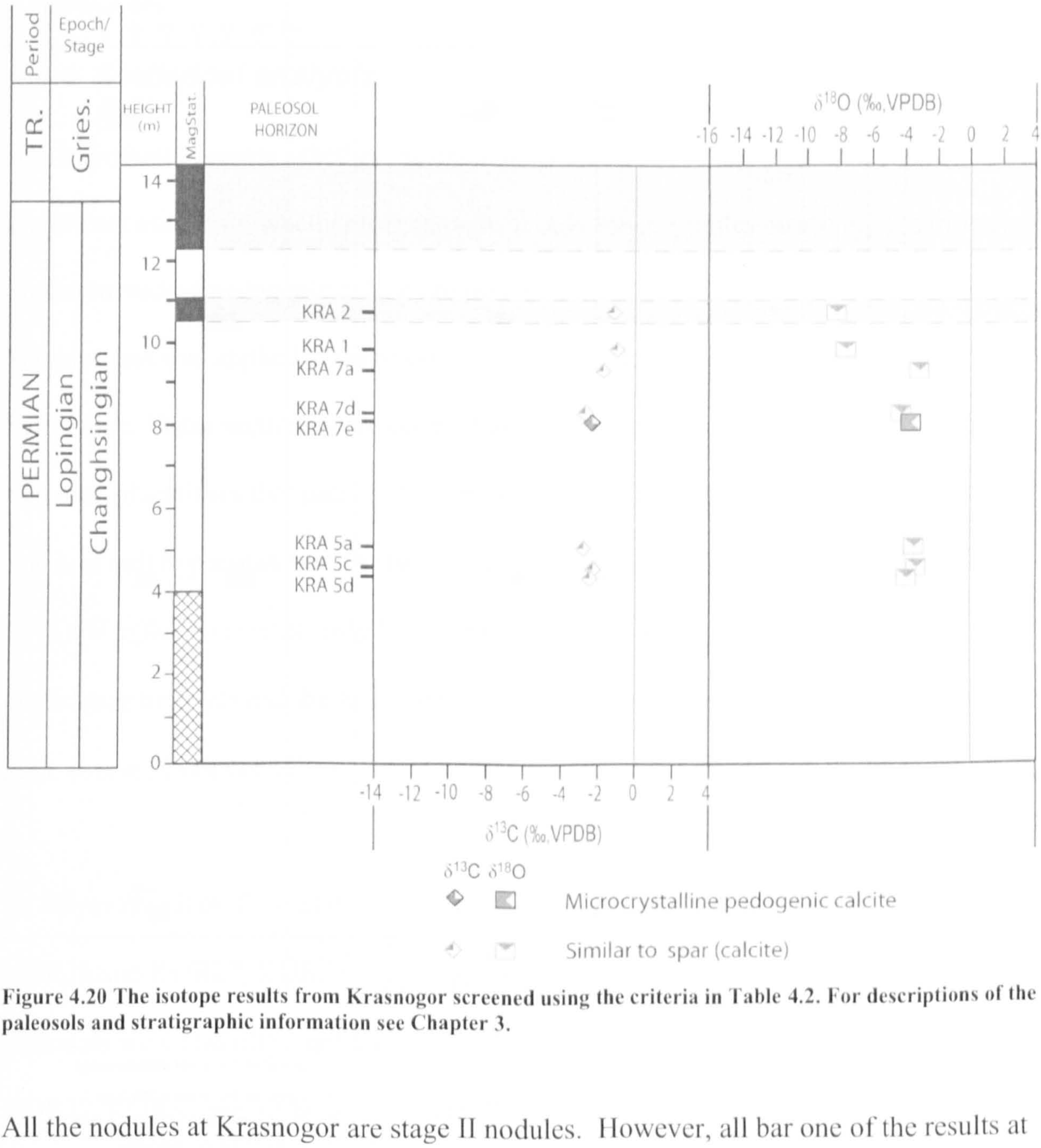


**Figure 4.20 The isotope results from Krasnogor screened using the criteria in Table 4.2. For descriptions of the paleosols and stratigraphic information see Chapter 3.**

All the nodules at Krasnogor are stage II nodules. However, all bar one of the results at Krasnogor appear to be over printed by the spar forming event. This is probably due to the fact that, as stated in Chapter 3, the Krasnogor palaeosols were formed on more porous fine sandstone rather than the mud and siltstone seen elsewhere in the basin. The one sample that has not been over printed by the spar forming event has values very

close to those which have been altered. This may suggest that this nodule was also altered but as it lacked any cracks or voids, there was nowhere for the spar to form. Alternatively the spar formed very early in the diagenetic history of the rock and had a similar geochemical signal to the meteoric water.

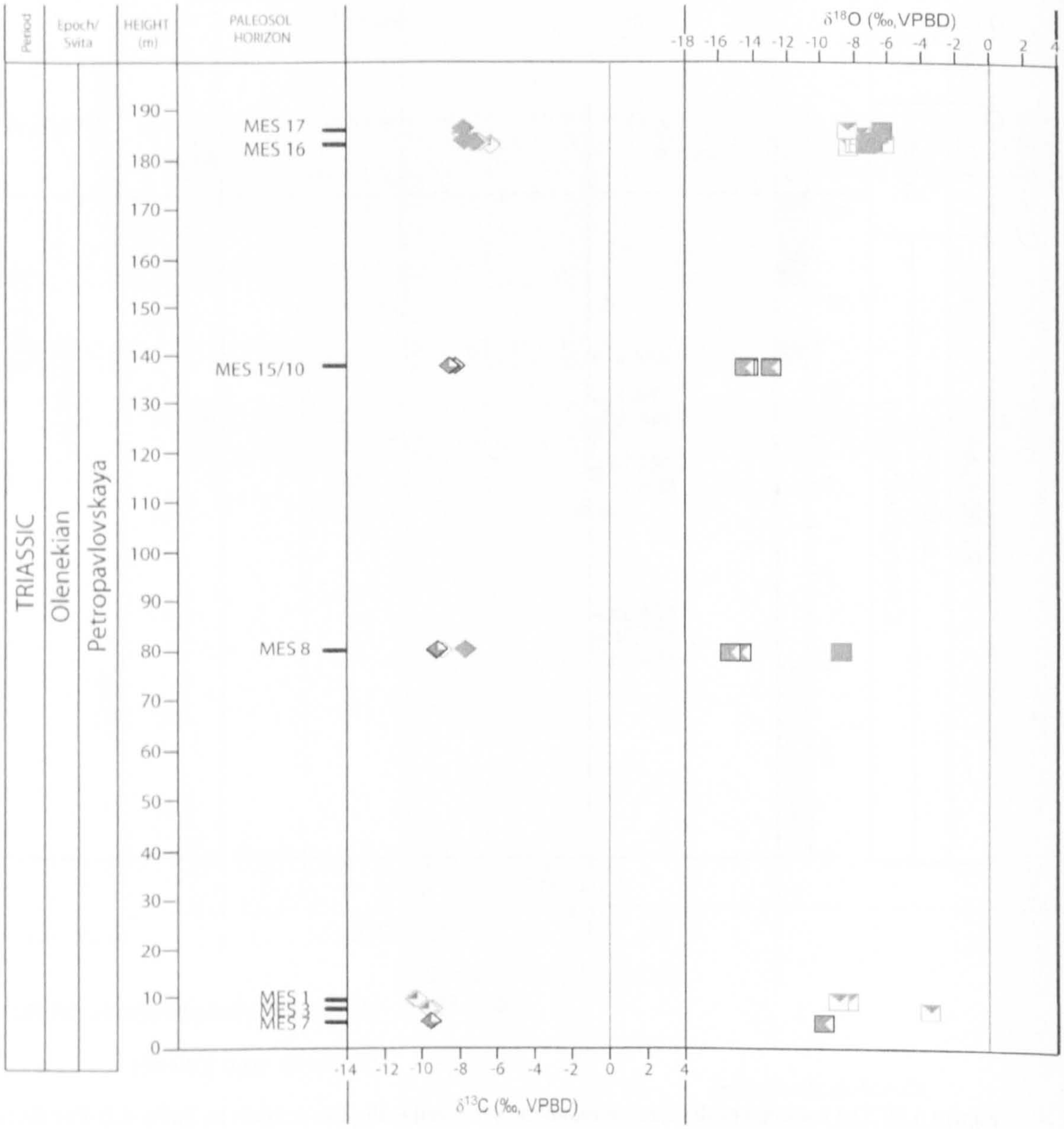


**Figure 4.21 The isotope results from Mescheryakovka screened using the criteria in Table 4.2. For descriptions of the paleosols and stratigraphic information see Chapter 3.**

Mescheryakovka is the only Olenekian section analysed and appears to have significantly more negative isotopic values than the Permian (minimum values of $\delta^{13}C$ –10.62‰ and $\delta^{18}O$ –17.66‰) (Figure 4.21). Figure 4.21 shows that most of these

extreme negative values are the result of a spar overprint or related to potential groundwater alteration. There are four analysis which have not been overprinted by the spar forming or groundwater alteration (MES8.2, MES16.6, MES16.1, MES17.9 see Table 1and Appendix 2.1). These have remarkably similar isotopic values of $\delta^{13}C$ –7.71‰ (±0.28‰ 1σ std) and $\delta^{13}C$ –8.15‰ (±1.22‰ 1σ std).

### *4.4.1 Statistical analysis*

It is important to assess whether the excursions identified in the Russian data are significant and, if so, whether this changes if only those nodules positively identified as unaltered vadose pedogenic calcite are used (Table 4.2). For this purpose the Mann-Whitney test was applied to consecutive screened paleosols at Boyevaya Gora and Sambullak. These sections were selected as they are the only ones which had significant numbers of analyses that passed all screening tests. The Mann-Whitney test assumes that as a null hypothesis that the two datasets are from the same population (Conover 1971). If $p \leq 0.1$ it is statistically likely that the null hypothesis is invalid (to a 95% confidence interval) and the two datasets are from separate populations (Dr R. Moyeed *pers. comm.*; Conover 1971).

At Boyevaya Gora, P1 was defined as comprising paleosol KOR35; P2 as KOR25, KOR26 and KOR27, KOR24; and P3 as KOR22 and KOR23. All the rest of the paleosols were classified as 'Background Permian' apart from KOR36, KOR33, KOR37, KOR32 and KOR34 which are Triassic (see Figure 4.17 and Appendix 2.5 for full results). At Sambullak, P3 is defined as comprising SAM23, SAM22, SAM13, SAM14 and SAM17; and P4 is SAM1, SAM4, SAM3, SAM2 and SAM12. The rest of the isotopic values from the paleosols are defined as being 'Background Permian'

| Section | Test | All data (p values) | | Pedogenic calcite only (p values) | |
|---|---|---|---|---|---|
| | | $\delta^{13}C$ | $\delta^{18}O$ | $\delta^{13}C$ | $\delta^{18}O$ |
| Boyevaya Gora | P1 (n=4,3) v 'Permian background' (n=119,13) | **0.0022** | **0.0011** | **0.0803** | 0.1064 |
| | P2 (n=4,3) v 'Permian background'(n=119,13) | **0.0007** | **0.0000** | **0.0693** | 0.2528 |
| | P3 (n=24,14) v 'Permian background' (n=119,13) | **0.0000** | **0.0000** | **0.0000** | **0.0005** |
| | Triassic (Tr1) (n=42,10) v 'Permian background' (n=119,13) | 0.6073 | **0.0000** | 0.4757 | **0.0003** |
| Sambullak | P3 (n=31,7) v "Permian background' (n=49,5) | 0.5036 | **0.0000** | 1.0000 | 0.5160 |
| | P4 (n=34,4) v 'Permian background' (n=49,5) | **0.0004** | **0.0000** | 0.2703 | **0.0200** |

**Table 4.3 Summary of statistical tests using the Mann-Whitney test (full results see Appendix 2.5) See section 1.2 for descriptions of the excursions. The bold values are those where there is a significant difference between the values of the excursions and those of the background (with a confidence interval of 95%). The n values are the numbers of analysis in the statistical test, the first is the unscreened number and the second is the screened number.**

Table 4.3 shows the summary of all the statistical tests. When all the isotope results are compared anomalies P1, P2, P3 and P4 are significant when all the data is considered. When only those analyses that pass all the criteria described in Table 4.2 are subjected to statistical analysis the picture changes. At Boyevaya Gora (Table 4.3) it now appears that the $\delta^{18}O$ excursions P1 and P2 are no longer significant. However, P3 and the oxygen excursion into the Triassic (Tr1) are both still significant as is the upper oxygen excursion at Sambullak (P4). Equally so are the $\delta^{13}C$ excursions P1, P2, P3 and P4. Both the lower carbon and oxygen excursions at Sambullak (P3) are no longer significant to a 90% confidence interval. However, especially when comparing the screened values there are very small numbers of analyses (see Appendix A2.5) and at such low numbers of input values the test may not be accurate as the values measured may not represent the total population distribution of the data (Dr R. Moyeed *pers. comm.*). The screening proposed in Table 4.2 is to remove some of the statistically significant excursions identified in the isotope signal (section 4.2).

## 4.5 Discussion

### *4.5.1 Dolomite in the Russian sections*

The vast majority of the carbonate material in the studied sections in the Southern Urals is formed primarily of poorly cemented micro- to cryptocrystalline micritic mud, suggesting a pedogenic origin for the calcrete in these sections (sees Section 4.3.3). This is supported by the predominance of carbonate nodules, rather than hardpans and the presence of floating grains and clotted textures within the nodules themselves (cf. Quast *et al.* 2006). Unstained petrographic observation of the micritic material supports this. XRD analyses of the micritic carbonate and subsequent dolomite-specific staining of the petrographic slides has revealed that some of the nodules contain micritic dolomite. Dolomite is commonly associated with diagenesis in sedimentary rocks (Leeder 1999) but this conflicts with the petrographic morphology observations of the nodules.

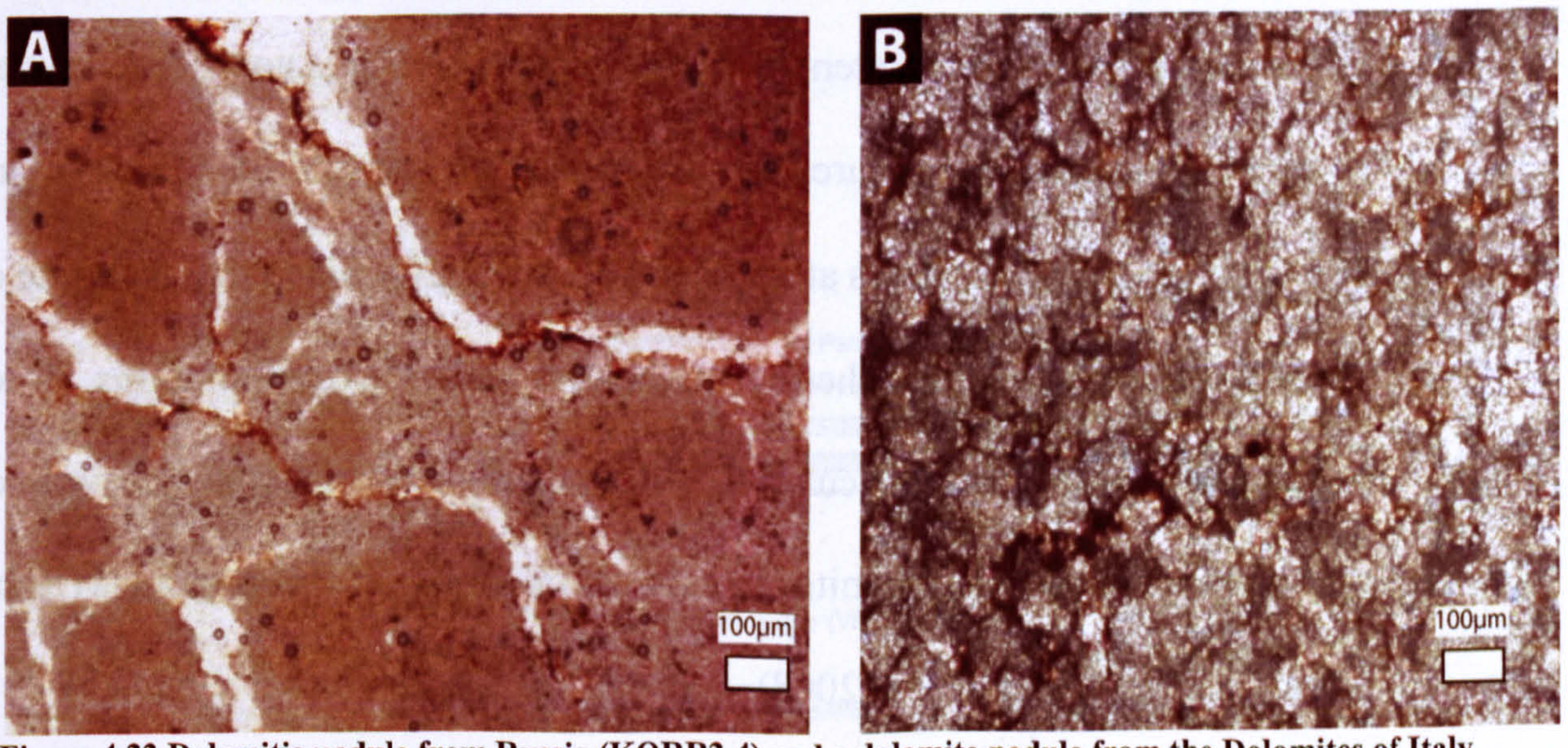


**Figure 4.22 Dolomitic nodule from Russia (KORR2.4) and a dolomite nodule from the Dolomites of Italy (RDA 41) Scale bar = 100µm.**

Comparing the texture of dolomitic nodules from Russia with diagenetically altered nodules from the Italian Dolomites (Figure 4.22, Appendix 5) shows that unlike the Italian dolocretes, those from Russia still preserve their primary pedogenic features (Figure 4.22) suggesting that the dolomite is not caused by diagenetic recrystallisation.

Another possibility is that the dolomite in Russian paleosols is derived from detrital dolomite from the source area of the fluvial sediments (in this case the Ural Mountains, see Chapter 3). This could explain the presence of dolomite in apparently pedogenic nodules (cf. Kraimer *et al.* 2005). The XRD analysis of different particle sizes within a nodule suggests that, unlike the nodules analysed by Kraimer *et al.* (2005), the dolomite derives primarily from the finest fraction which implies that it is related to the primary, micritic part of the nodule rather than clastic grains contained within matrix in which the nodules formed.

Primary pedogenic dolomite, formed through surface and groundwater processes rather than diagenetic or metamorphic processes has been recorded by several authors (Watts 1980, Wright and Tucker 1991, Colson and Cojan 1996; Alonso-Zarza *et al.* 1998; Capo *et al.* 2000; Bustillo and Alonso-Zarza 2007) and is usually associated with influence from lacustrine waters. Some have disputed if it is possible to crystallise dolomite at surface temperatures and pressures. Sherman and Barak (2000), in laboratory-based experiments at 25°C and 0.1 MPa $CO_2$ found that dolomite cannot directly precipitate at atmospheric temperatures and $CO_2$ concentrations. However, experiments using microbial cultures in both the field and laboratory have been shown to produce precipitated dolomites in natural waters at surface conditions (Roberts *et al.* 2004; Sánchez-Román *et al.* 2008).

There are two types of dolomitic paleosols present within the Russian sections: type A are those that are related to minor lacustrine limestones and as such are palustrine in origin (cf. Alonso-Zarza 2003); type B have no evidence of alteration or palustrine influence and yet the crypto- and microcrystalline component are formed principally dolomite.

Type A dolomitic profiles can be explained as there are many examples of such palustrine dolocretes in the geological record (Wright and Tucker 1991, Alonso-Zarza 2003). Similar examples have been recorded in Spanish Miocene dolocretes associated with groundwater and palustrine units (Alonzo-Zarza *et al.* 1998). Calvo *et al.* (1995) record dolomite occurring in soils close to lake margins that manifests as a crypto- to microcrystalline micrite nodules in the soil. It is thought that such asymmetric nodular dolocretes are precipitated in the vadose zone as the lacustrine body dried out (Colson and Cojan 1996; Quast *et al.* 2006). In semiarid climatic zones, evaporation of these ephemeral lakes would produce magnesium-rich waters which would precipitate dolomite rather than calcite (cf. Calvo *et al.* 1995). In such a system del Cura *et al.* (2001) suggest that cryptocrystalline (1-2μm crystals) dolomites can form directly from lake waters with an elevated carbonate/bicarbonate concentration. They suggest that the carbonate alkalinity will promote dolomite formation even at Mg/Ca ratios near 1, as there is plentiful $CO_3^{2-}$ solute present.

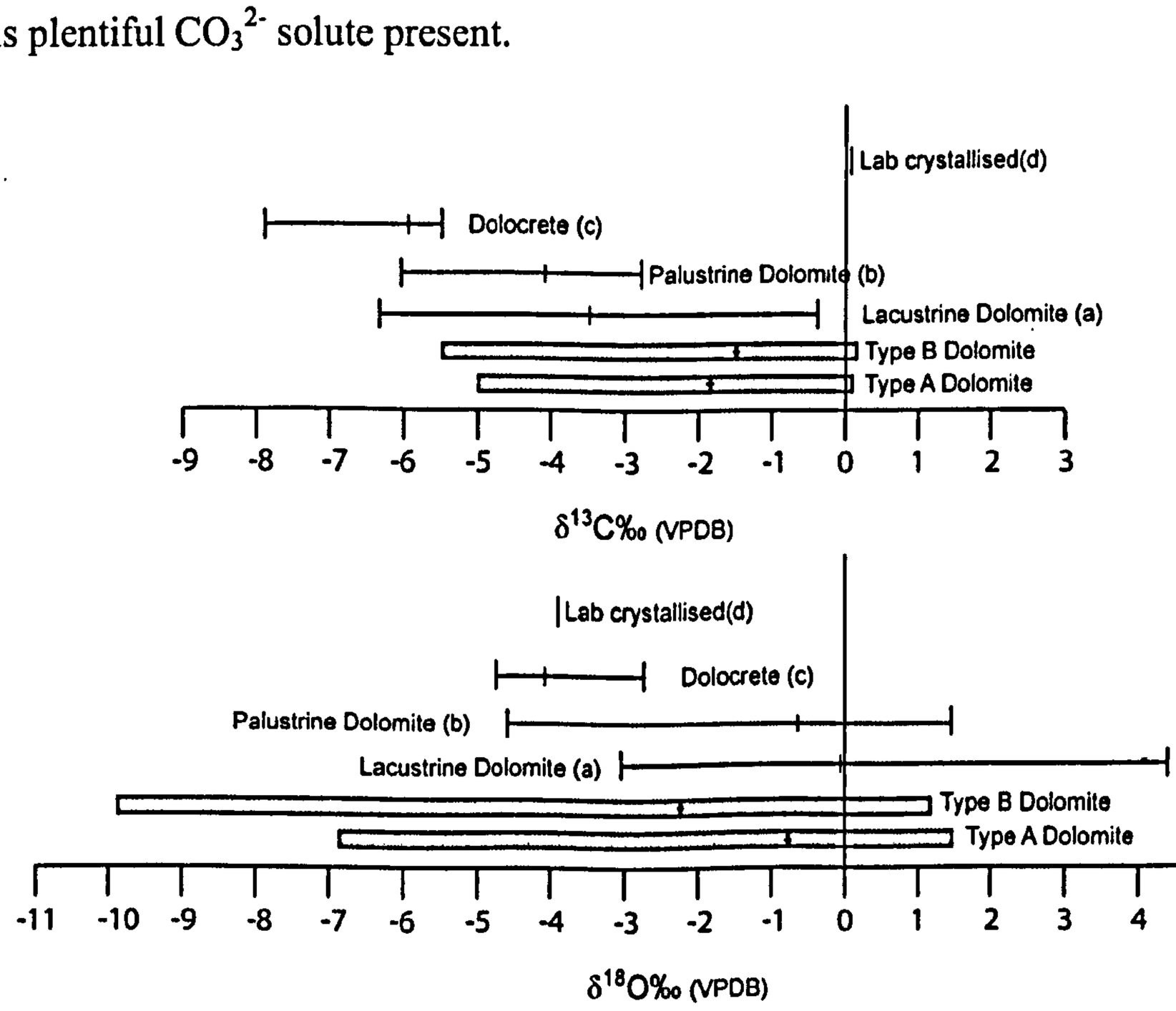


**Figure 4.23 The ranges and medians (median represented by tick) of Type A and Type B dolomite from this study compared to isotope results from other studies. (a) is lacustrine dolomite from the Pliocene central Spain (del Cura *et al.* 2001). (b) is palustrine dolomite values from the Madrid basin in the Palaeogene (Bustillo *et al.* 2002). (c) is lake margin dolocretes from the Middle Miocene, in the Madrid basin Spain (Calvo *et al.* 1995). (d) are the values produced by lab based experiments using microbial precipitation (Roberts *et al.* 2004).**

The $\delta^{13}C$ ranges of the Russian Type A dolomite fall within the ranges found in other lacustrine-formed dolomites (Figure 4.23). Similar values have been observed in the Pliocene of central Spain by del Cura *et al.* (2001). The relatively light $\delta^{13}C$ values (0 to–6‰) recorded in Russia (Figure 4.23) may suggest that plants had a role in the development of the dolomite (Calvo *et al.* 1995). Alternatively it may be a simple reflection of the more positive $\delta^{13}C$ atmospheric values in the Permian compared to the Cenozoic (cf. Veizer *et al.* 1999). Dolomite nodules associated with ephemeral lakes may have formed from a complex interplay between the desiccation of these bodies and the subsequent soil that formed after or during this process (Colson and Cojan 1996). The link between these type A dolomitic paleosols and lacustrine deposits is irrefutable as thin (5–6cm) limestones containing ostracods have been found as part of these soils.

A possible environmental analogue is the Loboi plain wetlands in Kenya (Bustillo and Alonzo-Zarza 2007). In periods of exceptionally heavy rainstorms, a river diversion takes place forming a wetland that becomes a shallow freshwater lake, which then evaporates producing progressively more saline waters. This saline water circulates through the surrounding soils and forms calcrete and dolocrete.

The $\delta^{18}O$ ranges of Type B dolomite sit partially outside the range of the lacustrine and lacustrine–associated dolomite (Figure 4.23). Equally the stratigraphic occurrence of Type B dolomite is harder to explain. Examples are found predominantly in paleosol horizons containing stage II carbonate nodules which are no different to their calcite counterparts. Equally they show no evidence of lacustrine influence, groundwater features or gleyed horizons (e.g. KOR6 Figure 4.24).

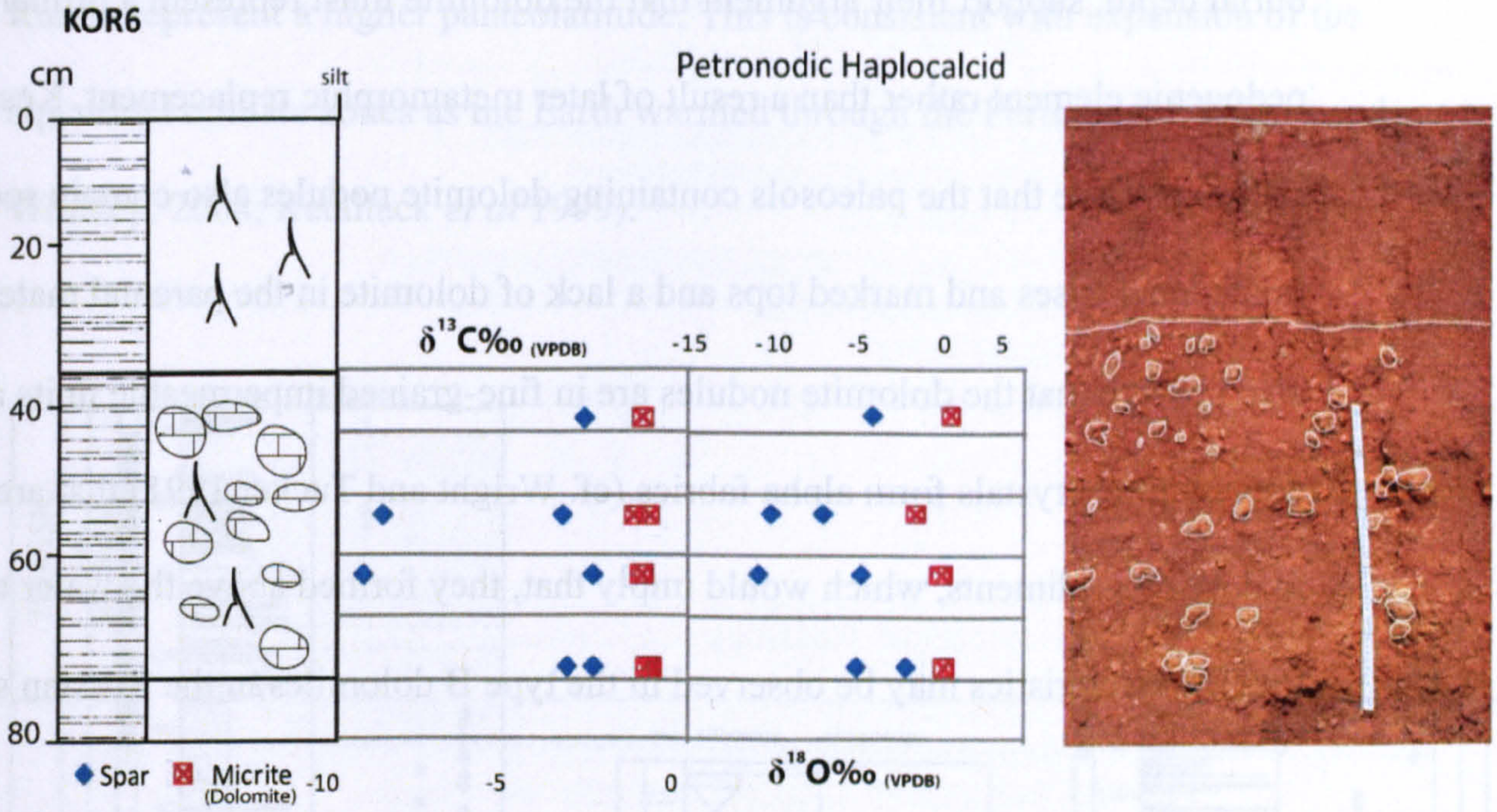


**Figure 4.24 A typical paleosol containing Type B dolomitic nodules from Boyevaya Gora. Scale bar in photos is 50cm.**

Type B dolomites are most evident in the 40 metres directly below the P/Tr boundary at Boyevaya Gora (Figure 4.17, Figure 4.25) where all the carbonate material is dolomite (see Appendix A2.1). This part of the section has the highest concentration of paleosols in the section. The paleosols have more developed Bk horizons than elsewhere in the section (up to stage V) and there is no evidence for ephemeral lakes associated with the paleosols. All paleosols are well rooted throughout with branching rootlets suggesting that the soil could not have been waterlogged for a prolonged period (Alonzo-Zarza 2003).

Paleosols showing a similar morphology as the Russian Type B dolomites have been previously identified in Vertisols from the Lower Permian (Wolfcampian to Leonardian) of New Mexico by Kessler *et al.* (2001) which at this time was at equatorial latitudes. These nodules are discrete, between <1cm to nearly 9cm in size, with a micritic texture to the dolomite crystals (≤30μm) and calcite filling the secondary veins. These observations, coupled with poor consolidation of the sediment and shallow

burial depth, support their argument that the dolomite must represent a primary pedogenic element rather than a result of later metamorphic replacement. Kessler *et al.* (2001) observe that the palcosols containing dolomite nodules also contain root traces, gradational bases and marked tops and a lack of dolomite in the parental material. They also observe that the dolomite nodules are in fine-grained impermeable units and that the dolomite crystals form alpha fabrics (cf. Wright and Tucker 1991) that are contained in dark red sediments, which would imply that, they formed above the water table. All these characteristics may be observed in the type B dolomites in the Russian sections.

Kessler *et al.* (2001) suggest that the origin of the dolomite crystallisation in their palcosols is a result of high Mg/Ca ratios caused by highly fluctuating water tables linked to high seasonality and a highly evaporative environment. Watts (1980) postulates that, in times of increased evaporation, magnesium will inhibit calcite nucleation and, if evaporation is greater than rate calcite nucleation, the Mg/Ca ratio would remain constant but the salinity would increase. Dolomite is then precipitated by 'forced crystallisation', and will thus not be in equilibrium with the precipitating fluids.

The type B dolocretes increase in occurrence after the negative $\delta^{13}C$ and $\delta^{18}O$ anomalies (excursion P3 see Figure 4.17) and below the P/Tr boundary at Boyevaya Gora and Sambullak (Figure 4.25). The soils of the lowest Triassic at Boyevaya Gora show no evidence ether Type A or B dolomite (Figure 4.25). This may suggest that the conditions that allowed the type B dolocrete to form may be directly related to the cause/consequences of the excursion P3. Using Kessler *et al.* (2001) as a guide, this suggests a dramatic increase in evaporation in the very latest Permian and a possible increase in seasonality. It must be noted that the example of Vertic dolosols in New Mexico is at near-equatorial palaeolatitude (Kessler *et al.* 2001) while the sections in

Russia represent a higher palaeolatitude. This is consistent with expansion of the equatorial climate zones as the Earth warmed through the Permian (cf. Kidder and Worsley, 2004; Retallack *et al* 1999).

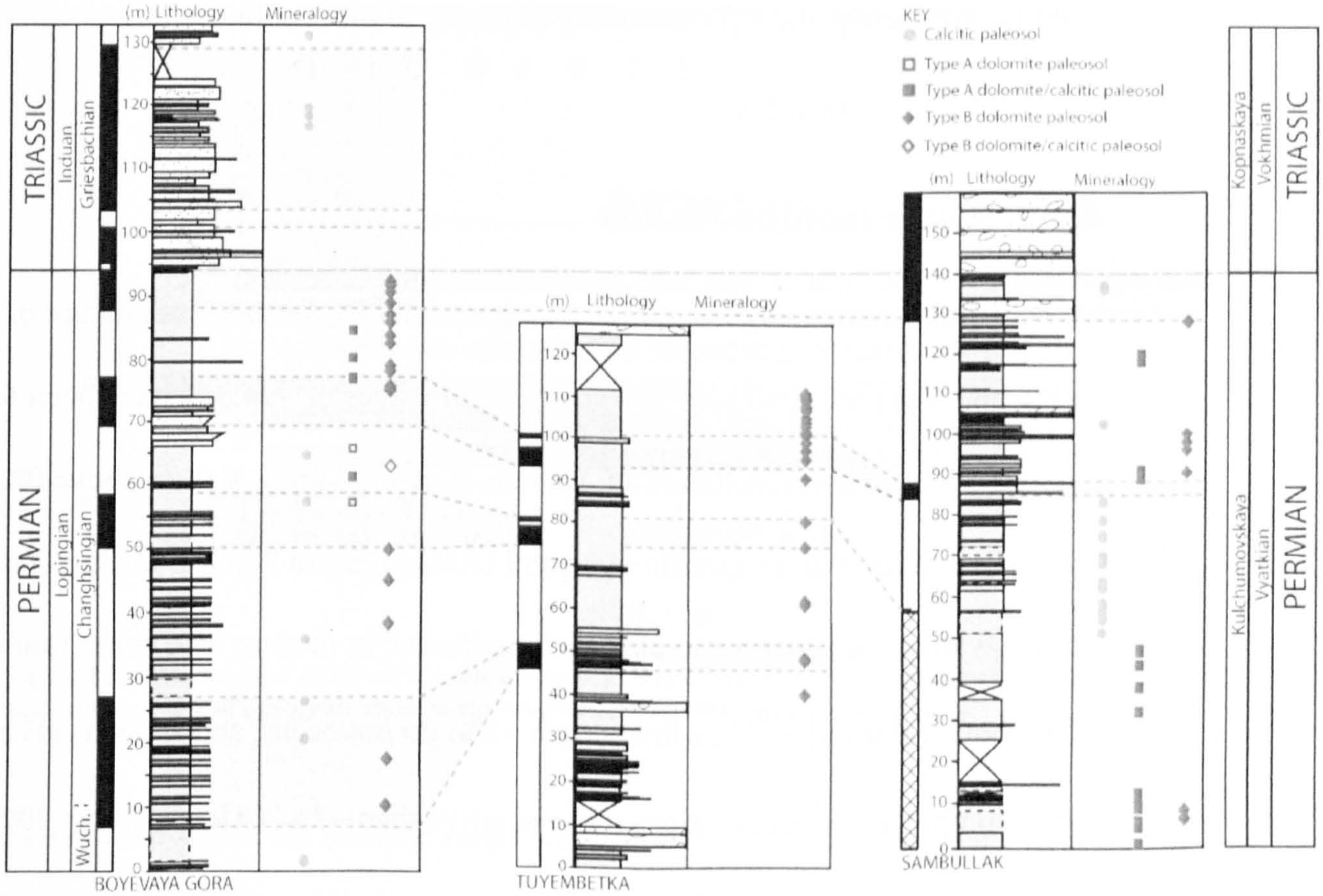


**Figure 4.25 The distribution of Type A and B dolomite through the Permian sections in Russia. Note there is no pedogenic dolomite present in the Triassic (Kearsey et al. in submission).**

The paleosols of the Triassic are, however, all calcitic and not dolomitic (Figure 4.21 and Figure 4.25), indicating that the specific conditions that resulted in the formation of primary, pedogenic dolomite peaked in the latest Permian, but did not continue in the Triassic. The complete absence of Lower Triassic dolocretes may indicate that evaporation rates, seasonality and monsoonal activity were reduced compared to the latest Permian. However, the Triassic paleosols at Mescheryakovka and Petropavlovka show evidence of fluctuating water tables, deep rooting, pedogenic slickensides, and pseudo-gleys, all indicating an increase in seasonality rather than a decrease (Chapter 3). An alternative hypothesis is that pedogenic dolomite formation is not linked to

extreme evaporation rates; rather it is reflecting a dramatic change in soil conditions across the P/Tr boundary. If bacteria were a key component in pedogenic dolomite formation (cf. Roberts *et al.* 2004, Sánchez-Román *et al.* 2008), then perhaps the disappearance of pedogenic dolocrete reflects a dramatic reduction in the soil microbial communities across the P/Tr boundary (Kearsey *et al.* in submission).

### *4.5.2 Stable isotope results*

Modern and recent pedogenic carbonates have a $\delta^{18}O_{carb}$ isotopic signature of between −13‰ and 0‰ (Alonso-Zarza 2003), although values of −14.3‰ have been found in modern calcite from Saskatchewan, Canada (Cerling 1984). Values above 0‰ are considered to have an evaporitic overprint (Alonso-Zarza 2003; Dworkin *et al.* 2005). $\delta^{18}O_{carb}$ values are sensitive to climatic conditions: in modern arid zones (annual rainfall <250 mm), values of $\delta^{18}O_{carb}$ lower than −5‰ do not occur, and areas receiving less than 350mm have $\delta^{18}O_{carb}$ values more positive than −2‰ (Alonso-Zarza 2003). The only exceptions are areas influenced by monsoonal rains, which have especially negative isotopic values. Pedogenic carbonates from areas influence by monsoons can have $\delta^{18}O_{carb}$ values up to 6‰ more negative than carbonates of non-monsoonal areas (Alonso-Zarza 2003).

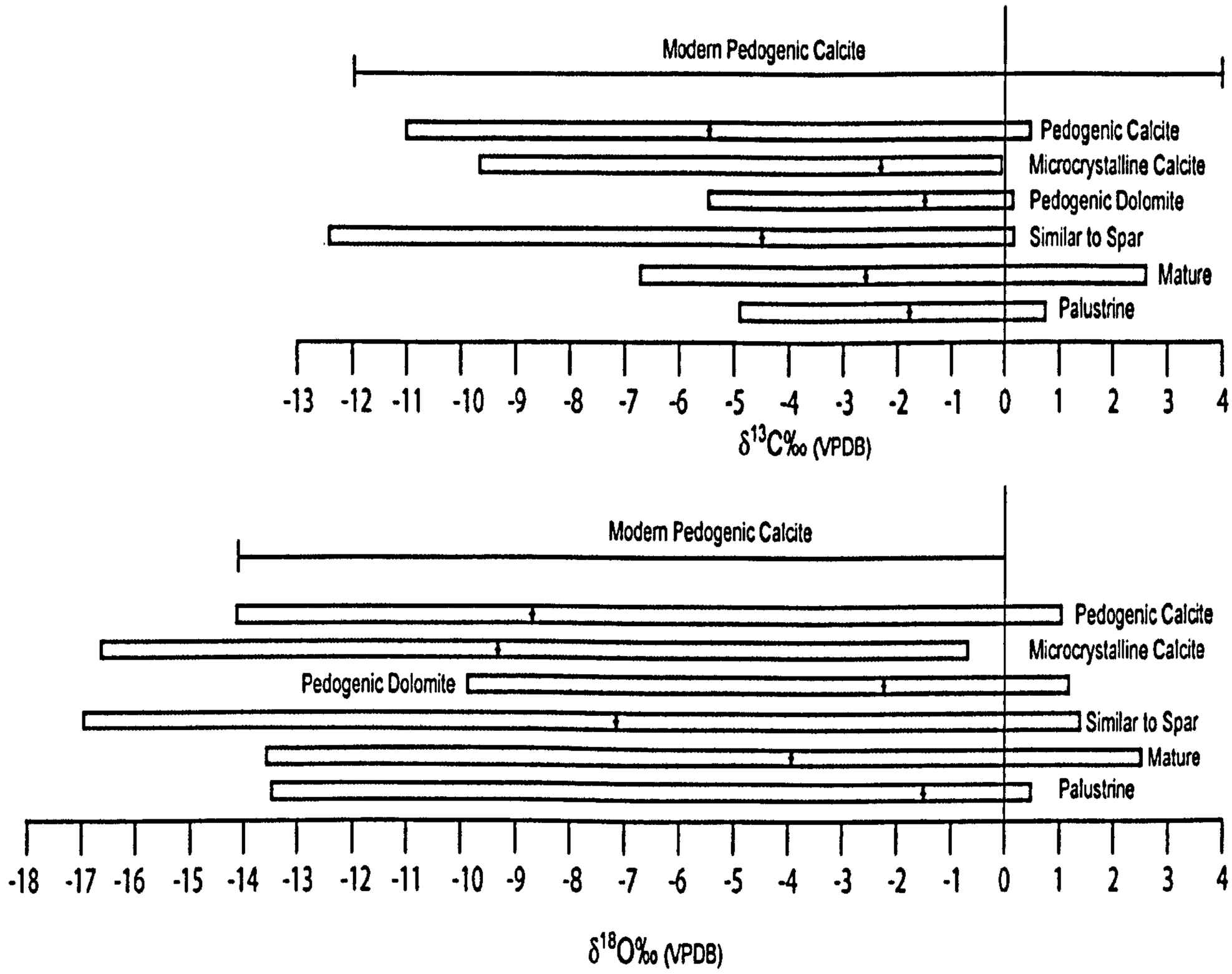


**Figure 4.26 The ranges of different micritic carbonate components found in Russia (Appendix A2.1) plotted against the ranges of pedogenic modern carbonate (Cerling 1984, Alonso-Zarza 2003).**

Figure 4.26 shows the isotopic ranges of the various types of carbonate identified in Table 4.2. from the Permian – Triassic paleosols of Russia. Apart from a few results from nodules where micritic values have been altered by the spar forming event, all values sit within the range of modern $\delta^{13}C_{carb}$ pedogenic calcite. The maximum $\delta^{18}O_{carb}$ values of the pedogenic calcite, pedogenic dolomite, mature calcrete and palustrine calcrete are within the range of modern calcite. However, all three types of carbonate have maximum values above 0‰ suggesting they may have been affected by evaporation. Those micritic values which were similar to the spar component of the nodule show the most negative isotopic values. This is similar to the observations of Cerling (1991) and Quast *et al.* (2006) where non-pedogenic and recrystallised calcretes are more negative than pedogenic values. In the three nodules where poikilotopic and neomorphic features were positively identified (SAM2.2, KOR2.4, KOR21.9) the spar component was significantly more negative than the micritic component (see Appendix

A2.1). For instance SAM2.2 has a micritic value of $\delta^{13}C_{carb}$ –2.48‰ and $\delta^{18}O_{carb}$ –5.52‰ and spar values of $\delta^{13}C_{carb}$ –4.24‰ and $\delta^{18}O_{carb}$ –10.66‰. The overlap between isotopic results from those nodules with micritic values similar to the spar component and those nodules which can be positively identified as being unaltered pedogenic calcite and dolomite (Figure 4.26) suggests that the spar-forming event happened at shallow depths or possibly even when the paleosol was active. This has been observed in modern Vertisols where microspars have grown in voids in an active soil (Ghosh *et al.* 2001). It also the micrite sampled from palustrine and paleosols more mature than stage II have a more positive range in $\delta^{18}O_{carb}$ than the other forms of carbonate observed in Russia (Figure 4.26) suggesting they are affected by evaporation to a greater extent than the stage II nodules, This was also recorded by Liu *et al.* (1996) and Ekart *et al.* (1999).

It is suggested that pedogenic carbonates with a crystal size >20μm are formed by groundwater rather than meteoric water (Quast *et al.* 2006), and it is evident that some of the microcrystalline carbonates have $\delta^{18}O_{carb}$ isotopic values which are more negative than those of the pedogenic calcite (Figure 4.26). This suggests that at least some of these calcretes may be formed from a different fluid to that which formed the pedogenic component. However, the fact that within many paleosol horizons, such as KOR15 (see Figure 4.17, Table 4.2 and Appendix A2.1), the vadose pedogenic values and microcrystalline values overlap suggesting they were formed from the same fluid.

| | Age | Locality | $\delta^{13}C$ (‰,VPDB) | $\delta^{18}O$ (‰,VPDB) | Author |
|---|---|---|---|---|---|
| Triassic | 234 Ma | Otter Sandstone (UK) | -9.9 | - | Ekart *et al.* 2000 |
| | Mid Triassic (240Ma) | Satpura basin, Central India | -5.8 to -7.2 | -5.5 to -10.9 | Ghosh *et al.*2001 |
| | Lower Anisian (>242Ma) | Utah (USA) | -5.5 to -7.6 | -3.7 to -6.2 | Prochnow *et al.* 2006 |
| | Upper Olenekian | Mescheryakovka | -7.29 to -7.92 | -7.00 to -9.85 | This Study |
| | Lowest Induan | Boyevaya Gora | -0.27 to -6.13 | -7.36 to -11.77 | This Study |
| | Earliest Triassic (28.0 metres [a]) | Karoo (South Africa) | -5.2 to -5.7 | -11.2 to -11.6 | Tarbor *et al.*2007 |
| Permian | Latest Permian (4.5 metres [a]) | Karoo (South Africa) | -5.6 to -7.1 | -13.4 to -14.1 | Tarbor *et al.*2007 |
| | Wuchiapingian to Changhsingian | Boyevaya Gora and Sambullak | 0.46 to -11.06 | 1.03 to -14.15 | This study |
| | 251 Ma | Quartermaster (Texas) | -7.4 | - | Ekart *et al.* 1999 |
| | Mid-Permian (260mMa) | Satpura basin, Central India | -5.1 to -7.9 | -8.4 to -14.4 | Ghosh *et al.*2001 |

**Table 4.4 Ranges from micritic pedogenic calcite values from other paleosol studies across the P/Tr boundary. [a] heights are from an arbitrary level placed at the bottom of Carlton heights, see Tarbor *et al.* (2007) for stratigraphic discussion. See figure 17, 18 and 21 and Appendix A2.1 for values from this study.**

The negative (–14‰) $\delta^{18}O_{carb}$ unaltered pedogenic calcite values seen in the Permian at Sambullak and Boyevaya Gora compare well to previously published values which have been rigorously tested and identified as being pedogenic, especially the time equivalent values from the Karoo basin (Table 4.4). However, the positive end of this range is much greater than recorded in other studies, again suggesting that evaporation may have had some control over the isotope values recorded in Russia. Equally the range of $\delta^{13}C_{carb}$ unaltered pedogenic calcite values is greater in the Permian in Russia than in other studies (Table 4.4). In the lowest Triassic the $\delta^{18}O_{carb}$ values compare well with those from Karoo (Tarbor *et al.* 2007; Table 4.4) but the range of the $\delta^{13}C_{carb}$ is greater than that seen at Karoo (although the Karoo values are only based on two data points; cf. Tarbor *et al.* 2007). The $\delta^{13}C_{carb}$ values for the Olenekian from Russian compare well to those from the Lower Anisian of Utah while the $\delta^{18}O_{carb}$ values are slightly more negative than seen in Utah (Table 4.4).

Of the four excursions identified in the Permian (P1, P2, P3 and P4 – see Figure 4.17) P1 is probably a result of diagenetic alteration as the nodule that has the negative values (KOR 35.3) is within error of the spar values from that paleosol (Figure 4.17). P2 is

identified as being unaltered pedogenic calcite, although it is only constrained by two horizons (Figure 4.17; Appendix A2.1). The extremely negative values recorded at Boyevaya Gora for excursion P3 also appear to be pedogenic and many of the isotopically positive values recorded in the same paleosols (such as KOR22) are related to the spar forming event (Figure 4.17). P4 is also defined by unaltered pedogenic calcite at Sambullak (Figure 4.18). The reason it is not recorded at Boyevaya Gora is that at this point in the section all the pedogenic material is entirely dolomite rather than calcite, which shows more positive $\delta^{18}O_{carb}$ values than calcite (cf. Quast *et al.* 2006) (Figure 4.18). P4 at Krasnogor has the same isotopic values as the spar components of the same nodules suggesting that they are a result of the spar-forming event (Figure 4.20). However, the fact that P4 at Sambullak appears to be pedogenic, while at it Krasnogor is possibly altered, may suggest that the fluid that formed the spar at Krasnogor was similar to the pedogenic fluid at Sambullak as they both show the excursion. Finally, the Triassic excursion recorded at Boyevaya Gora in the $\delta^{18}O_{carb}$ values also appears to be pedogenic (Figure 4.17) especially as it is similar to vadose pedogenic values in Karoo of a similar age (Table 4.4).

Negative $\delta^{13}C_{carb}$ excursions in organic carbon, carbonate and bone, have been observed in many P/Tr sections round the world (e.g. Krull and Retallack 2001; deWit *et al.* 2002; Kidder and Woresley 2004; Payne *et al.* 2004; Retallack and Jahren 2008) and all have been linked to the cause or an effect of the mass extinction event. Most of these terrestrial excursions occur in the first few metres of the Triassic (cf. Retallack *et al.* 2005; Retallack and Jahren 2008).

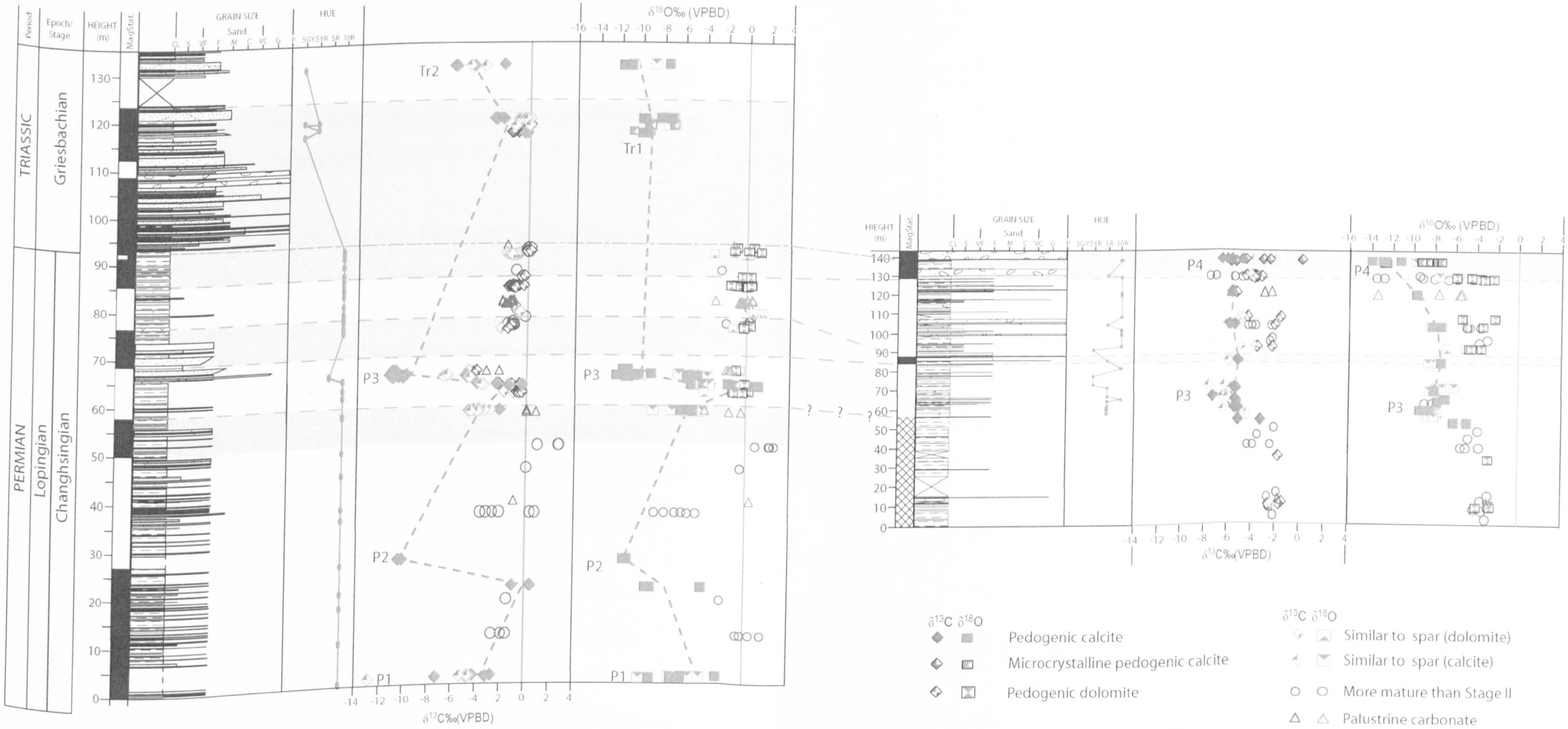


**Figure 4.27 Screened data from Boyevaya Gora (left) and Sambullak (right) correlated using magnetostratigraphy from the same sections (Taylor *et al.* 2009). Lithological data from unpublished field data from Dr A Newell and Dr R. Twitchett.**

No such excursion is seen in the basal Triassic in Russia (Figure 4.17). This is not to say that a negative excursion at the P/Tr boundary did not occur in Russia, but due to the change to coarser facies, there are no paleosols for 20 metres above the boundary. So it is possible that the global $\delta^{13}C_{carb}$ excursion seen in other areas also occurred in Russia in the basal Triassic, but as there was no carbonate being precipitated in the section studied or organic carbon preserved at that time, it has not been recorded.

In Russia, however, there is evidence for at least one negative excursion in $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values in the mid-Changhsingian (P3) (Figure 4.27). This excursion is recorded in carbonate nodules which have not been overprinted by later spar forming events and show no groundwater or lacustrine associations or morphologies. Furthermore this excursion can be observed in the same magnetochron at both Sambullak and Boyevaya Gora (Figure 4.27) indicating that it is a basin wide event. Finally, this excursion is also statistically different from the background values, and the increase in the range of isotope values in paleosols that contain the excursion may indicate that they formed at a time of climate change rather than under homogenous climate conditions (cf. Pendall *et al.* 1994).

## 4.6 Summary

The stable isotopic composition of carbonate in paleosols is potentially influenced by many factors. Deciphering these factors is essential for any palaeoclimatic study, especially as they have an influence over whether the isotope results can be used for palaeotemperature and $pCO_2$ estimates (Ekart *et al.* 1999, Quast *et al.* 2006). While there is some evidence of minor alteration in the sections in Russia but it is possible to separate this from the primary pedogenic carbonate results. The similarity between some of the 'altered' results (especially

the microcrystalline carbonates) and the pedogenic carbonates isotope results suggests they are formed from the same fluid and may represent meteoric values or that some of the 'diagenetic' processes occurred when the paleosols were still active (cf. Ghosh *et al.* 2001):

1. There is evidence of an $\delta^{18}O_{carb}$ negative shift across the P/Tr boundary which starts in the last beds of the Permian (Sambullak P4) and continues into the Triassic (Boyevaya Gora, Tr1). There may have been a negative $\delta^{13}C_{carb}$ excursion at the P/Tr boundary, as recorded in the southern hemisphere, but this has to have occurred in the ~15m between the P/Tr boundary and the first Triassic paleosol (Figure 4.27);
2. However, there are four isotope excursions in the Changhsingian, identified in the Russian paleosols, which have not been recorded in the southern hemisphere. Of these, P3 is the best constrained. P3 can be identified in pedogenic calcite at Boyevaya Gora and, to a lesser extent, Sambullak and represents a negative shift of 6–4‰ in the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values;
3. There is evidence that the paleosols were affected by intense evaporation, recorded $\delta^{18}O_{carb}$ isotopic values greater than 0‰ and the occurrence of pedogenic dolomite. Pedogenic dolomite has been identified in the palaeo-equatorial Lower Permian (Kessler *et al.* 2001) but this is the first evidence of it at latitudes as high as 30-35°N at the P/Tr Boundary;
4. Also there may be a relation between the isotope anomalies and the appearance of pedogenic dolomite as at Boyevaya Gora as after the main Permian isotope excursion (P3) all the pedogenic carbonate above this point up to the P/Tr boundary is dolomite. This suggests that the excursion P3 marks the start of a period of extreme evaporation, and seasonality which continues up to the P/Tr boundary.

# 5 Palaeoclimatic analysis of the Southern Urals of Russia

## 5.1 Introduction

The variation in morphology and isotopic composition within paleosols can be used to investigate broad changes in climate and atmospheric conditions as described in previous chapters. However, it is also possible to use the relative depths of certain paleosol horizons and the isotope results as proxies for the amount of mean annual precipitation (MAP), mean annual temperatures (MAT) (e.g. Retallack 2005b and Dworkin *et al.* 2005). These can be used to investigate temperature and rainfall tends in the sections studied which are essential to test palaeoclimatic models (e.g. Ziegler *et al.* 1997: Kiehl and Shields 2005; Roscher and Schneider 2006).

### *5.1.1 Pedological and mineralogical indicators of changes in climate*

Tracking sedimentological, pedological and mineralogical variation can be the most direct way of investigating how climate changes through the sections. The variation of such features, such as the presence or absence of pedogenic dolomite, can be used to indicate changes in the amount and intensity of evaporation (e.g. Kessler *et al.* 2001), and increase or decrease in ambient temperature through the section. These features can be used to test the results of any palaeotemperature estimates. Changes in soil colour and development and morphology of Bk horizons can also give an indication of changes in MAP and the intensity of monsoonal rains (Retallack 2005b).

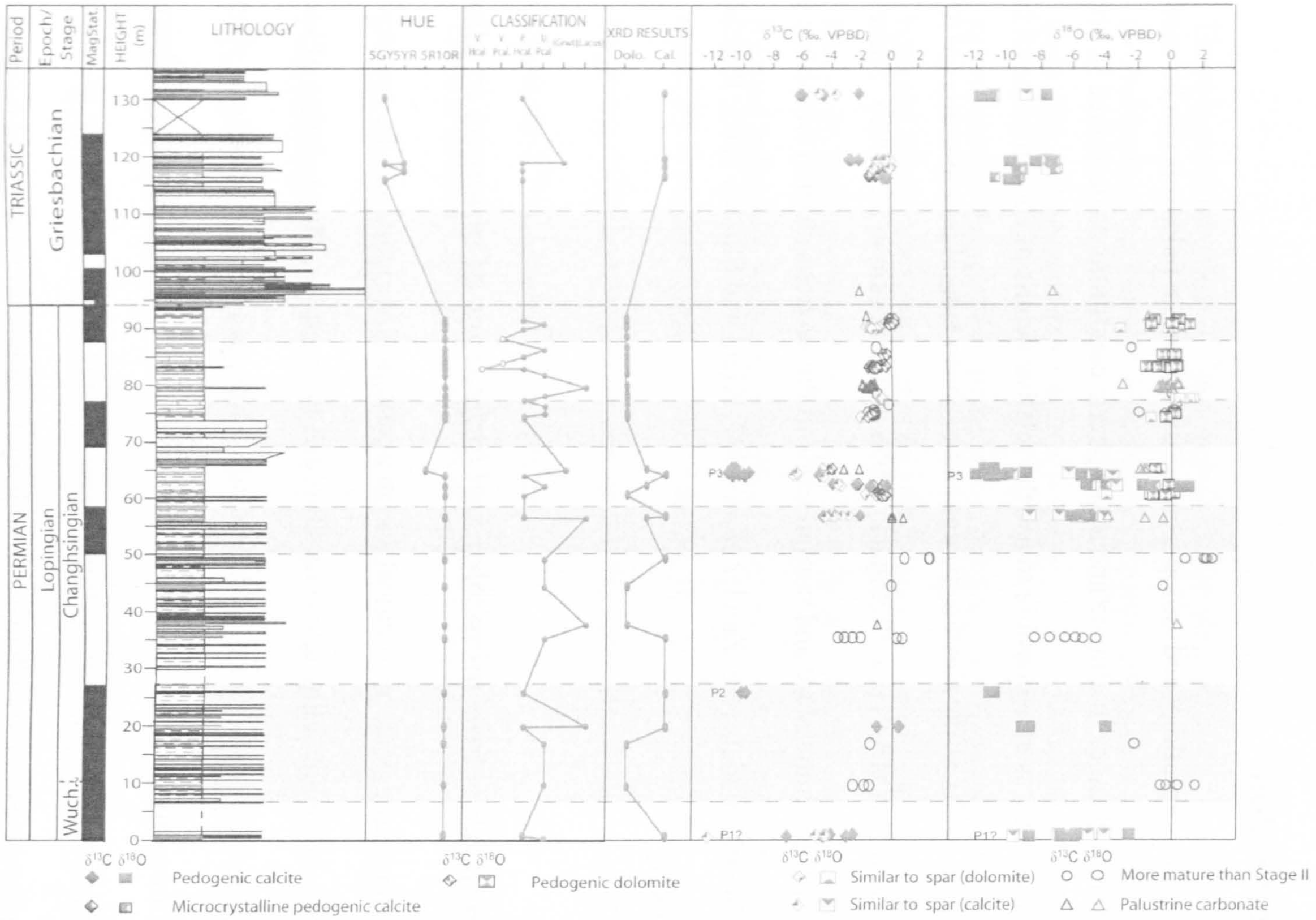


**Figure 5.1 Summary of the pedological and isotopic features seen at Boyevaya Gora (see Chapter 3 and 4 for details).**

Morphological changes in the type and development of paleosols have been observed in Antarctica (Retallack and Krull 1999; Retallack *et al.* 2007) and in the Karoo basin (Retallack *et al.* 2003) across the P/Tr boundary, associated with the isotopic anomalies seen in organic carbon (Retallack and Krull 2006) and pedogenic carbon (MacLeod *et al.*2000; Ward *et al.* 2000). As mentioned in Chapter 3, similar morphological features have observed at Boyevaya Gora (Figure 5.1) including a colour shift from a brick-red (10R) to a browner hue in the earliest (5GY). The first paleosols of the Triassic at Boyevaya Gora are poorly developed and associated with an increase in coarse-grade sediments. This also appears to be linked with a negative shift in the $\delta^{18}O$ isotope values in the earliest Triassic paleosols (Figure 5.1; Chapter 4). Equally at Boyevaya Gora, between the large $\delta^{13}C$ and $\delta^{18}O$ anomaly (P3, Figure 5.1), all the carbonate found in the paleosols is pedogenic dolomite, suggesting a rise in evaporation possibly initiated by the event that caused the isotopic excursions.

At Sambullak, while excursion P3 is present, there is no dominance of pedogenic dolomite after the excursion as at Boyevaya Gora (Figure 5.2). There are two possible explanations for this. Firstly, the dominance of pedogenic dolomite is a localised and restricted to Boyevaya Gora only. This appears unlikely as pedogenic dolomite was found at both sections. Another explanation for the dominance of dolomite is that it is linked to a rise in evaporation or a fall in river output. This would have affected Boyevaya Gora more dramatically as being further way from the Ural Mountains, where the fluvial systems originate, it would be affected first as the river output dwindles.

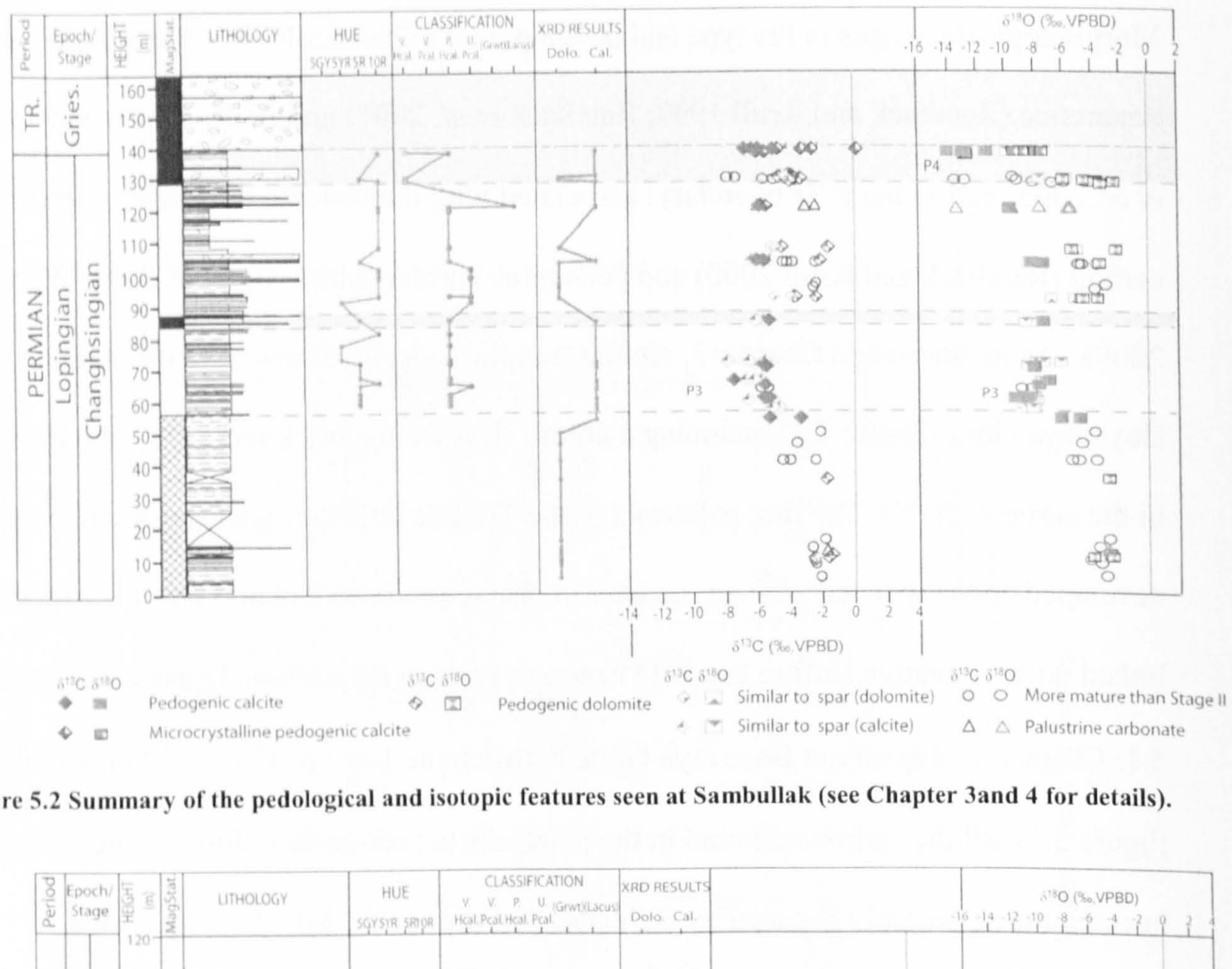


**Figure 5.2 Summary of the pedological and isotopic features seen at Sambullak (see Chapter 3and 4 for details).**

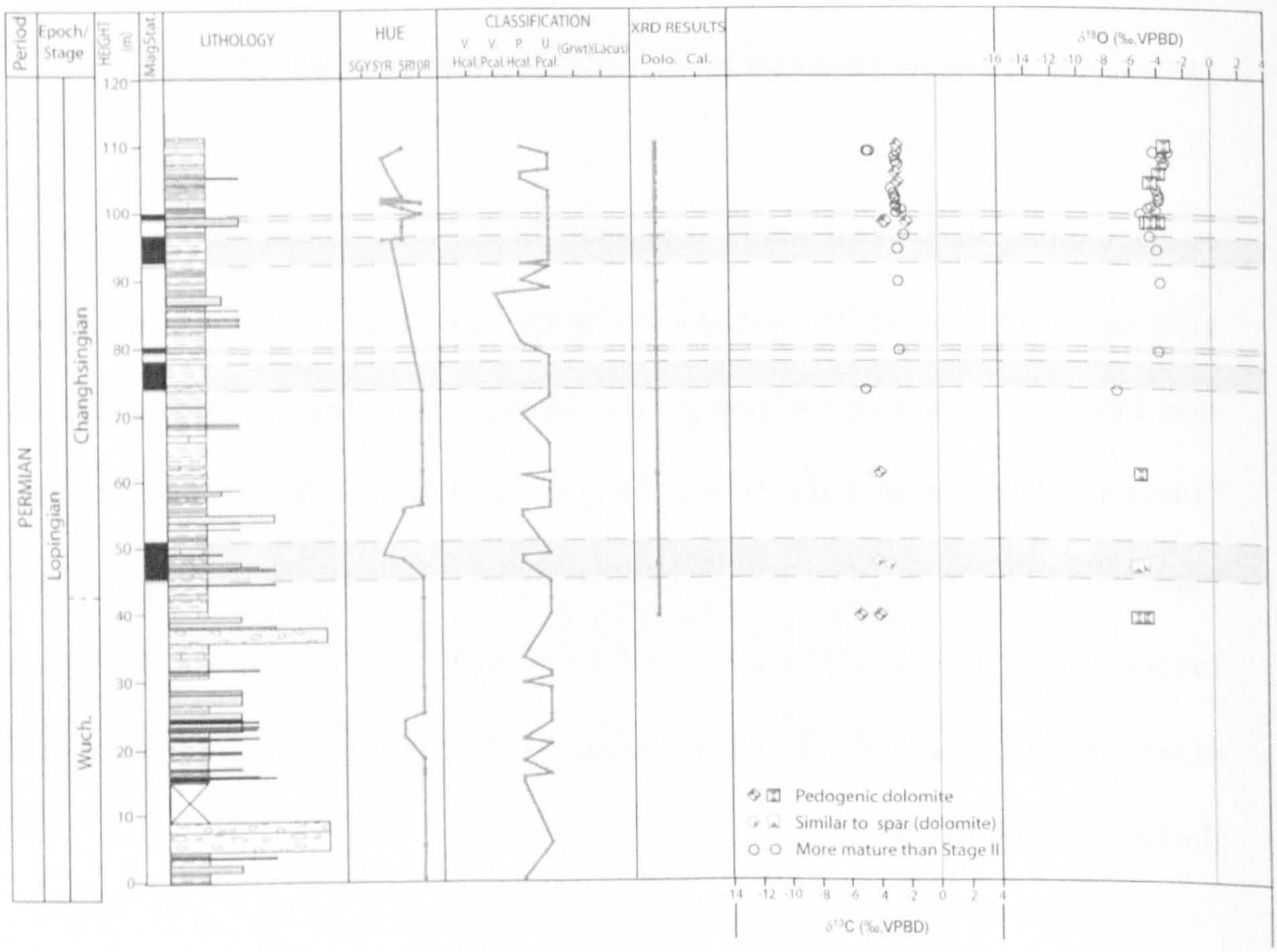


**Figure 5.3 Summary of the pedological and isotopic features seen at Tuyembetka (see Chapter 3 and 4 for details).**

Tuyembetka also covers this interval of time but as this section was probably on a palaeohigh (Chapters 3 and 4; and Taylor *et al.* 2009) it was already drier than the rest of the sections which explains why only dolomite was found there.

At Sambullak and Boyevaya Gora, in the interval just prior to the P/Tr boundary, there is an increase in the number of Vertisols again suggesting an increase in the amount of evaporation between P3 and the P/Tr boundary (Figure 5.1. and Figure 5.2).

By the upper Olenekian (Petropavlovskaya Svita) the basin has become more arid. For instance the carbonates found in the paleosols at Petropavlovka show groundwater morphologies suggesting that there was less influence from meteoric precipitation (Chapter 3). At Mescheryakovka, there is deep rooting, slickensides and carbonate related to arid environments (cf. Wright and Allen 1989; Stokes and Mather 2000). However, paleosols from Mescheryakovka also have the deepest average depth to Bk horizon which may indicate higher MAP (Chapter 3). The slickensides suggest that the paleosol must also have experienced times of drying and shrinking (Retallack 2001a; Kovda and Wilding 2005; Soil Survey Staff 2006) so perhaps the rains were more seasonal. This is supported by the strongly negative $\delta^{18}O$ values seen in this section (–14‰) possibly indicating monsoonal rains (cf. Alonso-Zarza 2003).

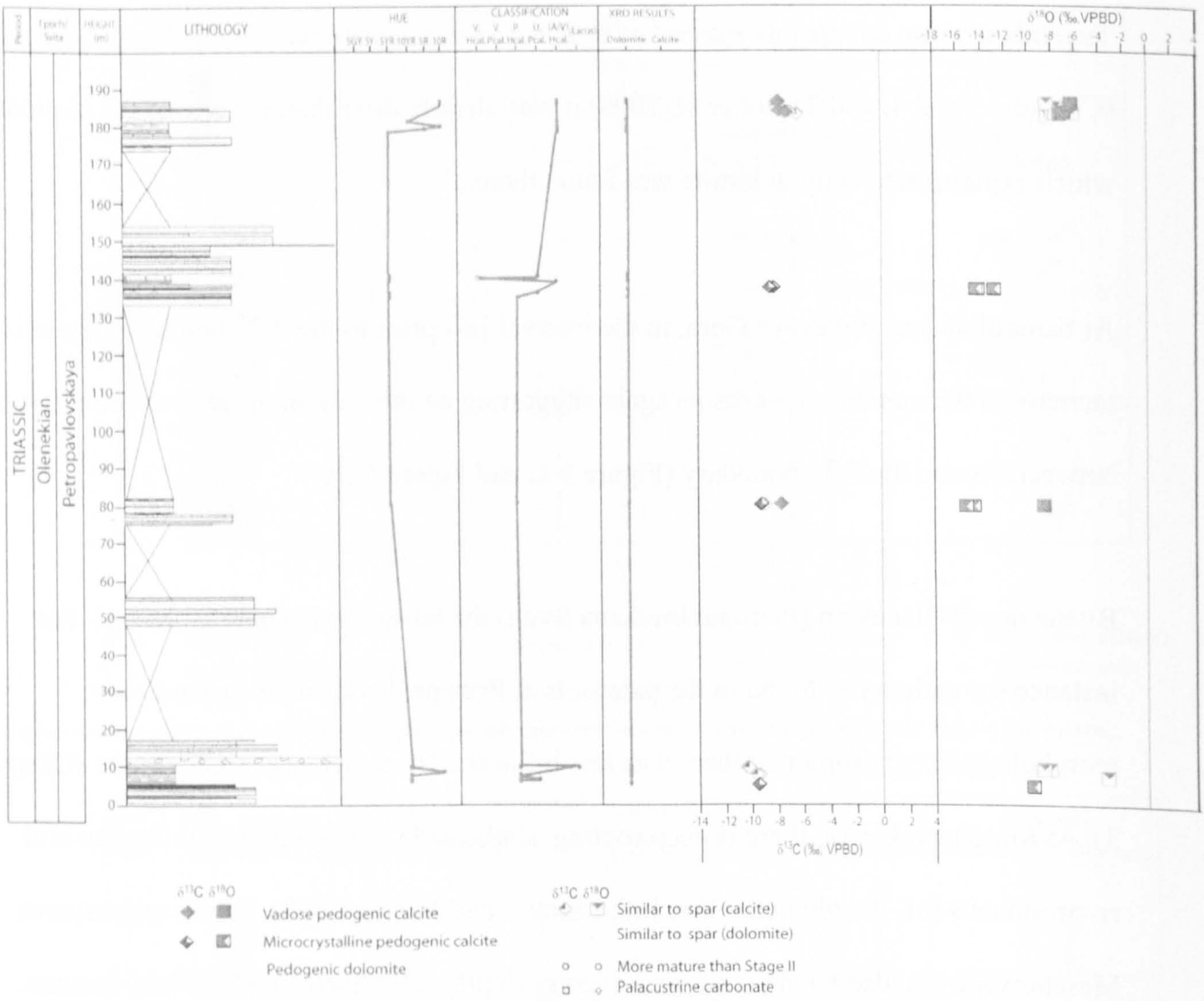


**Figure 5.4 Summary of the pedological and isotopic features seen at Mescheryakovka (see Chapter 3 and 4 for details).**

## 5.2 Palaeoprecipitation

The amount and severity of precipitation has a strong control on both the type of carbonate and the morphology of a paleosol. It has been suggested that the presence of carbonate in a paleosol indicates that the soil received between 100 and 1000mm of rainfall per year (Retallack 1994a, 2005a), although carbonate has been observed in modern Vertisols with a Mean Annual Precipitation (MAP) of 1400mm (Nordt *et al.* 2006).

It has also been observed that there is a quantitative link between the depth to the zone of carbonate (DTC) and mean annual precipitation (Jenny 1941; Retallack 1994a; 2001a; 2005b;

Nordt *et al.* 2006; Cleveland *et al.* 2008). This depth reflects the depth of biological respiration of the soil by available water during a year, and thus in years with less precipitation produces a shallower DTC. This relationship was first numerically described by Retallack (1994) based on 317 soils from the Quaternary. Since then this universal relationship has been revised with a more comprehensive dataset (Retallack 2005b). There have also been several models produced which link MAP to DTC for specific soil orders such as Vertisols (Nordt *et al.* 2006) and Aridisols (Cleveland *et al.* 2008).

The DTC can be hard to define as many nodule bands are diffuse rather than distinct horizons, particularly in monsoonal areas (Retallack 2005b). One definition of the DTC is the depth from the soil surface to the first occurrence of carbonate nodules; in monsoonal systems it is taken to be the zone of highest nodule abundance (Retallack 2005b). For this study the definition used will be that proposed by Nordt *et al.* (2006), which define the top of the DTC as the point in the paleosol when nodules make up 5% of the soil. 'Nodules' are defined as any form of carbonate segregation (nodule, soft mass, lump or concretion) (Nordt *et al.* 2006).

There is a question of the validity of applying the relationship between MAP and DTC to paleosols, especially Vertic-paleosols (Driese *et al.* 2000). This is partly because fluvial depositional sedimentary sequences are highly erosive, and while Bk horizons are relatively resistant to erosion, the A horizon is not and can be easily removed by overlying channels. In Vertisol sequences, layers that are several centimetres to a few decimetres thick have been observed to have been planed off by channel belt migration (Driese *et al.* 2000). There are other problems with the application of this relationship between the DTC and MAP to paleosol sequences. In fluvial stacked paleosol sequences, if the influx of sediment which buries a paleosol is less than the DTC, as controlled by precipitation, and a paleosol forms on

this new sediment the new paleosol can partially rework the top of the old paleosol, thus, truncating it without eroding it (Figure 5.5). Both erosion and this 'overprinting' have the effect of underestimating the DTC and thus the MAP. In the analysis of the Russian paleosols all those paleosols which had channels overlying them, or were part of a stacked paleosol sequence where there was no evident break between horizons, were noted as possible only representing the minimum rainfall.

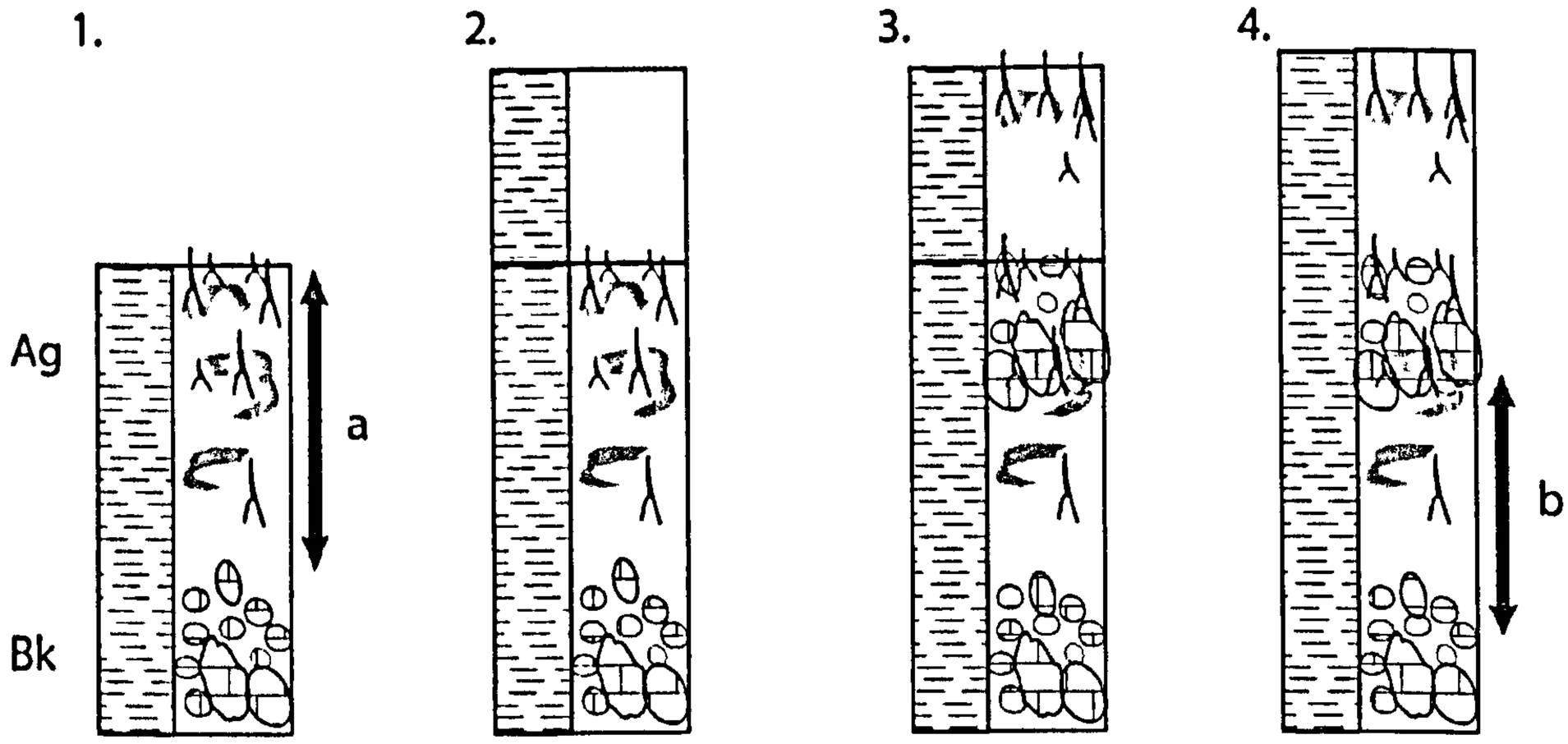


**Figure 5.5 Illustration how the depth to Bk horizon can be overprinted in stacked paleosols sequences. a) refers to the depth to Bk horizon in the original soil which then becomes covered by flood-derived silt (2) and a new soil forms reworking part of the lower soil profile (3). Thus, the depth to Bk horizon (b) is reduced (compare a and b) (4).**

The amount to which the paleosols have been compressed during lithification is another important factor to consider when applying precipitation estimates to paleosols. This study utilised the variant of the decompression algorithm proposed by Sheldon and Retallack (2001) for Aridisols (Equation 5.1). An estimated burial depth of 1.9km for the Russian sediments (Brunet *et al.* 1999; Andy Newell *pers. comm.*) was used in this equation.

$$C = \frac{-0.62}{\left[\left(\frac{0.38}{E^{0.17Dp}}\right) - 1\right]} \qquad (5.1)$$

$C$ is the compression factor and $Dp$ burial depth (km).

As mentioned previously, there are several variants of the palaeoprecipitation equation based on specific soil orders and overall relationships; this study utilises four of these. The first is the mean relationship proposed by Retallack (2005) based on a global dataset (Equation 5.2).

$$P=137.24+6.45D-0.013D^2 \qquad (5.2)$$

$P$ is the MAP in millimetres and $D$ is the DTC in centimetres.

A model specifically created for Vertisols was also used (Nordt *et al.* 2006). This equation comes in two variants, one for microlows (Equation 5.3) and another for microhighs (Equation 5.3a)

$$P=-4.00E-05D^2+4.251D+432.27 \qquad (5.3a)$$

$$P=-8.00E-04D^2+1.362D+1047.40 \qquad (5.3b)$$

$P$ is the MAP in millimetres and $D$ is the DTC in centimetres.

As these equations have been proposed purely for use in Vertisols, it has been suggested that they should only be used for DTC between 70 and 120cm (Cleveland *et al.* 2008).

Finally, the last relationship is the one formulated for Aridisols by Cleveland *et al.* (2008) (Equation 5.4). They suggest that this equation should only be applied to Aridisols with or paleosols containing pedogenic slickensides and that lack argillic horizons.

$$P=0.029(D-38)^2+2.7D+133 \qquad (5.4)$$

$P$ is the MAP in millimetres and $D$ is the DTC in centimetres.

It has been noted that in monsoonal conditions, Bk horizons become thicker reflecting the annual range of precipitation (Retallack 1991; Retallack 2005b). Retallack (2005b) uses this relationship to produce an equation that can predict the range of precipitation and thus the intensity of any monsoonal activity (Equation 5.5).

$$M=0.79T+13.71 \quad (5.5)$$

$M$ is the mean annual range of precipitation in millimetres and $T$ is the uncompressed thickness of the 'paleosol-with-nodules' in centimetres. The thickness of 'paleosol-with-nodules' in centimetres is defined as being the interval between the shallowest and deepest carbonate nodule (Retallack 2005b).

In the modern world the hydrological definition of monsoonal conditions is any region that receives the majority of its rain during a particular season (Webster 2005). For example, present day New Delhi (28° 34' 48" 77° 12' 00") has a mean annual range of precipitation of 235mm (based on 45-years' worth of measurements; IAEA/WMO, 2008) compared with Chihuahua in Mexico (28° 37' 48" -106° 4' 12") which has a range of 88mm (based on 27 years' worth of measurements; IAEA/WMO, 2008). Therefore, increases in mean annual range of precipitation can be seen as increases in seasonal conditions.

### *5.2.1 Palaeoprecipitation estimates for the Southern Urals, Russia*

Palaeoprecipitation estimates were calculated from paleosols at Boyevaya Gora, Sambullak, Tuyembetka and Mescheryakovka. These sections were chosen because 1) they are primarily pedogenic rather than groundwater–related, and 2) they are long sections and thus it is possible to track changes over time.

| Section | Average MAP (mm) | | | |
|---|---|---|---|---|
| | 5.2 | 5.3a | 5.3b | 5.4 |
| Boyevaya Gora (Permian) | 344(±118) | 293 (±74) | 956 (±178) | 217(±55) |
| Sambullak | 411(±114) | 268(±79) | 989 (±31) | 274(±63) |
| Tuyembetka | 409(±189) | 270(±102) | 989(±41) | 251(±89) |
| Boyevaya Gora (Triassic) | 185(±23) | 401(±15) | 1037(±5) | 180(±3) |
| Mescheryakovka | 541(±269) | 258(±43) | 961(±58) | 313(±151) |

**Table 5.1 The average MAP from the four longest Russian sections for the four different MAP equations (see Appendix 3.1 for calculations).**

At Boyevaya Gora equations 5.2, 5.3a and 5.4 produce averages within error of each other (Table 5.1) suggesting an average MAP of 300mm. Equation 5.3b on the other hand seems to produce a much higher value (Table 5.1). This is probably due to the fact that Equation 5.3b models microhighs and Boyevaya Gora was probably an active river channel (Newell *et al.* 1999) and not a microhigh.

Equations 5.4 show a gradual rise in precipitation of 175mm at the base of the section up to the P/Tr boundary and then a drop of 200mm across into the Triassic (Figure 5.6). Equation 5.3a gives the inverse of this relationship with a fall of precipitation of about 150mm up to the boundary and a rise of 200mm across the boundary. Equation 5.3b shows very little variation across the whole curve.

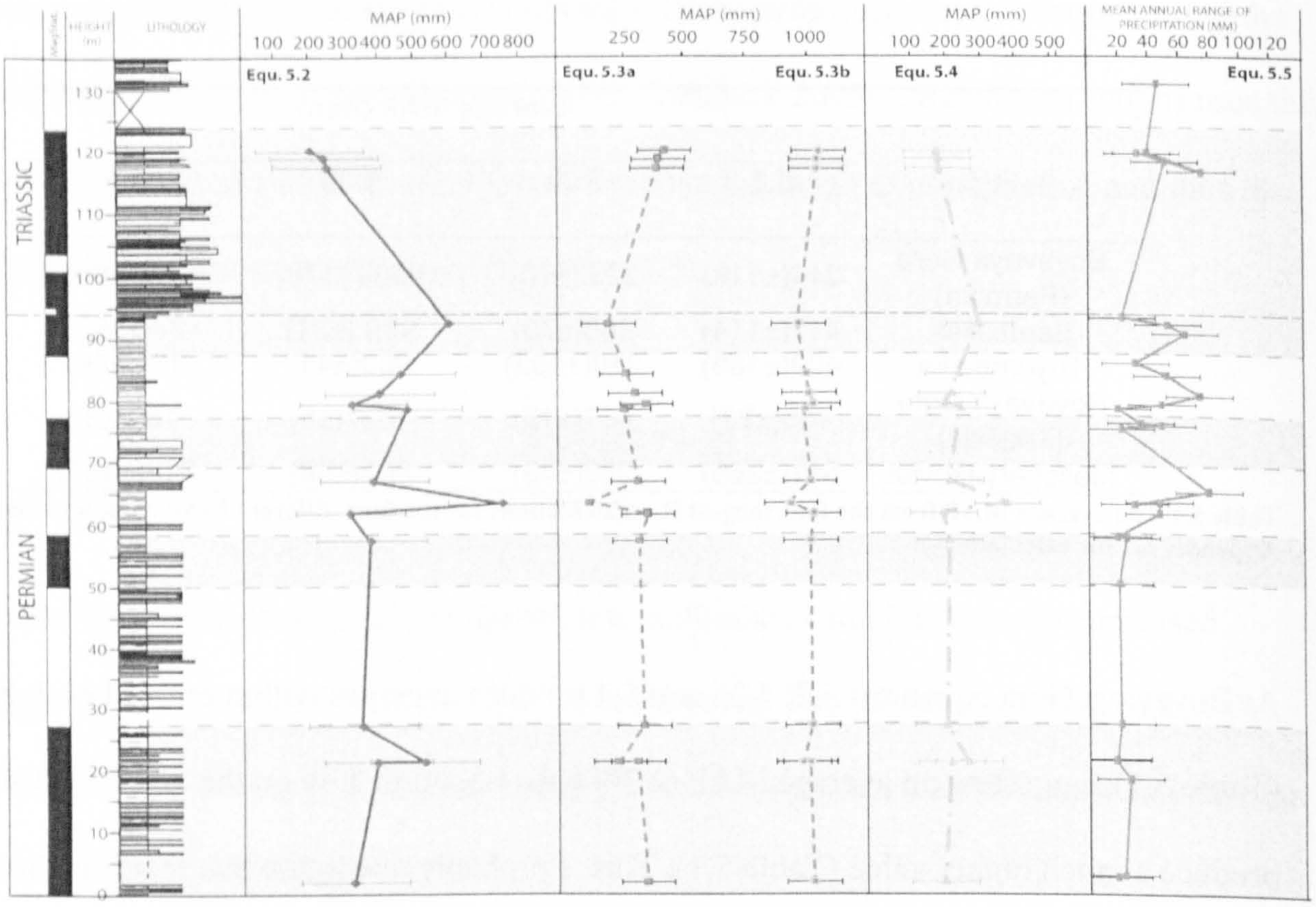


**Figure 5.6 MAP and Mean Annual Range of Precipitation estimates using at Boyevaya Gora (see Appendix 3.1 and 3.2 for calculations).**

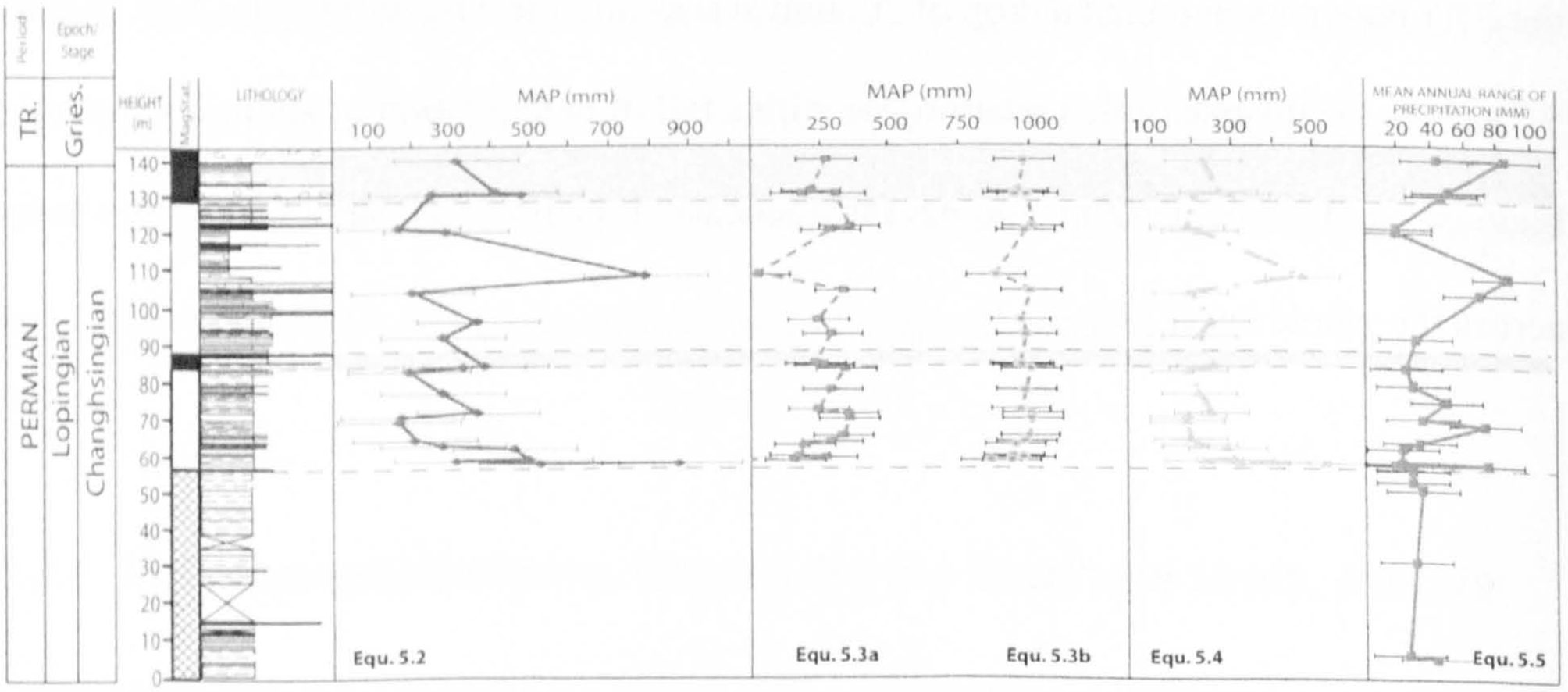


**Figure 5.7 MAP and Mean Annual Range of Precipitation estimates using at Sambullak (see Appendix 3.1 and 3.2for calculations).**

The average MAP values for Sambullak are greater than those seen at Boyevaya Gora (Table 5.1) and show a greater range of values, although a lot of the variation may be due to two anomalous paleosols, one at the base of the section and one at 110m which equation 5.2 and 5.4 models as a dramatic rise in MAP. Equations 5.2 and 5.4 show a minor rise in precipitation of 200mm as at Boyevaya Gora, while equation 4 shows a fall of about 200mm and equation 5.4 shows little variation. The mean annual range of precipitation shows a increase in the range in the last R-N-R-N magnetochrons of the Permian (Figure 5.7) which is similar to the average increase after the excursions seen at Boyevaya Gora (Figure 5.6), suggesting the increase in seasonality at Boyevaya Gora after P3 also occurred at Sambullak.

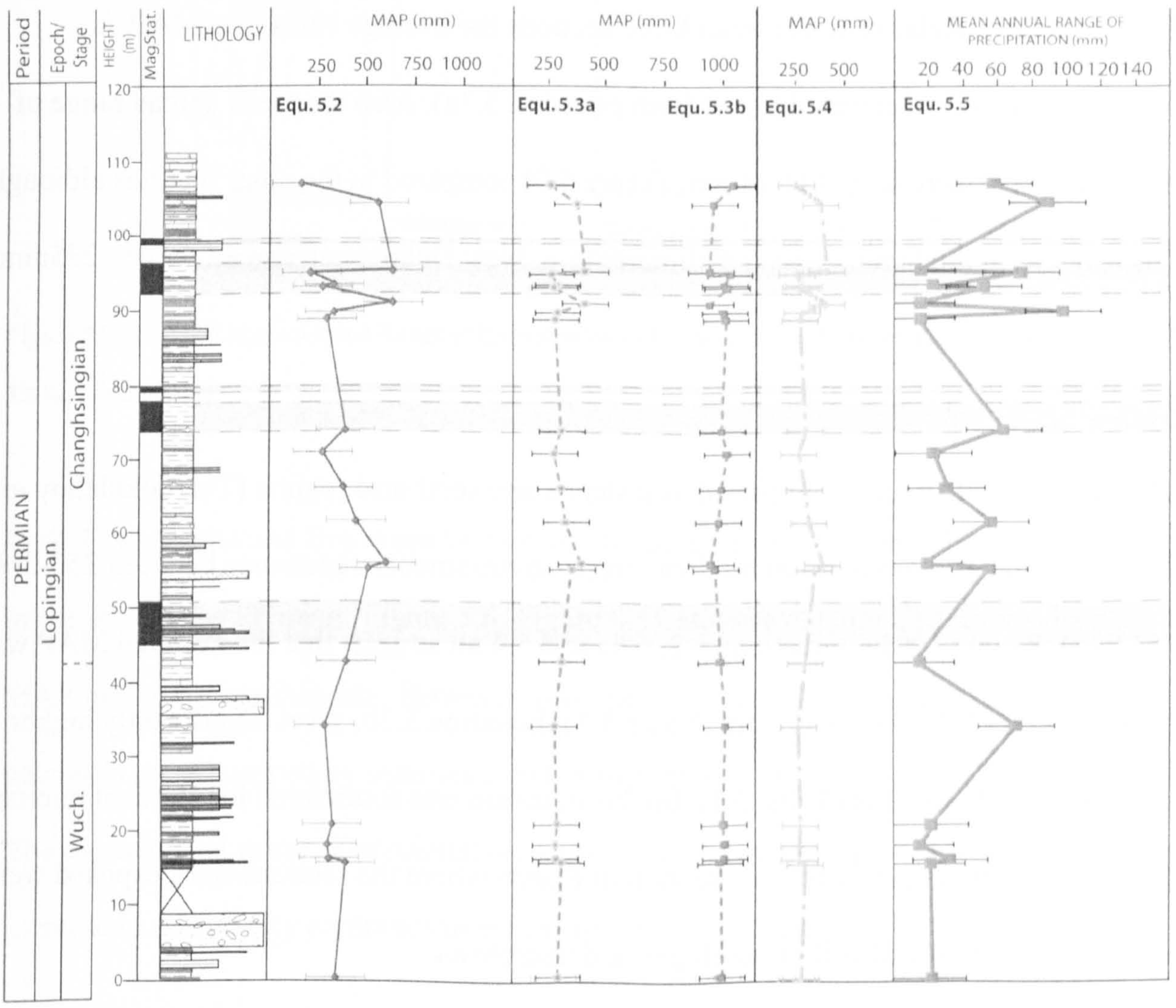


**Figure 5.8 MAP and Mean Annual Range of Precipitation estimates using at Tuyembetka (see Appendix 3.1 and 3.2 for calculations).**

The average values for Tuyembetka for equations 5.2 and 5.3b are similar to those for Boyevaya Gora and Sambullak which is expected as all three sections overlap stratigraphically. At the top of the section (above 90m, Figure 5.8) there appears to be an increase in MAP which may be linked to a rise in the mean annual range of precipitation seen at this point.

All three section show an increase in an increasing the range of mean annual precipitation (equation 5.5) up to the P/Tr boundary (Figure 5.6, Figure 5.7, Figure 5.8) from 17–44 (±22)mm range per year to 56–90 (±22)mm. Indicating an increase in seasonality up to the P/Tr boundary. Relative to the other three sections the average values for MAP at Mescheryakovka are elevated (apart from equation 5.3a). Also the mean annual range of precipitation is increased (134-18mm, Figure 5.9) compared to the other sections although this is not as in modern monsoonal climates (e.g. New Delhi mean annual range =235mm IAEA/WMO, 2008)

The Permian of Russia is interpreted as a steppe and semi-arid regime (Tverdokhlebov *et al.* 2005). Similar environments in modern steppe environments experience between 250-500mm MAP (McKnight 1999). Equations 5.2, 5.3a and 5.4 all suggest that the Permian MAP was between 227(±25)-500 (±144) mm (Table 5.1). Equation 5.3b, gives significantly higher estimates for all sections (Table 5.1), but his equation was formulated for Vertisol microhighs (Nordt *et al.* 2006) and there is no section in Russia where the sections were exposed well enough to positively identify microhighs and microlows.

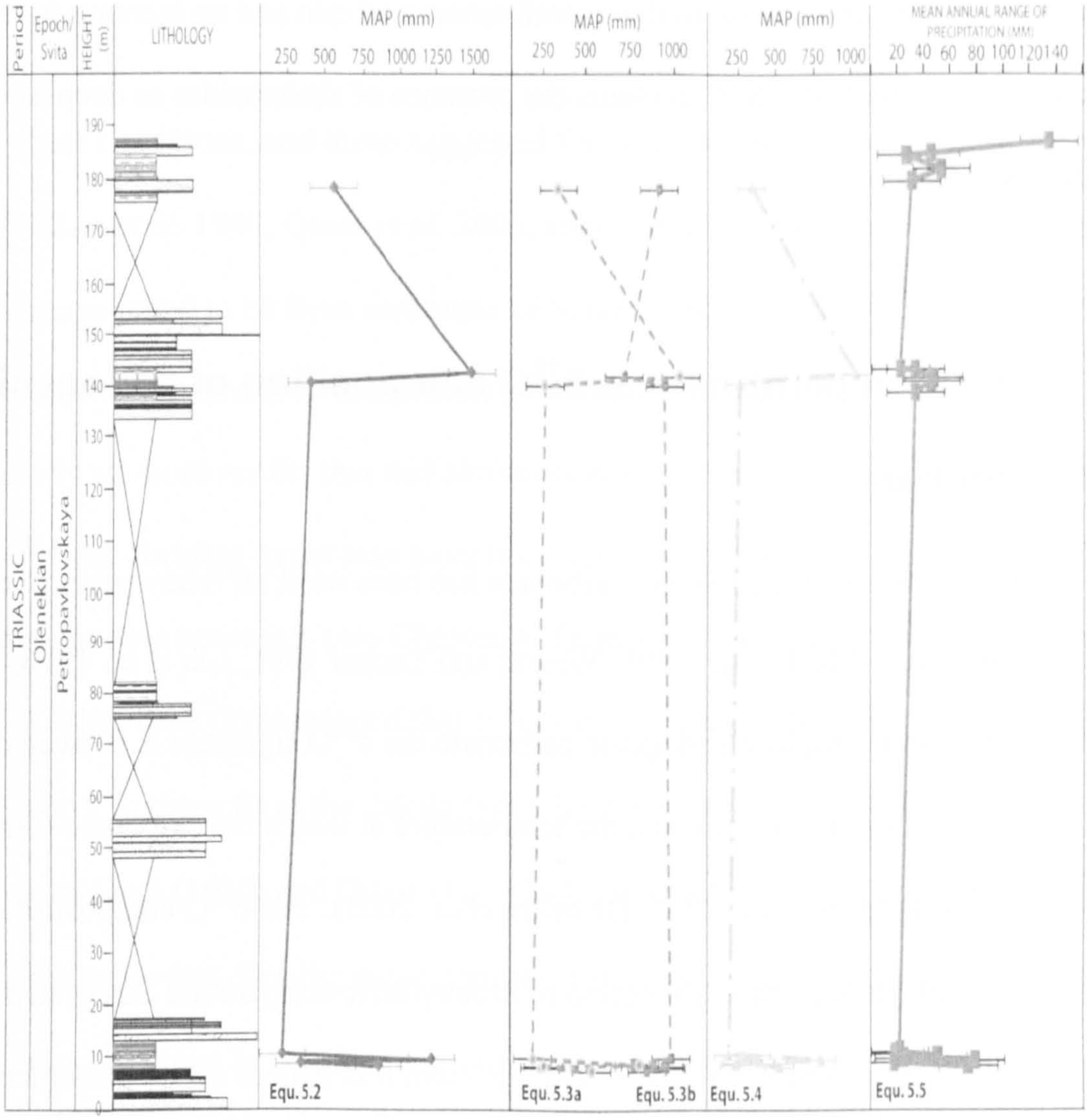


**Figure 5.9 MAP and Mean Annual Range of Precipitation estimates using at Mescheryakovka (see Appendix 3.1 and 3.2 for calculations).**

Both Tuyembetka and Boyevaya Gora show an increase in mean annual range of precipitation in the uppermost Permian (Figure 5.6, Figure 5.8). Boyevaya Gora also shows decrease in MAP in the earliest Triassic. However, this may be an erroneous result as the Triassic paleosols are all capped by sandstone beds which may have eroded the paleosols (Figure 5.6). The mean annual range of precipitation stays increased into the Triassic suggesting that the increase in seasonality continues in the earliest Triassic (Figure 5.6).

By the Olenekian it appears that both mean annual range of precipitation and MAP are elevated relative to the Permian and Earliest Triassic sections (Table 5.1, Figure 5.9).

This suggests both an increase in the overall amount of rain and an increase in the seasonality of that rain (Figure 5.9) which explains the presence of slickensides as deep as the Bk horizon (see Chapter 3).

## 5.3 Palaeotemperature and $\delta^{18}O$ composition of pedogenic carbonate

The $\delta^{18}O$ composition of pedogenic carbonate has been used for many years to estimate palaeotemperature (Mack *et al.* 1991; Wright and Tucker 1991; Liu *et al.* 1996; Dworkin *et al.* 2005). In primary vadose pedogenic carbonate the $\delta^{18}O$ signature is derived directly from meteoric precipitation (rainfall), and the temperature at which the carbonate formed (Cerling and Quade 1984; Mack *et al.* 1991; Dworkin *et al.* 2005). The $\delta^{18}O$ composition of the meteoric precipitation itself is a function of atmospheric temperature that precipitation formed at (Mack *et al.* 1991; Fricke O'Neil 1999). As such, it is a more useful palaeotemperature proxy than using $\delta^{18}O$ data derived from marine sediments as pedogenic carbonate is not affected by the isotopic fractionation in sea water (Wright and Tucker 1991; Dworkin *et al.* 2005).

Dworkin *et al* (2005) advise that, due to multiple different temperatures, chemistries and isotopic composition of the fluids from which pedogenic carbonate forms; particular attention must be taken to screening out these effects. They note that pedogenesis will 'pin' the oxygen isotopic composition to local precipitation and temperature so the most pressing issues are diagenetic modification and alteration in re-exposure. (Dworkin *et al* 2005). To this end only nodules that are made of anhedral grains of calcite of micritic or microspar size should be used for palaeotemperature analysis (c.f. Dworkin *et al* 2005).

Based on these conditions, and those suggested for screening paleosol carbonate for $pCO_2$ estimates (Ekart *et al.* 1999, Quast *et al.* 2006, see Chapter 4), only the isotope results which could be demonstrated to be from carbonate of Stage II and below, and not associated with palustrine carbonate, were used to calculate palaeotemperature estimates (see Chapter 4 Table 4.2). Similarly all those results that had similar isotopic values to the spar were excluded as, although the spar-forming event may have been very early, it may not represent active, vadose, soil-forming processes (see Chapter 4, Table 4.2). The pedogenic dolomite is also excluded as it has been demonstrated that $\delta^{18}O$ values from the dolomite are isotopically more positive relative to those from the calcite (see Chapter 4 Table 4.2). This is consistent with the findings of Land (1980) and Quast *et al.* (2006) that dolomitic $\delta^{18}O$ values are fractionated relative to the soil water. Finally, those nodules that show a microcrystalline texture are also problematic as they may be formed by groundwaters (Quast *et al.* 2006). However, the overlap with those nodules that were of unaltered cryptocrystalline micrite (see chapter 4) suggests that those nodules are also pedogenic, so they were included in the palaeotemperature estimates but only where they are similar to unaltered vadose pedogenic carbonate values from the same paleosol. As only Boyevaya Gora, Sambullak and Mescheryakovka have isotopic values that are definitely unaltered pedogenic calcite; these were used to calculate palaeotemperature estimates (see Chapter 4 Table 4.2).

### *5.3.1 Different Methods*

Friedman and O'Neil (1986) described the relationship between the $\delta^{18}O$ value of calcite and temperature but their equation requites the isotopic value for the liquid from which that calcite precipitated from. To accurately estimate palaeotemperature, the effects of both meteoric

precipitation and temperature on the $\delta^{18}O$ of the pedogenic carbonate must be modelled. This relationship was first described by Friedman and O'Neil (1986):

$$\delta^{18}O_{carb} - \delta^{18}O_p = 2.78(10^6 T^2) - 2.89 \quad (5.6)$$

where $\delta^{18}O_{carb}$ is the isotopic composition of the pedogenic carbonate (relative to VSMOW) from the; $\delta^{18}O_p$ is the isotopic composition of the meteoric precipitation (relative to VSMOW) and $T$ is the Mean Annual Temperature (°K). This is converted to °C using the conversion °C = °K – 273.15 (Bureau International des Poids et Measures 2008). This equation needs inputs of $\delta^{18}O_{carb}$ which is measured from the field data (Chapter 4) and $\delta^{18}O_p$ which has to be estimated.

It has been shown that the $\delta^{18}O$ of meteoric precipitation ($\delta^{18}O_p$) varies with latitude (Fricke and O'Neil 1999) and thus it is important to consider the palaeolatitude of the Southern Urals when trying to calculate palaeotemperature. In the Permian–Triassic period the Southern Urals were between 30–35 °N (Newell *et al.* 1999; Torsvik and Anderson 2002; Cocks and Torsvik 2007; Taylor *et al.* 2009). In the modern day rainfall from these latitudes has an isotopic range of between 11.06‰ and –15.51‰, (IAEA/WMO 2008). However, as SMOW is 1‰ any modern value greater than this must be fractionated by evaporation (Dr Stephen Grimes *pers. comm.*) and thus can be excluded, giving a range of –1.12 ‰ to –15.51‰ with a mean of –5.52‰ (Fricke and O'Neil 1999; IAEA/WMO 2008). Using the minimum, maximum and mean values for $\delta^{18}O_p$ and screened pedogenic carbonate values from Sambullak, Boyevaya Gora and Mescheryakovka, it is possible to produce temperature curves for the maximum, minimum and mean $\delta^{18}O_p$ curves using equation (5.6) (Figure 5.10)

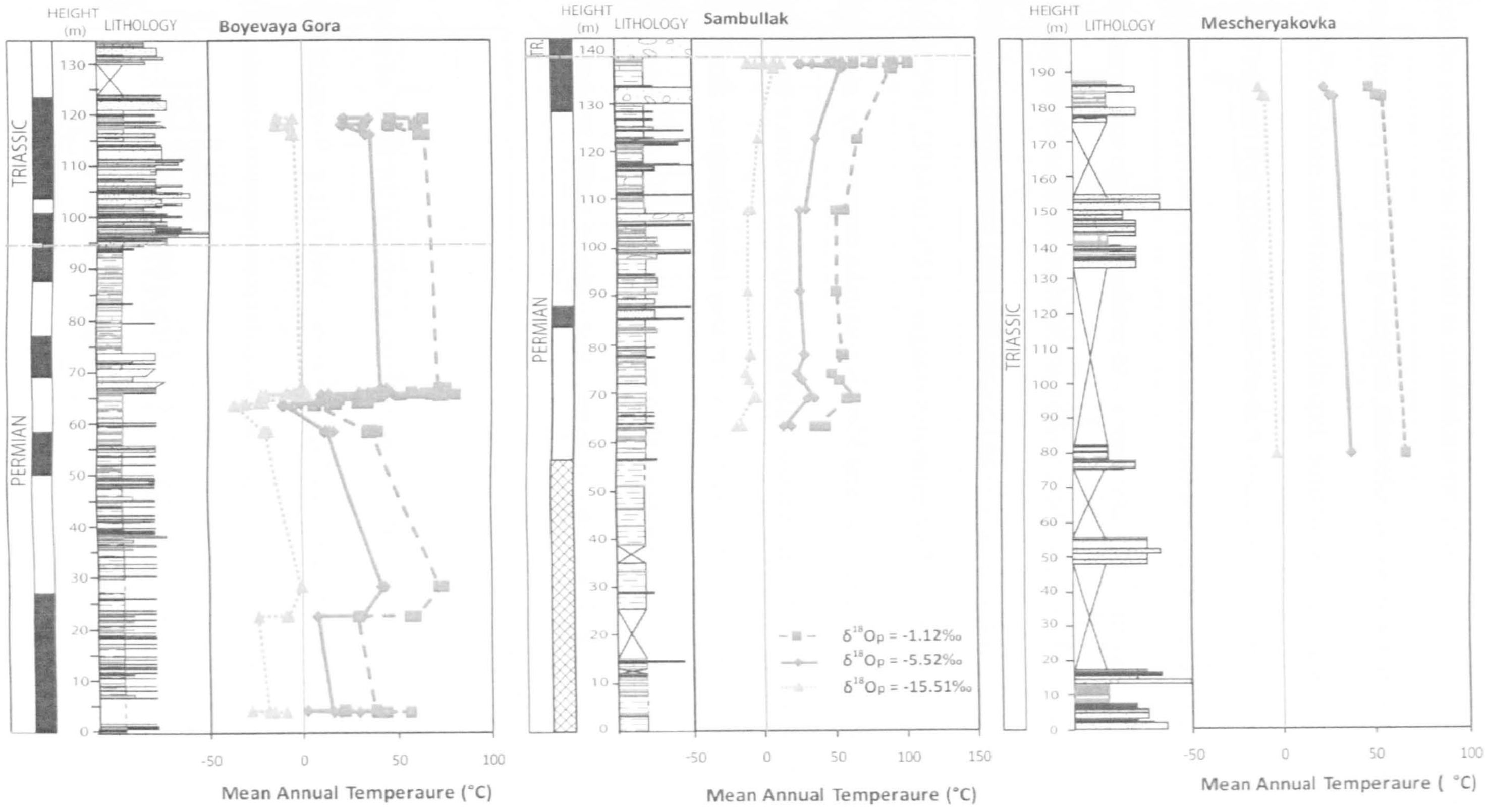


**Figure 5.10 Palaeotemperatures produced by equations (5.6) using the max, min and mean modern values for $\delta^{18}O_p$ from 30–35°N (see Appendix 3.3 for calculations).**

In all cases the minimum $\delta^{18}O_p$ value gives temperature values which are below freezing (averages of -9°C, -6°C, -7°C, for Boyevaya Gora, Sambullak and Mescheryakovka respectively see Figure 5.10). These are unrealistic as there is no evidence of ice wedging or prolonged formation in the Russian paleosols, suggesting that these paleosols never went below 0°C for a prolonged period of time. Equally the maximum modern $\delta^{18}O_p$ value for this latitude produces maximum temperatures that are unrealistically hot (ranges 6°C to 80°C, 6°C to 102°C, 48°C to 66°C for Boyevaya Gora, Sambullak and Mescheryakovka respectively, see Figure 5.10). The mean $\delta^{18}O_p$ value appears to produce realistic temperatures (Figure 5.10 and Figure 5.11) and suggests that there was an increase of 20°C and 26°C across the $\delta^{18}O_{carb}$ excursions seen at Boyevaya Gora (P3) and Sambullak (P4) respectively. However, this value also produced a large range in MAT estimates (ranges −11°C to 48°C, 14°C to 64°C, 48°C to 66°C for Boyevaya Gora, Sambullak and Mescheryakovka respectively, see Figure 5.11) some of which are below 0°C which again there is no physical evidence for in the sections.

Using a single value for $\delta^{18}O_p$ throughout a section may be problematic: firstly it assumes that using a modern average $\delta^{18}O_p$ value accurately represents the $\delta^{18}O_p$ of meteoric precipitation in the Permian–Triassic of Russia and, secondly, that $\delta^{18}O_p$ is unaffected by changes in atmospheric temperature.

Also at modern sites, there is a 5-10 per mil difference between the $\delta^{18}O$ of precipitation, between sites with the same mean annual temperature (MAT) (e.g. Rozanski *et al.*, 1993) and this would produce an uncertainty of ±5°C to any palaeotemperature estimates (Dr Nathan Sheldon *pers. comm.*).

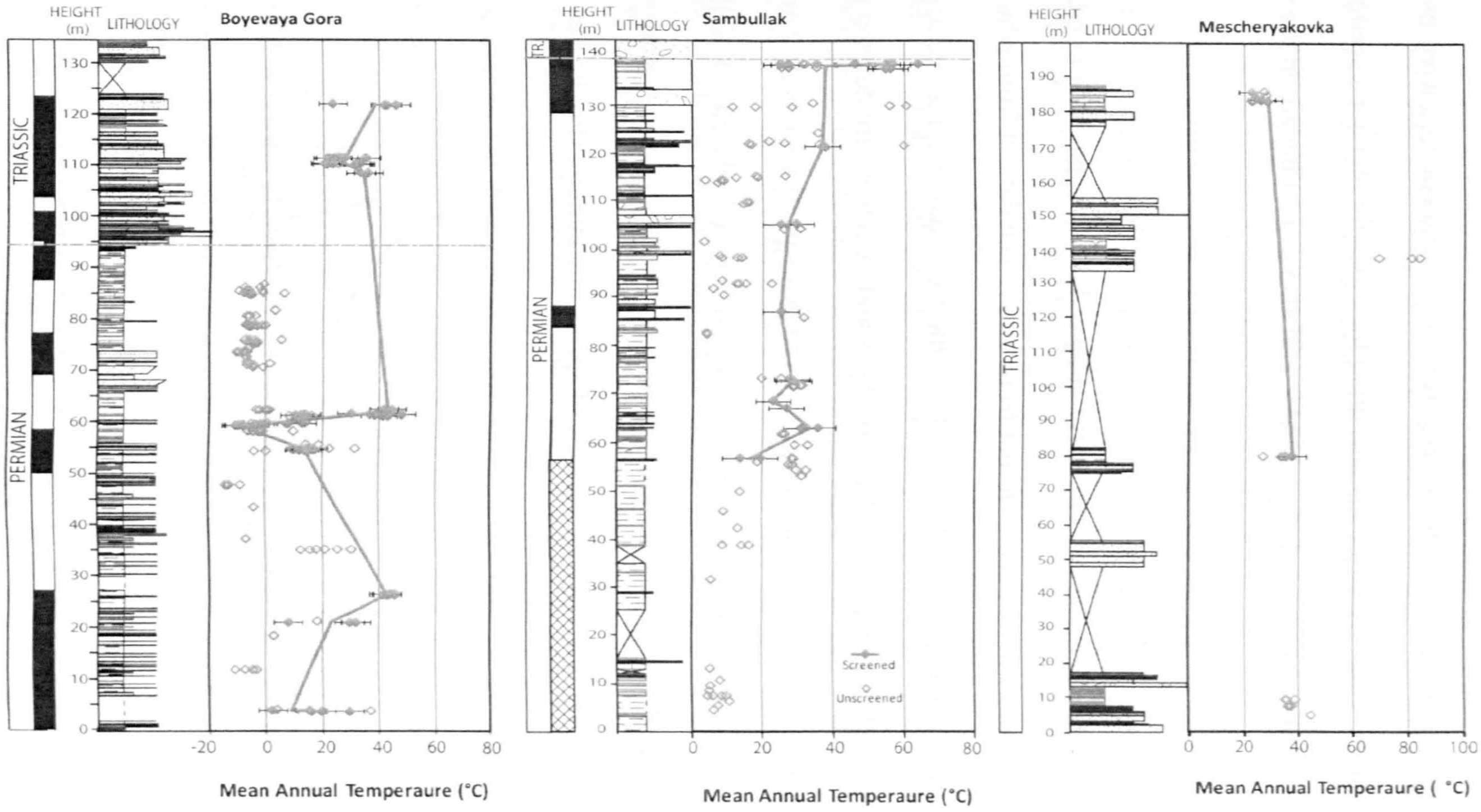


**Figure 5.11 Palaeotemperature produced by equations (5.6) using the mean modern values for $\delta^{18}O_p$ from 30–35°N of –5.52‰ (Fricke and O'Neil 1999; IAEA/WMO, 2008) (see Appendix 3.3 for calculations).**

Modelling the effect of temperature on meteoric precipitation, Fricke and O'Neil (1999) found that there was a positive relationship between the isotopic composition of meteoric precipitation ($\delta^{18}O_p$) and the local ground temperature in modern terrestrial environments (Figure 5.12). They found that, across the world, as local air temperature increases, the $\delta^{18}O_p$ becomes more positive. Thus, using a constant figure for $\delta^{18}O_p$ throughout a section will produce erroneous results as changes in local MAT will also cause changes in the value of $\delta^{18}O_p$.

By using the relationship described by this curve (Figure 5.12) it is possible to predict past $\delta^{18}O_p$ even if the absolute values were different from today. The dataset from which this relationship is derived (Figure 5.12) is based only on the 'seasonal extreme' values rather than the full annual dataset (Fricke and O'Neil 1999). 'Seasonal extremes' are defined as being the summer months (June, July and August, in the northern hemisphere) and winter months (December, January and February, in the northern hemisphere) (Fricke and O'Neil 1999). These months were used as they are thought to isolate seasonal extremes in climate variables and $\delta^{18}O_p$ values from the 'transitional' seasons of spring and autumn (Fricke and O'Neil 1999).

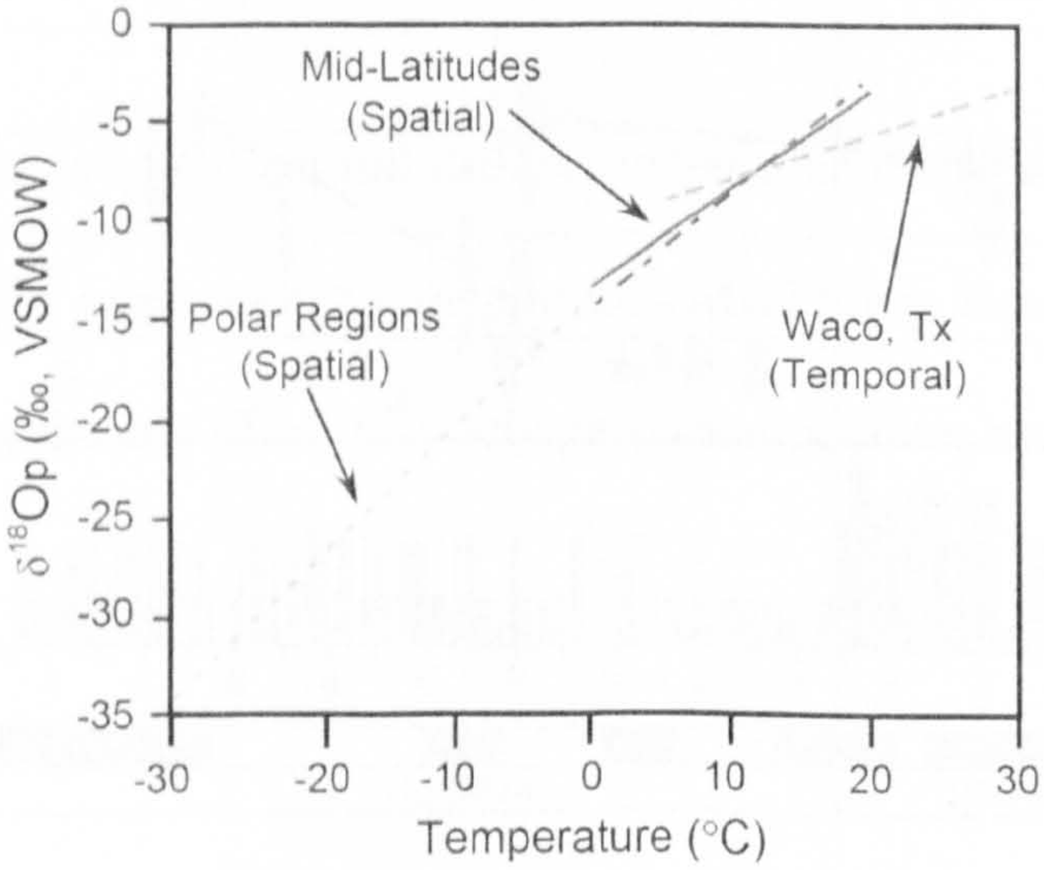


**Figure 5.12 The modern day relationships between $\delta^{18}O_p$ and temperature described by Fricke and O'Neil (1999) and Dworkin *et al.* (2005) (figure adapted from Dworkin *et al.* 2005).**

This relation between changes in MAT and $\delta^{18}O_p$ has been expressed as a 'spatial' relationship (equation 5.7a), referring to the relationship between long-term (annual) averages of $\delta^{18}O_p$ and surface air temperature at different latitudes round the globe (Rozanski *et al.* 1992; Fricke and O'Neil 1999; Dworkin *et al.* 2005).

$$\delta^{18}O_p = 0.50(T - 273) - 13.20 \qquad (5.7a)$$

where $\delta^{18}O_p$ is the isotopic composition of the meteoric precipitation (relative VSMOW) and $T$ is the Mean Annual Temperature (°C).

It has also been observed that there is a difference in the relationship between surface air MAT and the long-term (annual) average $\delta^{18}O_p$ at a single geographical location when compared to the global pattern (Fricke and O'Neil 1999), and this relationship may be more relevant for palaeoclimate analysis (Rozanski *et al.* 1992). This is because the $\delta^{18}O_p$ of meteoric water at a given location is controlled by regional-scale processes, such as conditions at the source of the vapour, transport patterns of vapour in the atmosphere, average "rain-out history" of the air masses precipitating in a given place, and cloud-base temperature, and these have varying effects at different localities (Rozanski *et al.* 1992).

In their study Dworkin *et al.* (2005) use the modern summer and winter $\delta^{18}O_p$ data (method after Fricke and O'Neil 1999) from a station in Waco Texas (the closest modern weather station to their field area) to generate this relationship (equation 5.7b).

$$\delta^{18}O_p = 0.22(T - 273) - 8.31 \qquad (5.7b)$$

where $\delta^{18}O_p$ is the isotopic composition of the meteoric precipitation (relative VSMOW) and *T* is the Mean Annual Temperature (°C). This is referred to as a 'temporal' relationship (Rozanski *et al.* 1992; Fricke and O'Neil 1999; Dworkin *et al.* 2005). The closest modern weather station to the Russian field area which has records of $\delta^{18}O_p$ of rain water for over three consecutive years is at Saratov, in the Russian Federation (51° 34' 00" / 46° 1' 60" / altitude 166m), (using the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval Database, IAEA/WMO, 2008). Using the methods proposed by Fricke and O'Neil (1999) and Dworkin *et al.* (2005) based only on comparing $\delta^{18}O_p$ to air temperature from the summer and winter months (Figure 5.13) it is possible to produce an equivalent equation (5.7c) for Saratov.

$$\delta^{18}O_p = 0.278(T - 273) - 12.91 \qquad (5.7c)$$

where $\delta^{18}O_p$ is the isotopic composition of the meteoric precipitation (relative VSMOW) and *T* is the Mean Annual Temperature (°C).

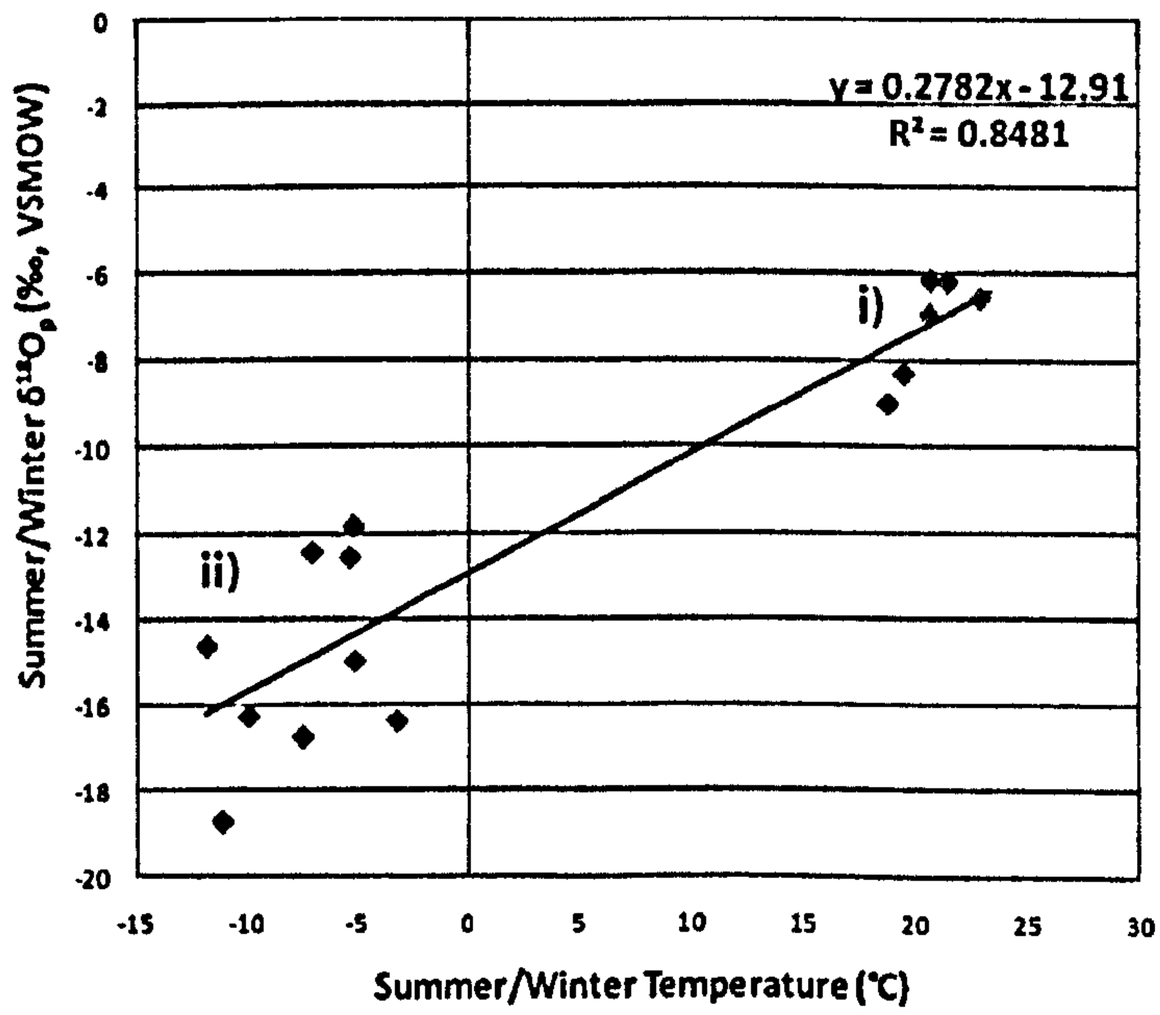


**Figure 5.13 The summer/winter comparison from the same data used to produce equation (5.7c). i) is the summer data and ii) is the winter data following method from Fricke and O'Neil (1999).**

Using equations (5.7a), (5.7b) and (5.7c) it is now possible to model how $\delta^{18}O_p$ changes with MAT in the Russian data. Combining these relationships with that described by Friedman and O'Neil (1977) (equation 5.6), Dworkin *et al.* (2005) and Prochnow *et al.* (2006) produced equations which can be used to model palaeotemperature without a known value for $\delta^{18}O_p$. They generate these equations by simultaneously solving equations (5.6) and (5.7a), and (5.7b) for temperature, and produce a third-order cubic polynomial for both a spatial relationship (5.8a) (Dworkin *et al.* 2005 and Prochnow *et al.* 2006) and a temporal relationship (5.8b) (Dworkin *et al.* 2005). Also, using the relationship created from the Saratov weather station (5.8c), it is possible to produce a temporal relationship specifically for the Russian field area (5.8c) following the method of Dworkin *et al.* (2005).

$$-0.50\,T^3+(\delta^{18}O_{carb}+152.04)\,T^2-2.78\times10^6=0 \quad (5.8a)$$

$$-0.22\,T^3+(\delta^{18}O_{carb}+61.99)\,T^2-2.78\times10^6=0 \quad (5.8b)$$

$$-0.28\,T^3+(\delta^{18}O_{carb}+92.24)\,T^2-2.78\times10^6=0 \quad (5.8c)$$

where $\delta^{18}O_{carb}$ is the isotopic composition of the pedogenic carbonate (relative to VSMOW); and $T$ is the Mean Annual Temperature (°K). This is converted to °C using the conversion °C = °K – 273.15 (Bureau International des Poids et Mesures 2008).

When equation (5.8a) is applied to the pedogenic carbonate values from Sambullak, Boyevaya Gora and Mescheryakovka, all sections produce MAT values below 0°C, some as low as –28°C, (Figure 5.14). As previously mentioned, there is no evidence of these soils being below freezing for a prolonged period of time. It is also questionable whether carbonate

nodules will be able form in such cold mean annual conditions. Equation (5.8a) also models the negative $\delta^{18}O$ excursion seen at Boyevaya Gora and Sambullak as a fall in temperature (Figure 5.14). This is the opposite of what has been observed in the marine realm where the $\delta^{18}O_{carb}$ negative excursion is linked to a temperature rise (e.g. Magaritz and Holser 1991; Kidder and Worsley 2004) in the range of 5–6°C (Magaritz and Holser 1991), although this single result may be due to changes in rock type or salinity (see Twitchett 2007 and references therein). The estimated drop in temperature seen in Russia also appears incongruent with the observed rise in aridity and evaporation seen in the morphology and mineralogy of the paleosols related to the oxygen excursions. Thus, it is possible to reject this equation as not accurately modelling the Russian sections.

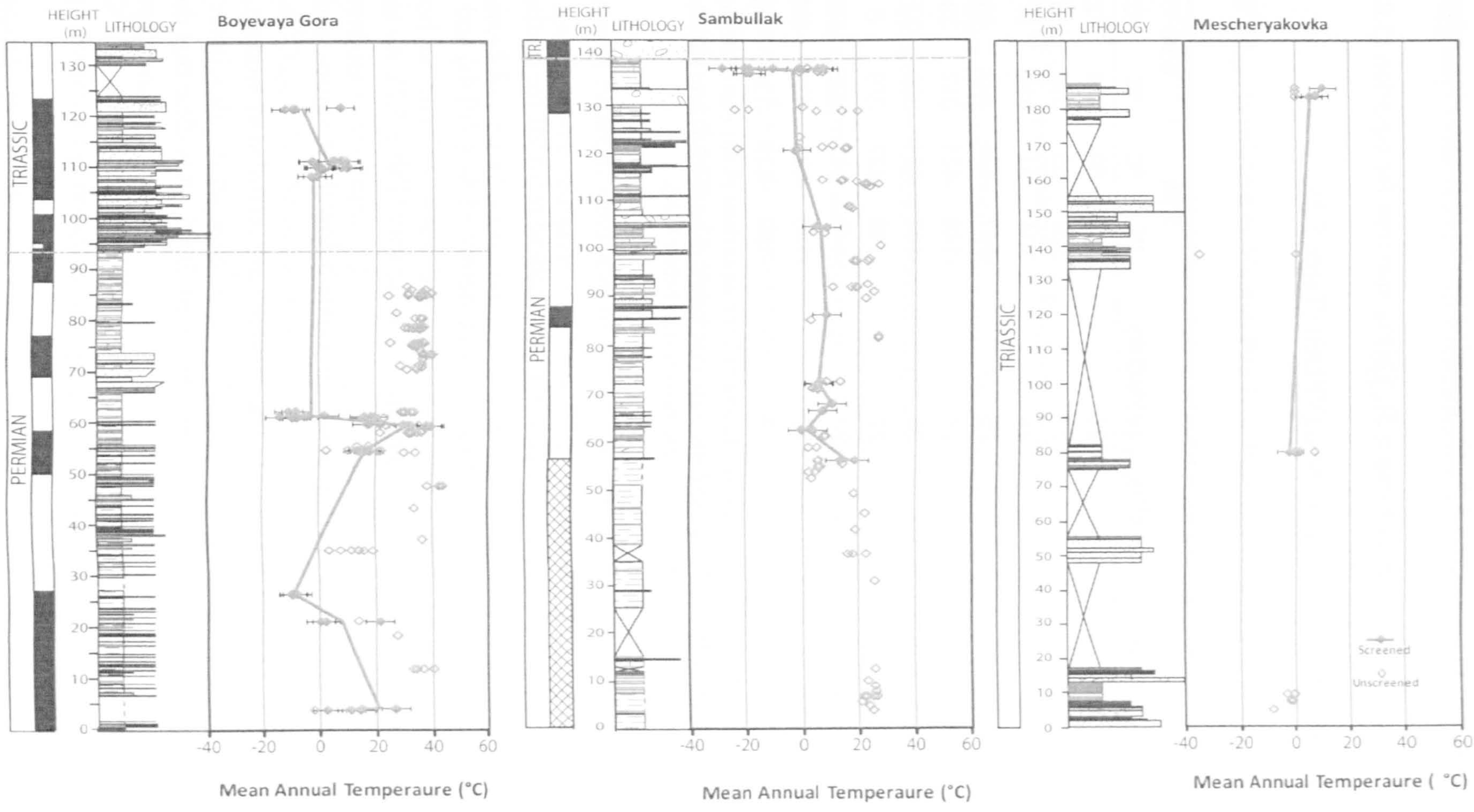


**Figure 5.14 Palaeotemperature estimates using equation (5.8a) for Boyevaya Gora, Sambullak and Mescheryakovka. The open diamonds are the nodules that failed the at least one of the screening tests applied (see Appendix 3.3 for calculations).Modelled temperatures below 0°C are incompatible with paleosol morphology (see text) and so Equation 5.8a can be rejected.**

When equation (5.8b) is applied to the screened pedogenic carbonate data from Russia, below pedogenic carbonate $\delta^{18}O$ values of –5 ‰ the equation produces temperature estimates of below –400°C, which is impossible (Table 5.2). This is also true for equation (5.8c) which exhibits this behaviour below values of –9‰ (VPDB) (Table 5.2).

| | | 5.8b | | 5.8c | |
|---|---|---|---|---|---|
| $\delta^{18}O_{carb}$ (VPDB) | $\delta^{18}O_{carb}$ (VSMOW) | °K | °C | °K | °C |
| -3 | 28 | 342 | 69 | 346 | 72 |
| -4 | 27 | 328 | 55 | 338 | 65 |
| -5 | 26 | 304 | 31 | 330 | 57 |
| -6 | 25 | **-147** | **-420** | 322 | 48 |
| -7 | 24 | **-148** | **-421** | 312 | 39 |
| -8 | 23 | **-148** | **-421** | 300 | 27 |
| -9 | 22 | **-149** | **-422** | 279 | 6 |
| -10 | 21 | **-149** | **-422** | **-136** | **-409** |
| -11 | 20 | **-150** | **-423** | **-136** | **-409** |
| -12 | 18 | **-150** | **-423** | **-136** | **-410** |

**Table 5.2 The mean annual air temperatures (in °K and °C) for equations (5.8b) and (5.8c) at a range of $\delta^{18}O_{carb}$ values from 0‰ (VPDB) to –12‰ (VPDB). Note that below -5 ‰ (VPDB) for (8b) and -9‰ (VPDB) for (5.8c) the equations produce unrealistic results (i.e. below 0°K).**

The reason for this sudden jump from positive values to extremely negative ones is due to the way a cubic polynomial is solved (see Chapter 2, mathematical methods for mathematical explanation). In the case of equations (5.8b) and (5.8c), below –5 ‰ (VPDB) and –9‰ (VPDB) the equations stop modelling the data in a realistic way (Table 5.2). As experimental values have been recovered from the pedogenic carbonate below these values, and since carbonate values below –5 ‰ (VPDB) and –9‰ (VPDB) are recorded in modern, unaltered pedogenic carbonates (Alonso-Zarza 2003; Dworkin *et al.* 2005), it is clear that these equations do not realistically model the relationship between temperature and $\delta^{18}O_{carb}$ in the Russian data and must also be rejected.

Dworkin *et al.* (2005) also produced an empirical method to calculate palaeotemperature from the modern linear relationship between MAT and modern pedogenic carbonates, from the data of Cerling and Quade (1993). This relationship is defined as:

$$\delta^{18}O_{carb} = 0.49(T) - 12.65 \quad (5.9)$$

where $\delta^{18}O_{carb}$ is relative to Vienna Pee Dee Belemnite (VPDB); and T is the Mean Annual Temperature (°C).

Equation (5.9), like equation (5.8a), models a negative excursion in $\delta^{18}O_{carb}$ as a drop in temperature (Figure 5.15). The values for all three sections are slightly warmer than those calculated from equation (5.8a) but with not quite the same range, that is to say the difference between the maximum and minimum estimates is not as great (Figure 5.15). However, as with equation (5.8a), this equation produces MAT estimates of below 0°C (see Sambullak Figure 5.15) and thus can be rejected as modelling MAT in the Russian sections.

The overall palaeotemperature estimates from the Russian P–Tr boundary produced from equations (5.8a) and (5.9) are not consistent with the pedological observations. That is to say they produce MAT estimates below 0°C as noted earlier, yet there is no evidence of freezing in the sections (see Chapter 3). This suggests that either:

(1) the $\delta^{18}O_{carb}$ values from the pedogenic carbonate were not formed from meteoric water,

(2) the relationship between $\delta^{18}O_{carb}$, $\delta^{18}O_p$, and MAT was different in the Permian –Triassic in the southern Urals, or,

(3) there are other factors influencing this relationship which the Dworkin *et al.* (2005) equations do not take into account.

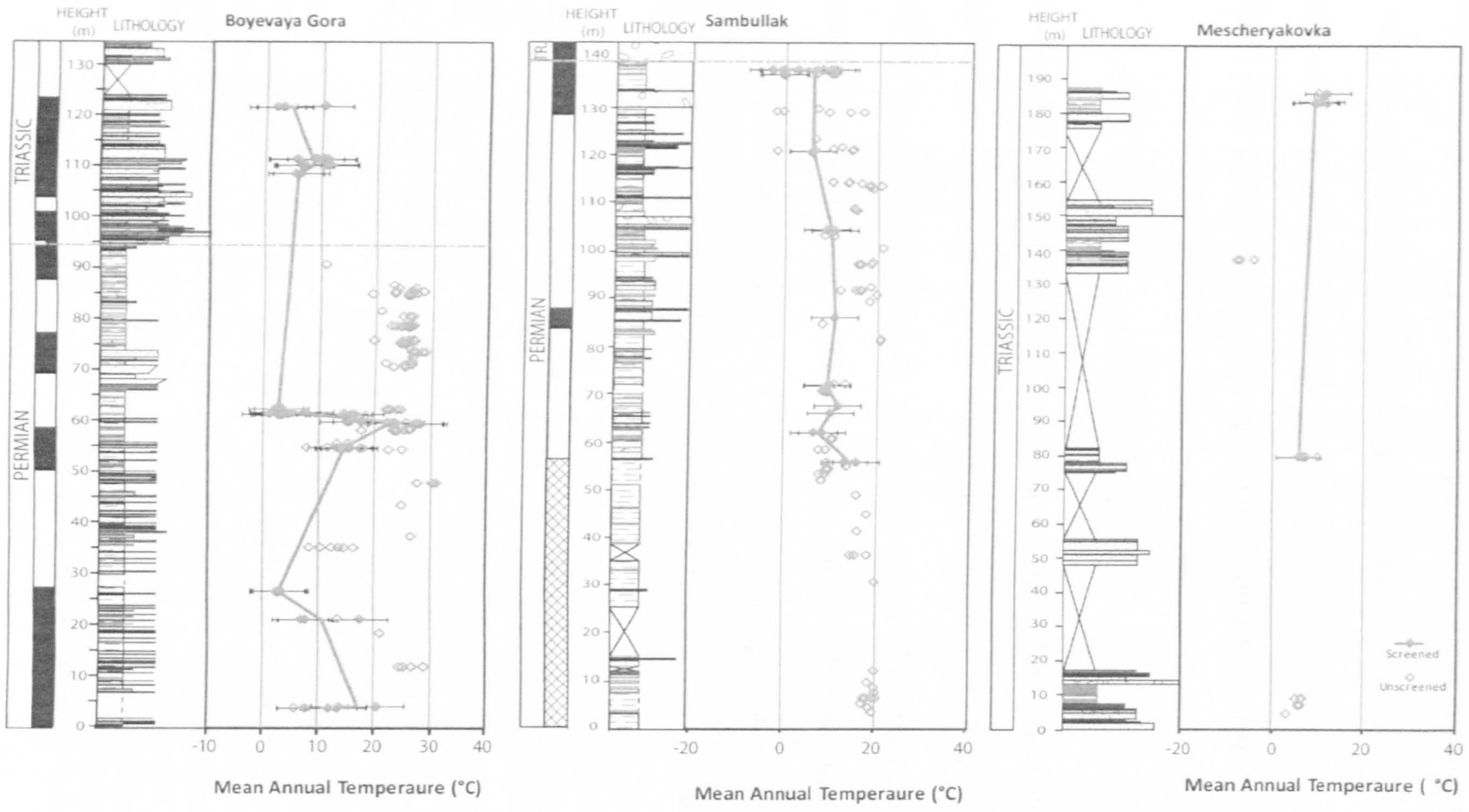


**Figure 5.15 Palaeotemperature estimates using equation (5.9) for Boyevaya Gora, Sambullak and Mescheryakovka. The open diamonds are the nodules that failed the screening process (see Appendix 3.3 for calculations).**

The screening criteria applied to the $\delta^{18}O_{carb}$ values (see Chapter 4) mean that point (1) can be rejected. The fact that equation (5.8a) has been successfully applied to similar paleosols in the Middle Triassic of Utah (Prochnow *et al.* 2006) suggests that the relationship described by equation (5.8a) is valid for at least some localities in the Triassic. Therefore it seems likely that another factor is influencing the $\delta^{18}O_{carb}$ composition of the pedogenic carbonate nodules in Russia which is causing equations (5.8a), (5.8b), (5.8c) and (5.9) either not to function or to produce anomalously cool temperatures.

The hypothesis that another factor not modelled by equations (5.8a), (5.8b), (5.8c) and (5.9) may also explain why these equations model a negative excursion in $\delta^{18}O_{carb}$ as a drop in temperature, rather than the expected rise. In order to produce a rise in temperature with a negative excursion in $\delta^{18}O_{carb}$ there must be a negative relationship between MAT and $\delta^{18}O_p$. This is the opposite of the relationship described by Fricke and O'Neil (1999). However, such relationships have been observed in the modern day. For instance in modern northern Italy it has been observed that a 3.5°C rise in temperature actually led to a $\delta^{18}O_p$ decrease of –3.82‰ in mean annual precipitation. The reason for this negative in northern Italy is because the rise in temperature caused a reduction in isotopically positive summer rain, shifting the weighted annual mean towards the isotopically negative autumn rains (Longinelli *et al.* 2006). This lowers the $\delta^{18}O$ of mean annual precipitation in the hotter years. This may suggest that in some localities just comparing the seasonal extremes to temperature (as proposed by Fricke and O'Neil 1999) fails to take into account when in the year the maximum precipitation falls and thus which isotopic composition is likely to have a controlling influence over the soil water.

This inverse relationship has also been observed at the Saratov weather station used to produce equation (5.7c), but only when the mean annual temperature is compared to the $\delta^{18}O_p$ of weighted mean annual precipitation (Figure 5.16). The method used to produce (5.7c) (as proposed by Fricke and O'Neil 1999) produces a positive relationship from the very same data (Figure 5.13).

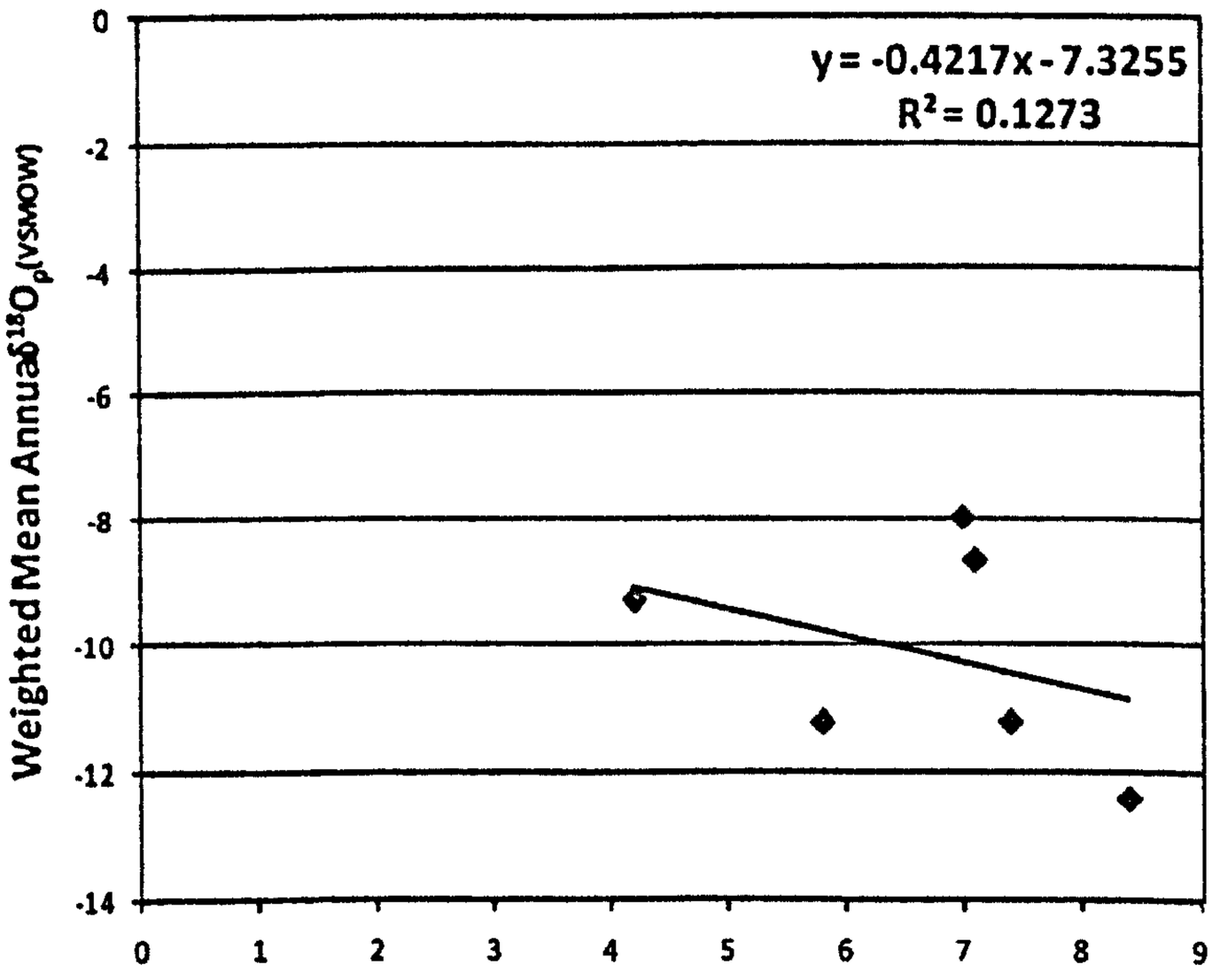


**Figure 5.16 A. Weighted mean annual precipitation for 6 years plotted against Mean annual temperature for Saratov station (51° 34' 00" / 46° 1' 60" / 166m).**

The reason for the difference between is that at Saratov (Figure 5.16), as in Italy (Longinelli *et al.* 2006), in the years with the highest MAT more precipitation falls in the winter, while in cooler years there is more precipitation in the summer months which is isotopically positive (Figure 5.17). This has the effect of shifting the annual mean of $\delta^{18}O_p$ negative while the actual isotopic values of summer and winter precipitation remain unchanged. Thus, it becomes essential to understand which of these methods best describes the $\delta^{18}O_p$ of soil water and thus that which is incorporated into pedogenic carbonate nodules.

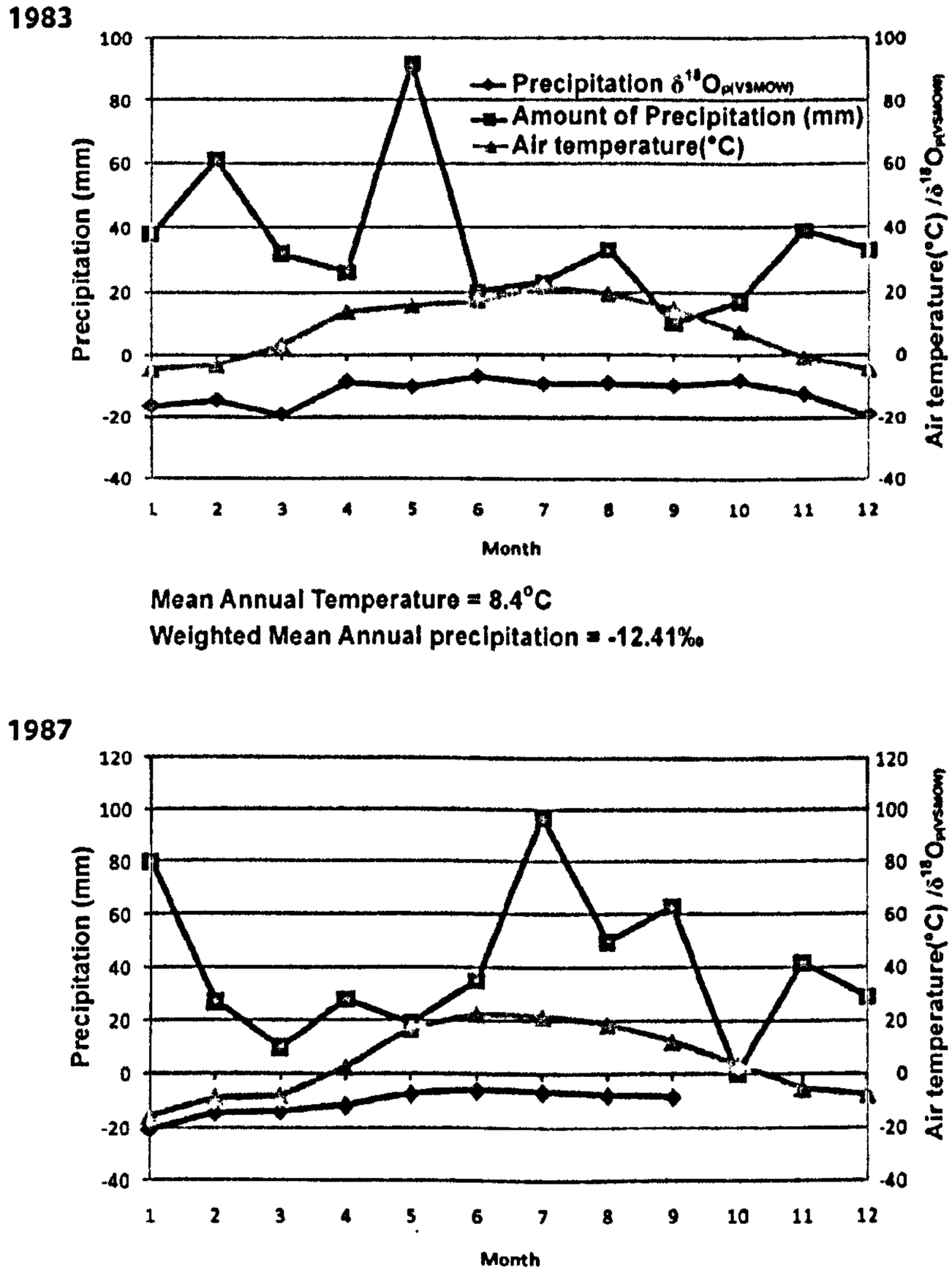


**Figure 5.17 The plots of the monthly data collected at Saratov for the hottest year in the dataset (1983) and the coolest (1987). Note the reduction in summer precipitation in the hotter year (1983) leading to a more negative weighted Mean Annual precipitation (data from IAEA/WMO, 2008).**

This negative relationship has also been observed in Russia (at Saratov and Rostov Na Donu), Japan (Ryori) and China (Chengdu, Hetian and Zhangye) (data from IAEA/WMO, 2008) (see Figure 5.18). However, when these values are all plotted together it is observed that although values from one locality may show a negative relationship over all they show a positive relationship with respect temperature. This suggests that the relationship described by Fricke and O'Neil (1999) is describing the global latitudinal variation of temperature and $\delta^{18}O_p$ while at single localities the opposite relationship may be true.

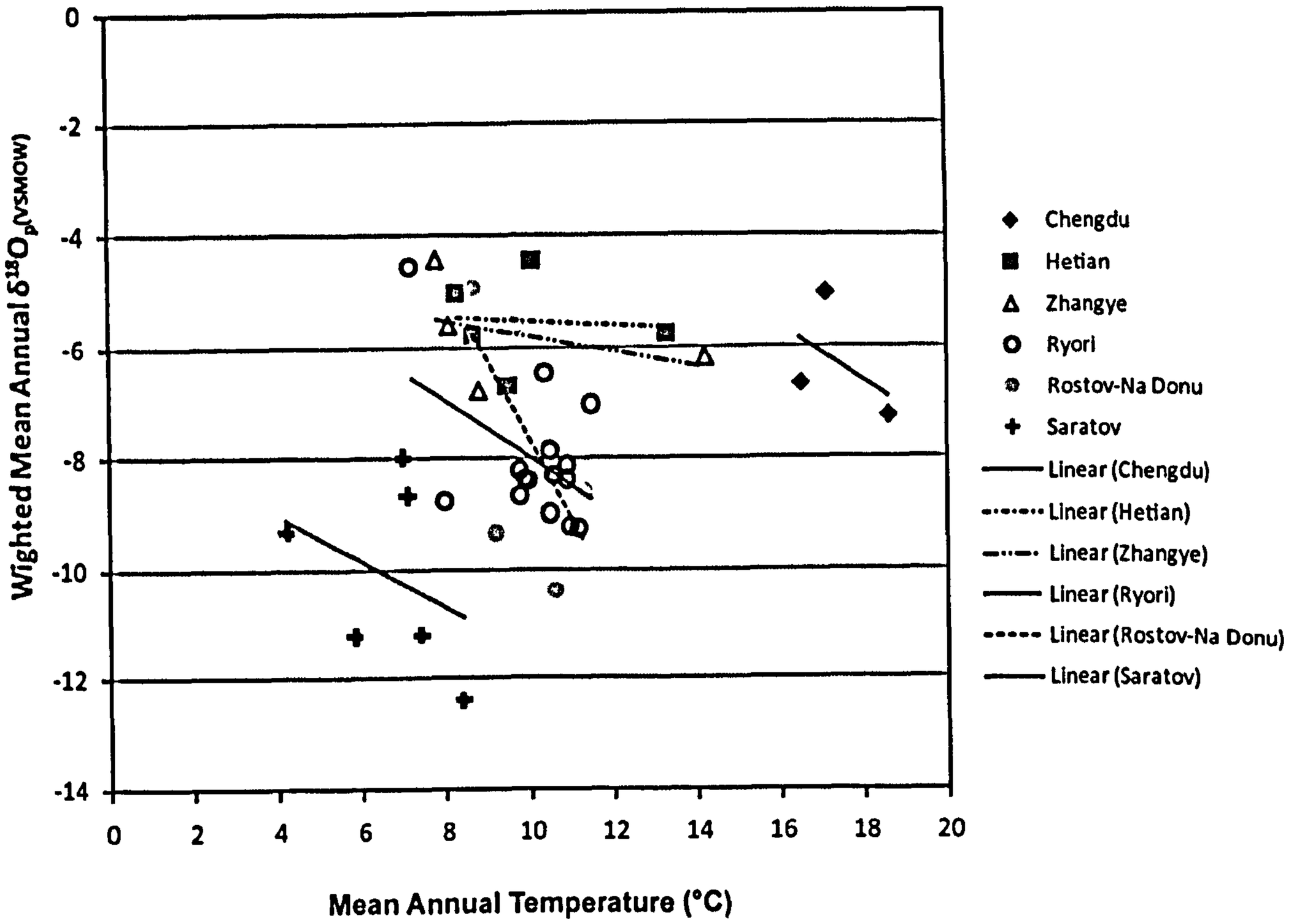


**Figure 5.18 Weighted mean annual precipitation plotted against Mean annual temperature for Chengdu (30° 40' 12" / 104° 1' 12" / 506m), Hetian (37° 7' 60" / 79° 55' 60" / 1375m), Zhangye(38° 55' 48" / 100° 25' 48" / 1483m) in China; Ryori (39° 1' 48" / 141° 48' 36" / 260m) in Japan; and Rostov-Na Donu (47° 15' 00" / 39° 49' 12" / 77m) and Saratov (51° 34' 00" / 46° 1' 60" / 166m) in Russia (data from IAEA/WMO, 2008).**

It has been suggested that long-term (inter-annual) changes in precipitation and surface air temperature are most appropriate for palaeoclimate reconstructions based on isotopic studies (Rozanski *et al.* 1992). In modern soils it has been observed that, in spite of significant seasonal variation in the isotopic value of the soil water at the surface, those nodules at depth show little inter-annual variation (Liu *et al.* 1996). This would suggest comparing MAT and MAP $\delta^{18}O_p$ rather than using the seasonal extremes as suggested by Fricke and O'Neil (1999), is more applicable to modelling the effect of $\delta^{18}O_p$ in soil carbonates. This approach has also been suggested by studies conducted on modern soils (Cerling and Quade 1993) which have

shown strong correlation between isotopic compositions of carbonate nodules and mean annual precipitation rather than seasonal extremes as used by Dworkin *et al.* (2005).

Using data from the MAT and weighted mean annual precipitation it is possible to model this relationship (Figure 5.16A). Combining this relationship with equation (5.6) it is possible to generate a temperature equation (5.10) that models the effect of reduction in isotopically heavy summer rain shifting the weighted annual mean at Saratov.

$$0.4217\,T^3 + (\delta^{18}O_{carb} - 124.88)\,T^2 - 2.78\times10^6 = 0 \qquad (5.10)$$

When applied to the Russian data this equation produces results that are not below 0°C and produces increases of temperature across the excursions rather than drops (Figure 5.19). Therefore, this method may more accurately model the results from Russia. However, the relative lack of data from the Saratov weather station and the weak coefficient of determination ($R^2 = 0.1273$) (Figure 5.16A) suggests that even though this relationship produces 'realistic' results (i.e. similar to what would be hypothesized) results may be treated with caution.

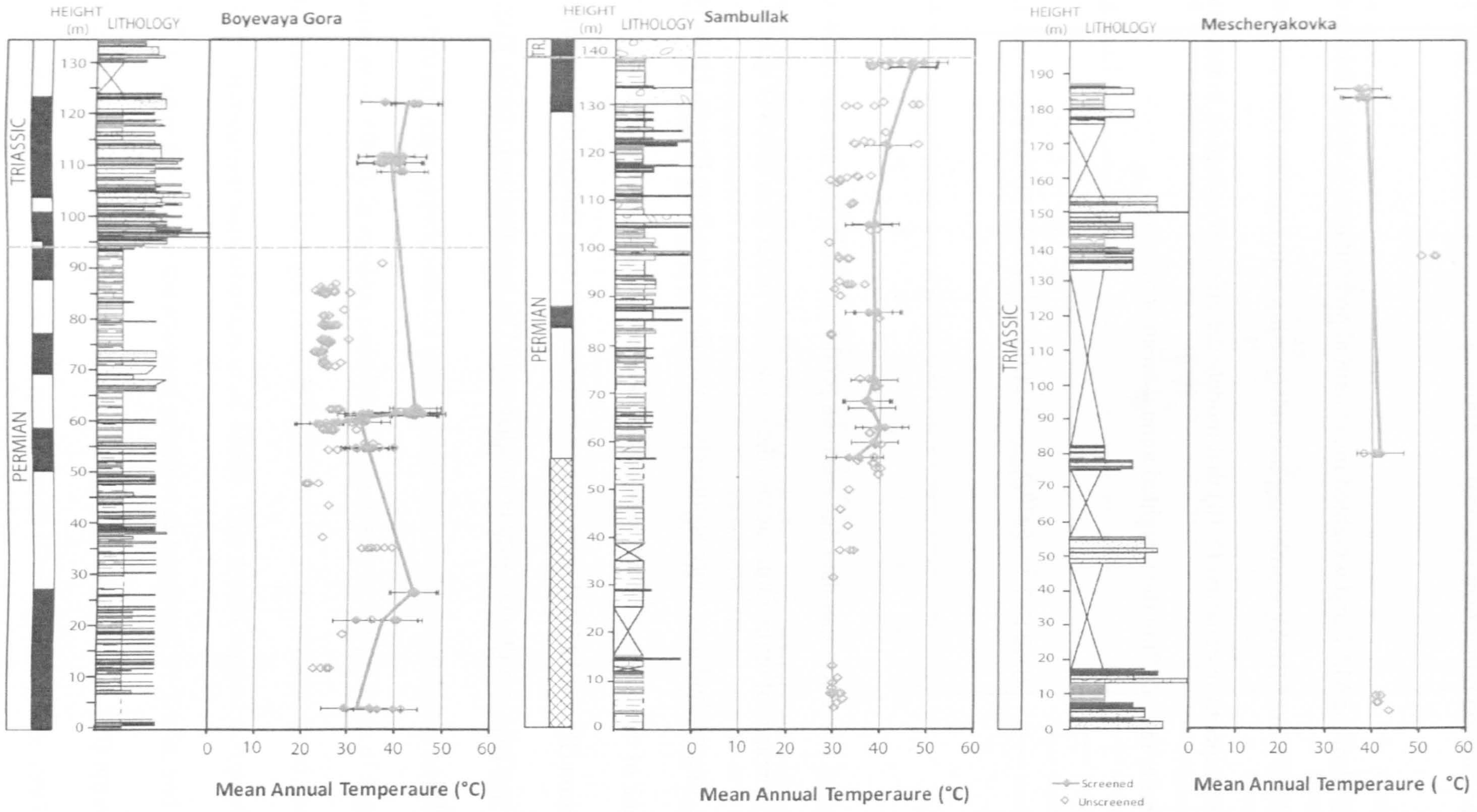


**Figure 5.19 Palaeotemperature estimates using equation (5.10) for Boyevaya Gora, Sambullak and Mescheryakovka. The open diamonds are the nodules that failed the screening process. (See Appendix 3.3 for calculations.**

### *5.3.2 Monsoonal effects on oxygen isotopes*

Physical processes can change over time and it is possible that modern meteoric precipitation–temperature relationships may not be valid in the past or for a specific locality (Fricke and O'Neil 1999, Dworkin *et al.* 2005). For instance changes in the $\delta^{18}O$ of the palaeo-oceanic source region of precipitation and, changes in the temperature difference between ocean surface temperature at the vapour source and the air temperature at the site of interest, can affect the $\delta^{18}O_p$ versus MAT relationship (Dworkin *et al.* 2005).

The isotopic composition of monsoonal or highly seasonal rain does not correspond to temperature, due to the 'amount effect' where higher amounts of rainfall are associated with a lesser $^{18}O$ content in the rainwater because, unlike normal precipitation, the air masses move vertically rather than horizontally (Dansgaard 1964: Hoffmann and Heimann 1997; Yadava *et al.* 2007). This can disrupt the relationship seen by Fricke and O'Neil (1999), as rainfall, in these areas will record strongly depleted isotope signals at the period of highest rainfall (Hoffmann and Heimann 1997). In some areas the temperature effect (positive $d\,\delta^{18}O_p/dT$) has been known to partially cancel out the effect of precipitation (negative $d\,\delta^{18}O_p/dP$) as the time of highest rainfall coincides with the time of highest temperature (Johnson and Ingram 2004). In localities affected by the Asian monsoon the standard positive $\delta^{18}O_p$ versus MAT relationship may be nonexistent (Hoffmann and Heinemann 1997; Johnson and Ingram 2004; Li *et al* 2007). In these regions the $\delta^{18}O_{carb}$ can be ~6‰ lighter than in non-monsoonal areas (Alonso-Zarza 2003). Due to a pronounced 'amount effect', rather than producing more negative values at higher latitudes, similarly depleted $\delta^{18}O_p$ values are found at lower latitudes (Hoffmann and Heinemann 1997). This becomes even more problematic if the strength of the monsoon varies over time. It has been observed in modern China that, depending on the strength of the monsoon, the dominant control on $\delta^{18}O_p$ can switch back and forth between the

precipitation (the amount effect) and temperature (Johnson and Ingram 2004). This could produce erroneous palaeotemperature estimates using equations (5.8a), (5.8b), (5.8c), (5.9) and (5.10) if an increase in monsoonal, or seasonality, activities occurs at the same time as an increase in temperature, since it could potentially cancel out or even reverse the positive excursion caused by temperature.

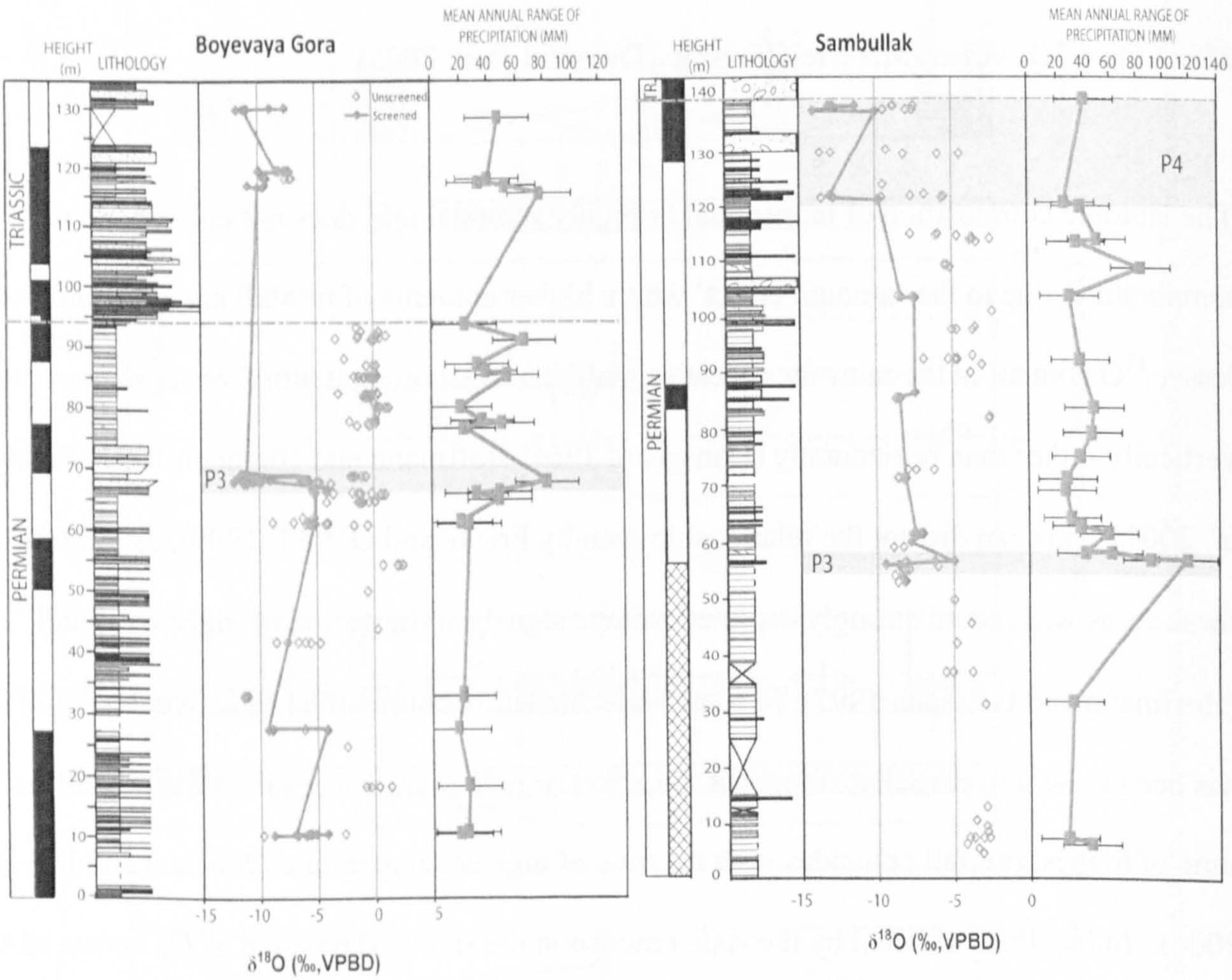


**Figure 5.20 Variation in $\delta^{18}O_{carb}$ of pedogenic carbonate plotted next to mean annual range of precipitation at Boyevaya Gora and Sambullak. Note how there is an apparent increase in seasonality activity after the negative $\delta^{18}O_{carb}$ at Boyevaya Gora (see Appendix 3.2 and 3.3 for calculations).**

If the annual range of precipitation is used as a proxy for changes in seasonality (cf. Retallack 2005b) and is plotted against the $\delta^{18}O_{carb}$ values it is notable that the negative excursion P3 is coincident with a marked rise in mean annual range of precipitation from 46mm (±22mm) to 76mm (±22mm) at Boyevaya Gora and 30mm (±22mm) to 90mm (±22mm) at Sambullak

(Figure 5.20). This is very similar to the difference in mean annual range of precipitation between monsoonal and non-monsoonal locations in the modern world (see Section 5.2) may suggests that the isotope excursion P3 may be caused by an increase in seasonality, and thus the influence of the amount effect, rather than temperature (Figure 5.20). Excursion P4, on the other hand, does not coincide with a rise in mean annual range of precipitation and thus probably relates to a change in temperature rather than seasonality activity (Figure 5.20).

## 5.4 Discussion

Some of the strongest evidence for environmental change associated with the P/Tr boundary is that from the palaeoprecipitation estimates. Using the palaeoprecipitation equation for Vertisol microlows (equation 5.3a) there is a 200mm rise in MAP across the P/Tr boundary compared to a rise of just less than 400mm across the P/Tr boundary recorded at Lootsberg Pass in the Karoo basin (Retallack 2003). However, the three other equations (5.2, 5.3 and5.5) all show the opposite relationship, suggesting a drop in MAP in the earliest Triassic. These three equations also all suggest an increase of MAP through the part of the section at Boyevaya Gora containing only pedogenic dolomite (Figure 1 and Figure 6) which may seem incongruous as pedogenic dolomite is probably linked to increases in evaporation (see Chapter 4). It has been noted that pedogenic dolomite in other sections is related to increased seasonality (Kessler *et al.* 2001), an observation borne out by the suggestion of an increase in the mean annual range of precipitation (seasonality) related to this rise in MAP (Figure 5.6). This increase in the mean annual range of precipitation is evident, both after the P3 event at Boyevaya Gora, over the P/Tr boundary and increasing into the Triassic, and is especially evident in the Olenekian where there is a strong increase in the range of mean annual precipitation. An increase in seasonality and MAP has also been observed at Karoo, in the

Earliest Triassic, (Retallack 2003) and in the Anisian of Utah in the USA. (Prochnow *et al.* 2006).

As stated by Retallack (1994), climate modelling can become very seductive and the results of any model must be tempered by real pedological and sedimentological data. This is especially pertinent when considering the results from the palaeotemperature equations. Thus, a holistic approach must be used, especially in cases where the evidence from different models is contradictory.

The pedological data and analysis of the sections in Russia (Chapter 3) suggest a steppe to semi-arid climate, as warm as or warmer than similar environments existing today. Modern dry steppe environments (BSh) have a MAT greater than 18°C (Peel *et al.* 2007). The increase in numbers of Vertic paleosols up to the P/Tr boundary seen in Russia suggests that the paleosols were being affected by more pronounced wetting and drying cycles, and the increase of pedogenic dolomite would suggest an increase in evaporation (Figure 1 and Chapter 4). This would all point to an increase in temperature up to the P/Tr boundary. Equally the evidence from the paleosols suggests that, by the Olenekian in the Early Triassic, the basin was more arid and possibly hotter than it was in the Permian. The occurrence of Triassic aeolian dunes in the Induan (Tverdokhlebov *et al.* 2002) would also indicate a hotter, more arid, climate in the Triassic than the Permian.

| | Permian (°C) | | | Triassic (°C) | | |
|---|---|---|---|---|---|---|
| Equation | Min | Mean | Max | Min | Mean | Max |
| 5.6 | -11 | 27 | 64 | 21 | 31 | 46 |
| 5.9 | -3 | 10 | 28 | 2 | 8 | 12 |
| 5.10 | 23 | 38 | 49 | 37 | 40 | 45 |

**Table 5.3 Values from the three palaeotemperature equations. Equation 5.6 uses a constant value of $\delta^{18}O_p = -5.52‰$) (see Appendix 3.3 for calculations).**

Based on the results of computer climate modelling, it is suggested that in the latest Permian the Southern Urals area summer temperatures were between 35 – 40°C, winter temperatures were between 0 – 5°C (Kiehl and Shields 2005) and soil temps of ~30°C (Roscher *pers. comm.*). Others have suggested a slightly lower global temperature of 25°C (35°C at the equator and 15°C at the poles) in the Late Permian rising to a global average of 30°C (40°C at the equator and 20°C at the poles) (Kidder and Worsley 2004). Based on these models it appears that equation 5.10 best fits the range they predict (Table 5.3) although it is on the high end of the range of these predictions. Palaeotemperature estimates from paleosols in the Karoo basin, using different proxies (B horizon chemistry), suggest a rise from 9.9°C (±4.4) in the Permian to 10.3°C (±4.4) in the Triassic (Retallack *et al.* 2003). However, in their paper Retallack *et al.* (2003) suggest that diagenetic changes may have offset their estimates. Also the Karoo sections are at higher latitude than the Russian sections (50-60°S Retallack *et al.* 2003 compared with 30-35°N Taylor *et al.* 2009)

As noted in Chapter 4 there are two negative $\delta^{18}O_{carb}$ anomalies which are recorded in pedogenic calcite and defined by more than one paleosol in the South Urals sections; one just before the P/Tr boundary at Sambullak (P4) and one 40m below the P/Tr boundary (P3) at both Sambullak and Boyevaya Gora. Both of these excursions represent rises in temperature of ~7°C, using equation (5.10). However, it is possible that the excursions are linked to other processes such as an increase in highly fractionated seasonal precipitation rather than changes in temperature and, if these dominated, they could obscure any signal caused by changes in local air temperature.

These factors can be divided into local and global factors (Figure 5.21). Local factors include changes in evaporation, plant cover and waterlogging of the soil. With respect to the isotope

excursions recorded in Russia, the increase in aridity linked with the possible reduction in plant cover would cause an increase in evaporation which would preferentially remove the lighter isotopes producing a positive excursion rather than a negative one (Wright and Tucker 1991: Cerling and Quade 1993; Liu *et al.* 1996). The influence of groundwater is thought also to cause enrichment in $^{18}O$ from more evolved groundwaters (Wright and Tucker 1991) although it has been observed that pedogenic carbonate is enriched with respect to groundwater cavity fills (Quast *et al.* 2006). This effect was observed in the difference between the spar and micritic component of the Russian nodules so, by screening the data and excluding all the results where these values were within error of each other, the effect of groundwater has been removed (Chapter 4).

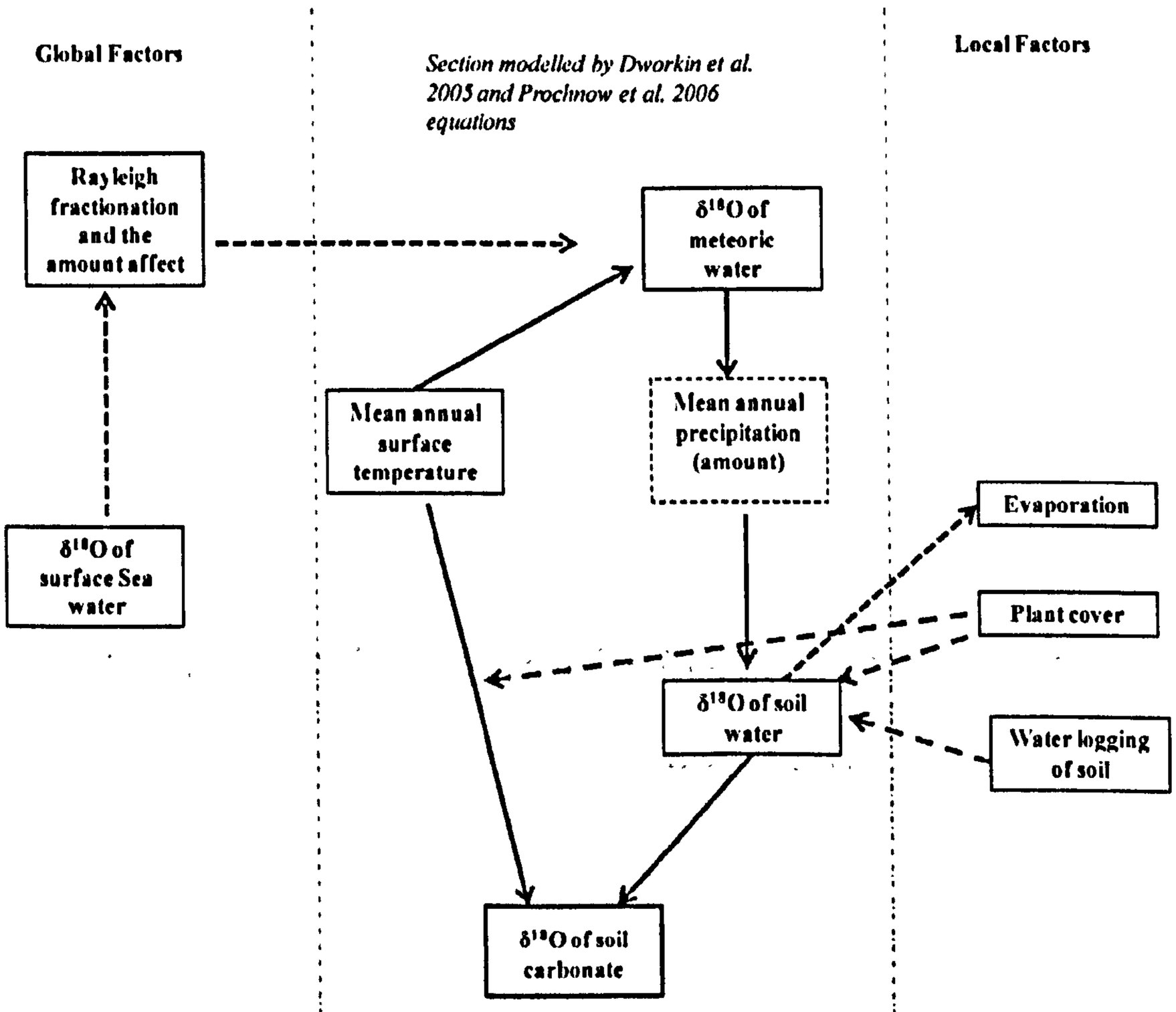


**Figure 5.21 The factors that can affect the $\delta^{18}O$ of soil carbonate. The central panel contains the factors described in the equations created by Dworkin *et al.* (2005). The other two panels refer to other factors that can affect the $\delta^{18}O$ of soil carbonate that are not included in the equations. Global factors refer to factors that normally are constant but at a time of mass extinction may vary and local factors are those in the local environment that could also affect soil carbonate.**

The global factors that could have obscured any change in local air temperature include changes in the $\delta^{18}O$ of the seawater source area and changes in circulation. However, it has been observed that changes in $\delta^{18}O$ of the seawater have only a minor effect on $\delta^{18}O_p$ (1–2‰ over geological scales) (Fricke and O'Neil 1999) compared to the effect caused by Rayleigh fractionation (the process of evaporation and condensation within the cloud base) which can vary up to 30‰ (Dansgaard 1964). One of the strongest influences of the $\delta^{18}O_{carb}$ of pedogenic carbonate is the effect of changes in monsoonal variability (Andrews *et al.* 1998; Alonso-Zarza 2003; Dworkin *et al.* 2005). The Russian paleosols of the Late Permian have dispersed carbonate nodules, which have been linked to the influence of monsoonal activity (Retallack *et al.* 2003; Retallack 2005b) and it has been suggested that there was an increase in monsoonal activity across the P/Tr boundary (Kidder and Worsley 2004). This increase in seasonal rain could have introduced isotopically lighter precipitation into the system, as has been recorded in the Late Pleistocene in India (Andrews *et al.* 1998) and in China (Johnson and Ingram 2004; Li *et al.* 2007).

The coincidence of a $\delta^{18}O_{carb}$ negative excursion (P3) with a marked increase in mean annual range of precipitation suggests that this excursion may be in part due to an increase in seasonality and thus the influence of the amount effect. It is possible to quantify the change in $\delta^{18}O_p$ that is needed to produce the recorded $\delta^{18}O_{carb}$ negative excursion, assuming temperature did not change, by using equation (5.6) (Table 5.4).

| | | $\delta^{18}O_{carb}$ (‰) | | Temp | $\delta^{18}O_p$ |
|---|---|---|---|---|---|
| | | VPDB | VSMOW | °C | ‰ |
| **Boyevaya Gora** | | | | | |
| | Excursion | -9.46 (±7.48) | 21.10 (±7.71) | 30 (±12) | 6.46 (±10.22) |
| | Pre excursion | -3.12 (±7.18) | 27.65 (±7.41) | 30 (±12) | -0.09 (±9.92) |
| Change in $\delta^{18}O_p$ needed to cause excursion | | | | | -6.54 (±0.31) |
| **Sambullak** | | | | | |
| | Excursion | -9.05 (±0.87) | 21.53 (±0.90) | 34 (±2) | 5.15 (±1.32) |
| | Pre excursion | -5.63 (±1.29) | 25.06 (±1.33) | 34 (±2) | 1.62 (±1.75) |
| Change in $\delta^{18}O_p$ needed to cause excursion | | | | | -3.53 (±0.43) |

**Table 5.4 The change in $\delta^{18}O_p$ to generate excursion P3 at Boyevaya Gora and Sambullak if temperature is held constant.**

It is theoretically possible to produce the negative excursion P3 without any change in temperature simply by reducing $\delta^{18}O_p$ by –6.54‰ to –3.53‰. In modern monsoonal areas (e.g. New Delhi) there is a –8.4‰ difference between the $\delta^{18}O_p$ in monsoonal months compared to non monsoonal months (IAEA/WMO, 2008). Thus, it is possible that the excursion P3 may be purely due to a change to monsoonal conditions. However, the negative $\delta^{18}O_{carb}$ excursion occurs at the same time as a similar negative $\delta^{13}C_{carb}$ excursion, suggesting a change in atmospheric conditions (cf. Kidder and Woresley 2004; Retallack and Krull 2006; Payne and Kump 2007).

A negative $\delta^{18}O$ excursion in the composition of therapsid tusks has been observed at Karoo across the P/Tr boundary and has been interpreted as a rise in temperature (Smith and MacLeod 1998; MacLeod *et al.* 2000; Retallack *et al.* 2003). If this is indeed the case at these localities, then an inverse relationship between temperature and $\delta^{18}O_p$ (e.g. as observed at Saratov Figure 5.17 B) must have operated. As if the global positive relationship observed by Fricke and O'Neil (1999) controlled the composition of $\delta^{18}O_p$ then these excursions too would be caused by a fall in temperature rather than a rise. This underlines the fact that when

applying palaeotemperature equations to data from ancient terrestrial systems, the models that have been created for the modern day may not necessarily hold true in the past and that there may be local conditions that have a stronger influence on the isotopic composition than global ones especially at times of changes in the seasonality of rainfall as seen in Russia.

## 5.5 Summary

In summary, the period spanning the Permian–Triassic in Russia is characterised by dramatic climate change. This climate change, however, seems to have started prior to the P/Tr boundary in the South Urals and is linked to the large negative carbon and oxygen excursion (P3). The palaeoclimatic investigations have revealed the following:

1. The negative carbon and oxygen excursion (P3) is followed by a period of only type B dolomite at Boyevaya Gora and an increase in type B dolomite at Sambullak;
2. MAP for the Permian is 392mm (±158, 1σ std) (eq.5.2) to 242mm (±72, 1σ std) (eq.5.5) and a possible of drop in MAP into the earliest Triassic at Boyevaya Gora to 185mm (±48, 1σ std) (eq.5.2) to 180mm (±6, 1σ std) (eq.5.5) followed by an increase by the Olenekian to 541mm (±269, 1σ std) (eq.5.2) to 313mm (±151, 1σ std) (eq.5.5);
3. There is an increase in mean annual range of precipitation from the excursion P3 up to the P/Tr boundary and an even bigger increase in the Olenekian to annual ranges similar to modern-day monsoonal areas (New Delhi) suggesting an increase in seasonality in the Triassic;
4. If the $\delta^{18}O_{carb}$ isotopic values are completely controlled by temperature, it appears that the paleosols in Russia, as at Saratov today, showed a lack of summer rain with an increase in air temperature causing the weighting of the mean annual precipitation towards more negative $\delta^{18}O_p$ values for warmer years;

5. Using equation (5.10) suggests an average Permian temperature of 38°C (± 14) and 40°C (± 8) in the Triassic. The excursions at Sambullak and Boyevaya Gora (P3 and P4) represent a rise in MAT of 7°C, although the weakness of the MAT/$\delta^{18}O_p$ relationship (Figure 5.17) on which equation (5.10) is based urges caution in the use of this estimate;
6. It is possible that excursion P3 (but not P4) represents an increase in seasonality and thus the amount effect with or without a rise in temperature.

# Chapter 6. Isotopic variation in marine carbonates of the Italian Dolomites[1]

## 6.1 Introduction

The potential multiple influences on the pedogenic $\delta^{18}O_{carb}$ values in Russia (see Chapter 5) means it is essential to understand whether the $\delta^{18}O_{carb}$ excursion seen in Russia are actually due to a change in temperature at P/Tr boundary or is due to another cause, such as changes in seasonality. Fossil brachiopods, due to their low-Mg calcite composition, which is a diagenetically more stable polymorph of calcite, have the potential to preserve a primary isotopic signal (Auclair *et al.* 2003). The comparison of the morphological and chemical structures of fossil brachiopods with modern brachiopods can thus determine if they have been recrystallised or altered by diagenesis (Auclair *et al.* 2003; Bojar *et al.* 2004; Korte *et al.* 2005a, b; van Geldern *et al.* 2006). As such they have been successfully used as proxies for both the $\delta^{13}C$ and $\delta^{18}O$ composition of ambient seawater (Popp *et al.* 1986; Veizer *et al.*1986; Grossman *et al.* 1996; Veizer *et al.* 1999; Brand 2004; Batt *et al.* 2007) and also to estimate palaeotemperature (Korte *et al.* 2005a, b; van Geldern *et al.* 2006) hence they could be used to test if the $\delta^{18}O$ excursion in the marine bulk rock record associated with the P/Tr boundary is a result of a change in temperature or a later diagenetic artefact.

In addition, understanding the $\delta^{13}C$ isotopic composition of palaeo-seawater is also essential when attempting to estimate $pCO_2$ from pedogenic carbonate from paleosols. This is because the paleosol $pCO_2$ model proposed by Cerling (1991) and modified by Ekart *et al.* (1999) needs an estimate of the $\delta^{13}C$ composition of the atmosphere ($\delta^{13}C_a$) which can be derived from the isotopic composition of carbonate precipitated in equilibrium with palaeo-seawater

[1] This chapter is adapted from a co-authored paper Kearsey *et al.* in review (see References)

(Mora *et al.* 1996; Ekart *et al.* 1999; Prochnow *et al.* 2006). Therefore, to produce an accurate $pCO_2$ estimate, especially over periods of extreme climatic change, accurate palaeo-seawater composition estimates are required.

The global marine negative carbon and oxygen isotope excursion associated with the P/Tr boundary has been observed in marine carbonate sections from the Italian and Austrian Dolomites (e.g. Magaritz *et al.* 1988; Baud *et al.*1989; Holser *et al.* 1991) which has been linked to a change rise in temperature (Holser *et al.* 1991). Equally, many of these sections have also been shown to contain brachiopod fossils (e.g. Posenato 2001; Chen *et al.* 2006). To investigate the difference between bulk rock and brachiopod isotope values the section at Val Brutta in the Italian Dolomites was micro-sampled and variations in lithology and recrystallisation were taken into consideration in order to determine whether lithology, diagenesis or primary processes were controlling the stable isotopic composition of the carbonates within the section. Biogenic calcite of brachiopod shells were recovered from this and another section (Tesero) to investigate how their isotopic composition compared with the bulk rock record with the aim of recovering a palaeotemperature and palaeo-seawater composition record.

## 6.2 Geological setting and stratigraphic position

The sampled localities for this study are Val Brutta (N 46° 0.539′, E 011° 26.685′) and Tesero (N 46° 17.191′, E 011° 31.211′) (Figure 1). The Val Brutta section has been previously described by Ghetti and Neri (1983) and Posenato (2001). It consists of 80 metres of shallow marine carbonates which extend through the upper part of the Bellerophon Formation and into the Tesero Member of the overlying Werfen Formation. The Bellerophon Formation consists

of interbedded grey micritic muds and recrystallised fossiliferous wackestones and packstones.

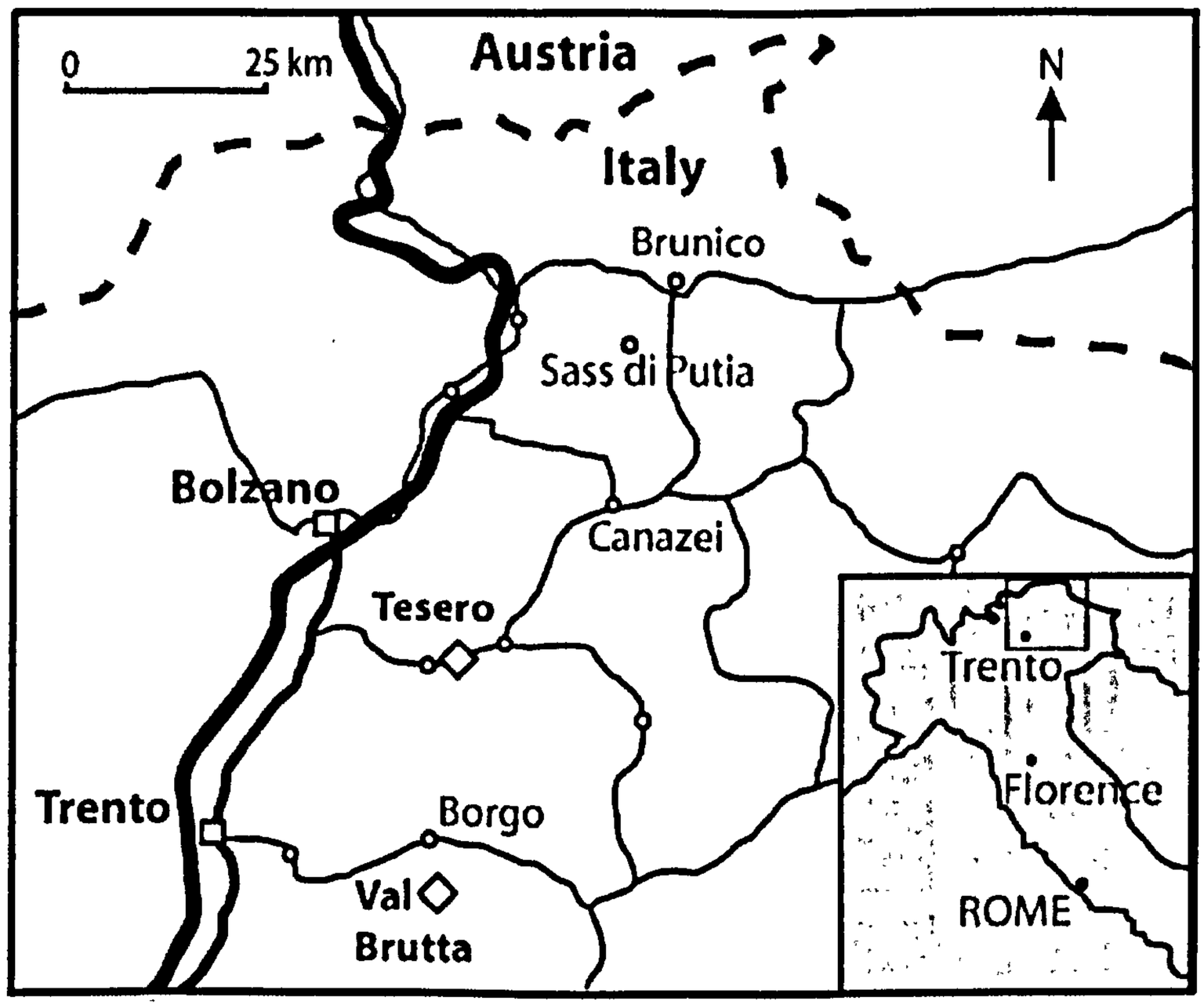


**Figure 6.1 Map of the South Tyrol region of Northern Italy with the study localities (Val Brutta and Tesero) marked (diamonds).**

The lower Tesero Member comprises thickly bedded oolitic grainstones which were deposited in sub-tidal, low energy, ooid shoals (Broglio Loriga *et al.* 1983; Farabegoli *et al.* 2007). The studied brachiopod material at Val Brutta has been mainly collected from the fossiliferous 'transitional beds' of Posenato (2001) between the Bellerophon and Werfen formations, which correspond to the Bulla Member of Farabegoli *et al.* (2007) (Figure 6.2). These beds consist of 0.30-0.24m of fossil rich bioclastic packstones, which are overlain by the first oolitic grainstones of the basal Tesero Member of the Werfen Formation.

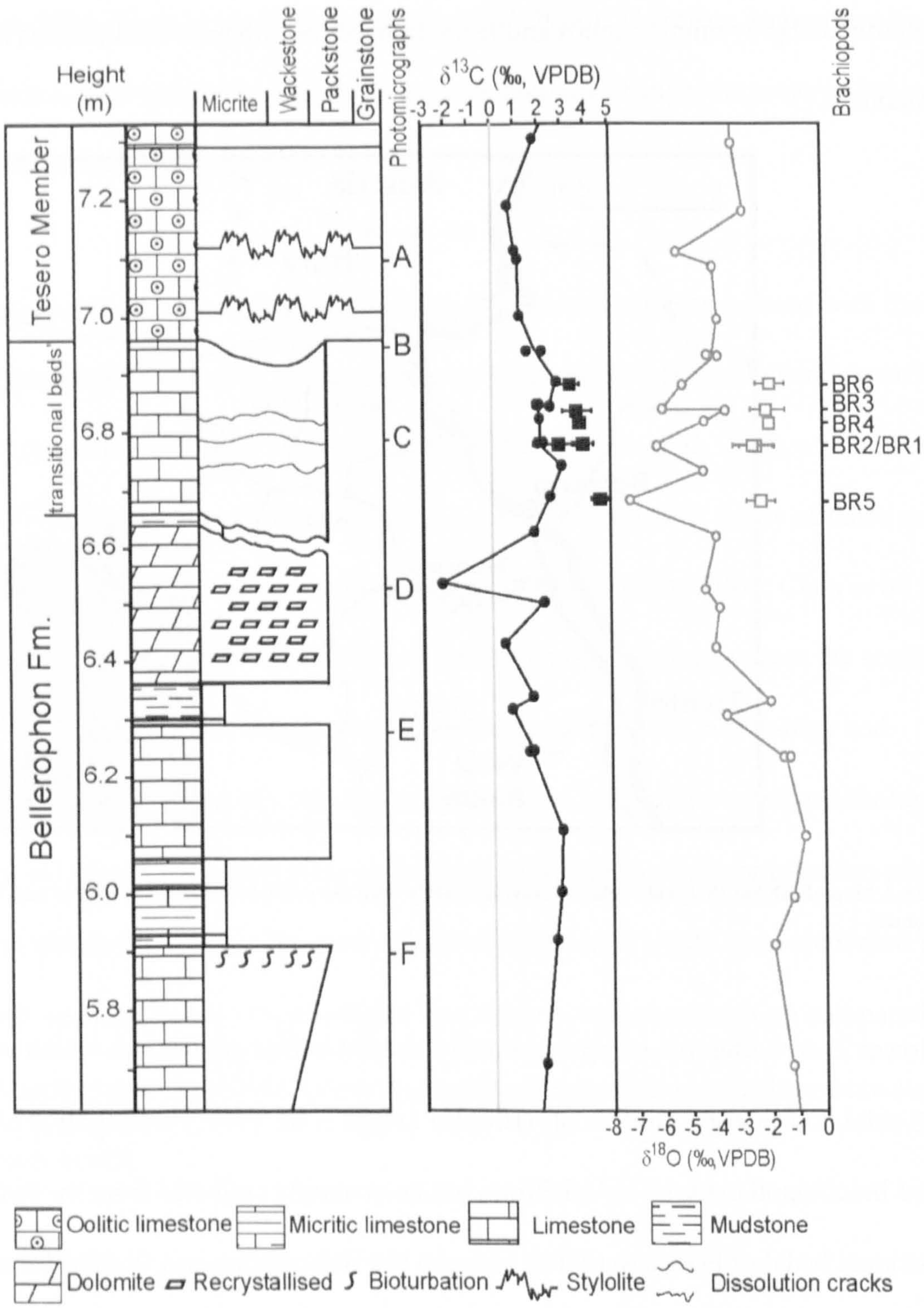


**Figure 6.2 Detail of the beds around the Bellerophon Formation, Tesero Member boundary and especially the 'transitional beds' (of Posenato 2001). The photomicrographs referred to in the figure are seen in Figure 6.4. Stable isotope results for both the brachiopods (square) and bulk rock (circles) and the brachiopods results have the relevant sample number next to them.**

The Tesero section has been previously described by Neri *et al.* (1986) and Broglio Loriga and Cassinis (1992). Only the uppermost Bellerophon Formation is exposed at Tesero and this consists of predominantly grey brown to whitish dolomites and shelly marls. Overlying this is a peloidal packstone which is taken to be the top of the Bellerophon Formation (Neri *et al.*

1986; Farabegoli *et al.* 2007). Above this point, as at Val Brutta, the peloidal packstone is overlain by the oolitic grainstones of the Tesero Member, interbedded with occasional ~10cm thick micritic mud bands. The brachiopod fossils were recovered from a micritic horizon 154cm above the base of Tesero Member.

Determining the precise position of the P/Tr boundary in the Southern Alps' sections has been problematic in the past, due to the absence of ammonoids in the lower Werfen Formation (e.g. Broglio Loriga *et al.* 1983). In marine Permian–Triassic sections conodonts are the preferred zone fossils of the P-Tr interval as the GSSP for the base of the Triassic is now defined as the first appearance datum of the conodont taxon *Hindeodus parvus* in Meishan, South China (Yin *et al.* 2001). However, due to the rarity of *H. parvus* in the Italian sections and the transgressive nature of the Tesero Member there is much debate about the position of the P/Tr boundary within the Werfen Formation. Wignall *et al.* (1996), placed the entire Tesero Member (= their Tesero Oolite Horizon) within the Changhsingian as they recorded *H. parvus* from the base of the Mazzin Member in the Tesero locality type section. In contrast, Farabegoli and Perri (1998, p. 302) placed the P/Tr boundary somewhat lower within the Tesero Member, following their analysis of the Bulla section. In southern Austria, *H. parvus* first appears at the top of Tesero Member in the Gartnerkofel-1 core, but at the base of the Tesero Member in the nearby outcrop sections (Holser *et al.* 1991).

Recently, Farabegoli *et al.* (2007) has correlated the Italian sections with the GSSP section in Meishan using a combination of facies interpretations and conodont biostratigraphy, and maintain that the P/Tr boundary lies within the Tesero Member. However, the extinction event occurs below the Bellerophon/Werfen Formation contact, with a further extinction horizon within the lower metres of the Tesero Member (Broglio Loriga and Cassinis 1992;

Cirilli *et al.* 1998; Rampino and Adler 1998). The brachiopods analysed in this study from Val Brutta derive from the Late Permian, just prior to the main local extinction event. The brachiopods recovered from the section at Tesero are from the Tesero Member, above the extinction horizon but below the first occurrence datum of *H. parvus* (Chen *et al.* 2006; Farabegoli *et al.* 2007).

## 6.3 Results – bulk rock stable isotopes

Bulk rock stable isotope analysis was undertaken at Val Brutta to pinpoint the isotope anomaly at that locality and to compare it to other Italian and global sections, and to the brachiopod values from the same locality (see Appendix A4.2 for results table).

At Val Brutta the $\delta^{13}C$ and $\delta^{18}O$ bulk rock values record a negative excursion which starts in the uppermost beds of the Bellerophon Formation (63m) (Figure 6.3). The $\delta^{18}O$ data record a negative excursion of –3.28‰ between 63m and 64m in the section. The $\delta^{18}O$ continue to record a negative trend of –1.58‰ up through the Tesero Member to the top of the section. The $\delta^{13}C$ data are more complicated. Coincident with the $\delta^{18}O$ excursion there is a $\delta^{13}C$ excursion of –2.04‰. Then at 65.6m there is an even greater excursion of –4.31‰, although this is only constrained by one analysis. By 67.6m the $\delta^{13}C$ values have returned to pre-excursion levels before showing a gradual negative shift of –2.58‰ into the Tesero Member and to the top of the section.

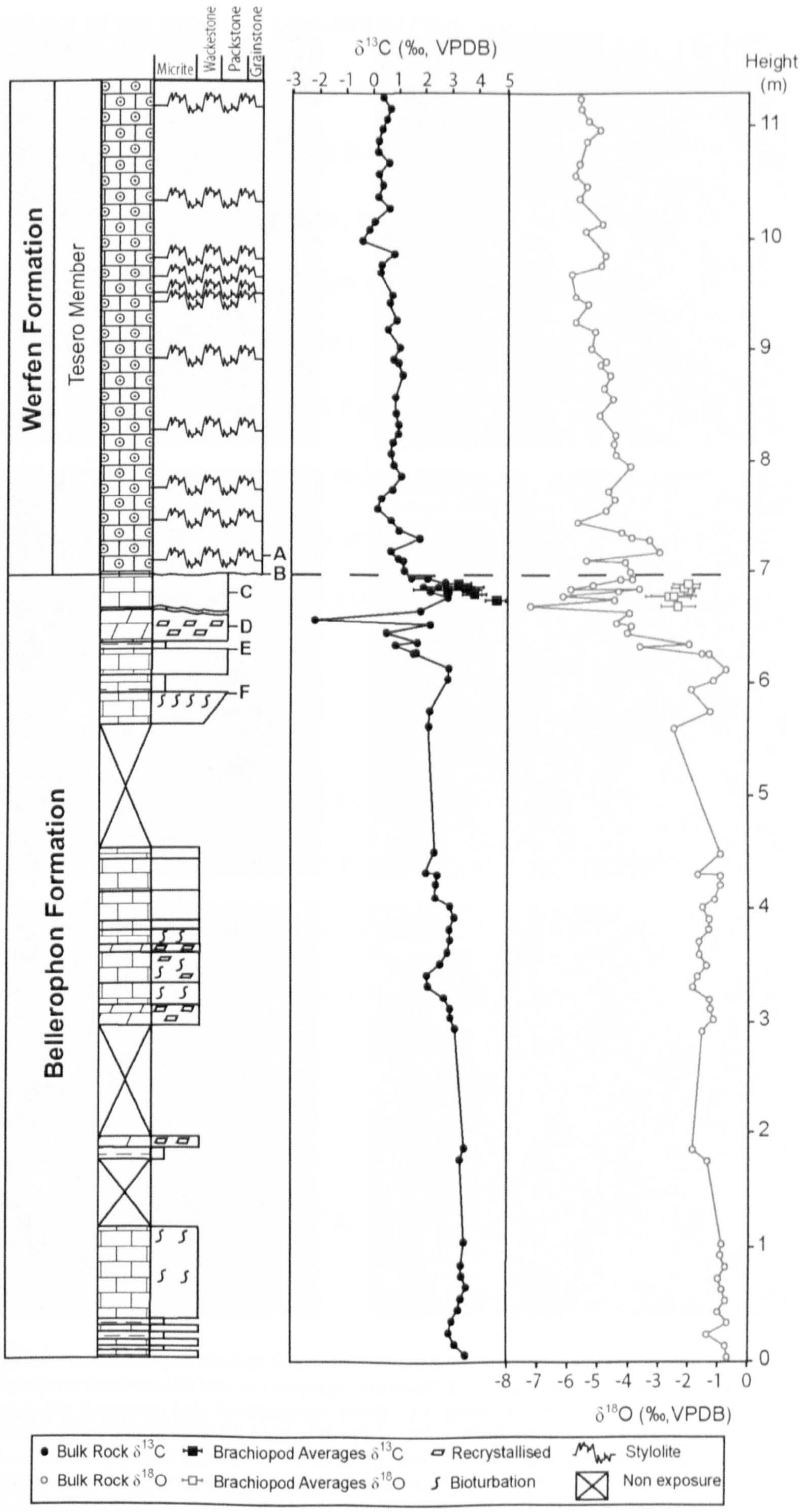


**Figure 6.3 Stable isotope results for both the brachiopods (square) and bulk rock (circles) through the section at Val Brutta plotted against lithology. The Bellerophon Formation consists of recrystallised and bioturbated wackestones inter bedded with micrite and the Tesero Member consists of stylolite-rich oolitic grainstones. The letters (A-F) refer to the photomicrographs in Figure 6.4.**

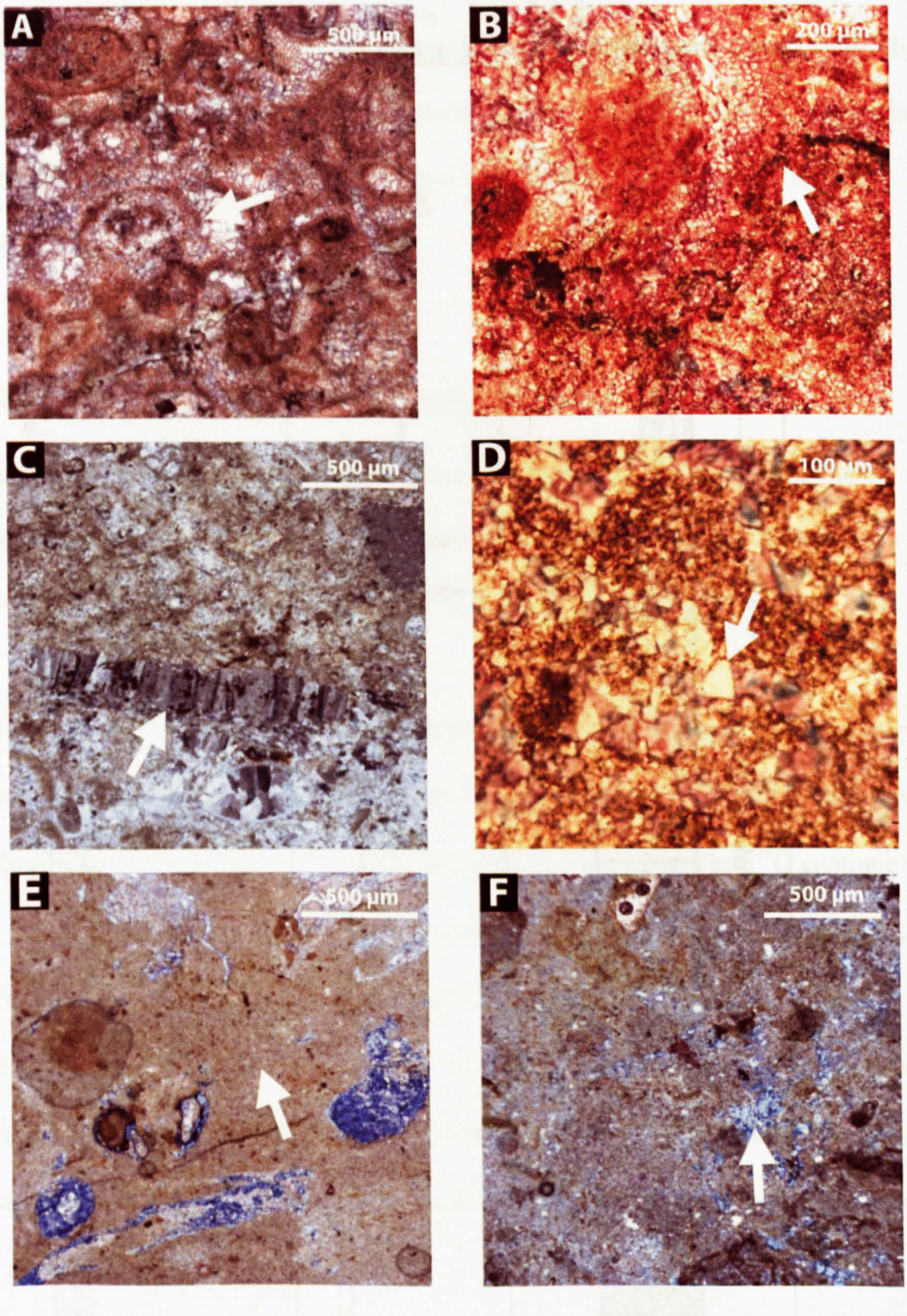


**Figure 6.4 The photomicrographs represent the different lithologies and correspond to the stratigraphic heights on the section log seen in Figure 6.2 and Figure 6.3. Photomicrographs (A) and (B) are both recrystallised oolitic grainstones from the base of the Tesero Member; (A) shows recrystallised ooid (arrowed) (B) shows a stylolite (arrowed). Photomicrograph (C) is from the 'transitional beds' where the brachiopod fossils were sampled. The arrow points to a fragment of brachiopod. Photomicrograph (D) is a strongly dolomitised horizon, showing large dolomite crystals (arrowed). This bed is over 75% dolomite by area. Photomicrographs (E) and (F) are less recrystallised packstones from the Bellerophon Formation; (E) has large area of unaltered micrite shown by arrow. The arrowed section of (F) points to an area of small dolomite crystals (12% by area) which are present in both (E) and (F). Note changes in scale in photomicrographs (B) and (D).**

There is evidence of variation in the amount of recrystallisation in the section. Petrographic analysis of the beds through the isotope excursions (Figure 6.4 and Figure 6.3) has revealed recrystallisation and dolomitisation in all the coarser-grained limestone samples (Figure 6.4 A and D). The amount of dolomitisation is, however, more variable throughout this part of the section. Within the Bellerophon Formation the wackestone beds that contain the excursions vary in the amount of dolomite rhomb by 12% – 75% by area of the slide (Photomicrograph E in Figure 6.4, and Photomicrograph D in Figure 6.4). There is a coincidence between the variation in amount of dolomite rhombs and the isotope signal. Petrographic analysis of bed that contains the negative $\delta^{13}C$ excursion at 65.6m above the base of the section shows it to contain 75% dolomite crystals (Figure 6.4D), while the bed directly beneath it only contains 12% (Figure 6.4E).

In the overlying Tesero Member there is an increase in the volume of dolomite crystals up to 19% (Figure 6.4b) and an increase in the level of recrystallisation (Figure 6.4b). Elemental analysis of bulk rock samples shows relative enrichment in Mn (178ppm) and Fe (945ppm) and depletion of Sr (330 ppm) with respect to the brachiopod samples from the same levels (Table 6.1).

## 6.4 Results – brachiopods stable isotopes

Six articulate brachiopods were analysed from Val Brutta including representatives of *Janiceps* and *Comelicania* and one from Tesero (*Crurithyris*). Brachiopods were recovered from just below the Bellerophon/Werfen Formation boundary (Figure 6.2) and from the Tesero Member just below the first appearance datum (FAD) of *H. parvus* as described by Farabegoli *et al.* (2007) (Figure 6.5). All of the brachiopods are more isotopically positive

than the equivalent bulk rock values at both localities (see Chapter 2 for preparation methods and Appendix A4.1 for results and Appendix A4.4 for the drill sites).

The brachiopod samples from Val Brutta $\delta^{18}O$ values range between –2.66‰ and –2.03‰ and $\delta^{13}C$ values between 4.65‰ and 2.83‰. This is quite different from the bulk isotope measurements from the same horizon which have average $\delta^{18}O$ values of –6.01‰ and $\delta^{13}C$ values of 2.39‰ (Figure 6.3). The brachiopod recovered from the Tesero section similarly has $\delta^{18}O$ values between –5.93‰ and –3.74‰ and $\delta^{13}C$ values between 1.13‰ and 1.74‰ compared to bulk rock values of $\delta^{18}O$ values of –6.6‰ and $\delta^{13}C$ values of 1.0‰ for the same horizon (Figure 6.5 and Appendix A4.1).

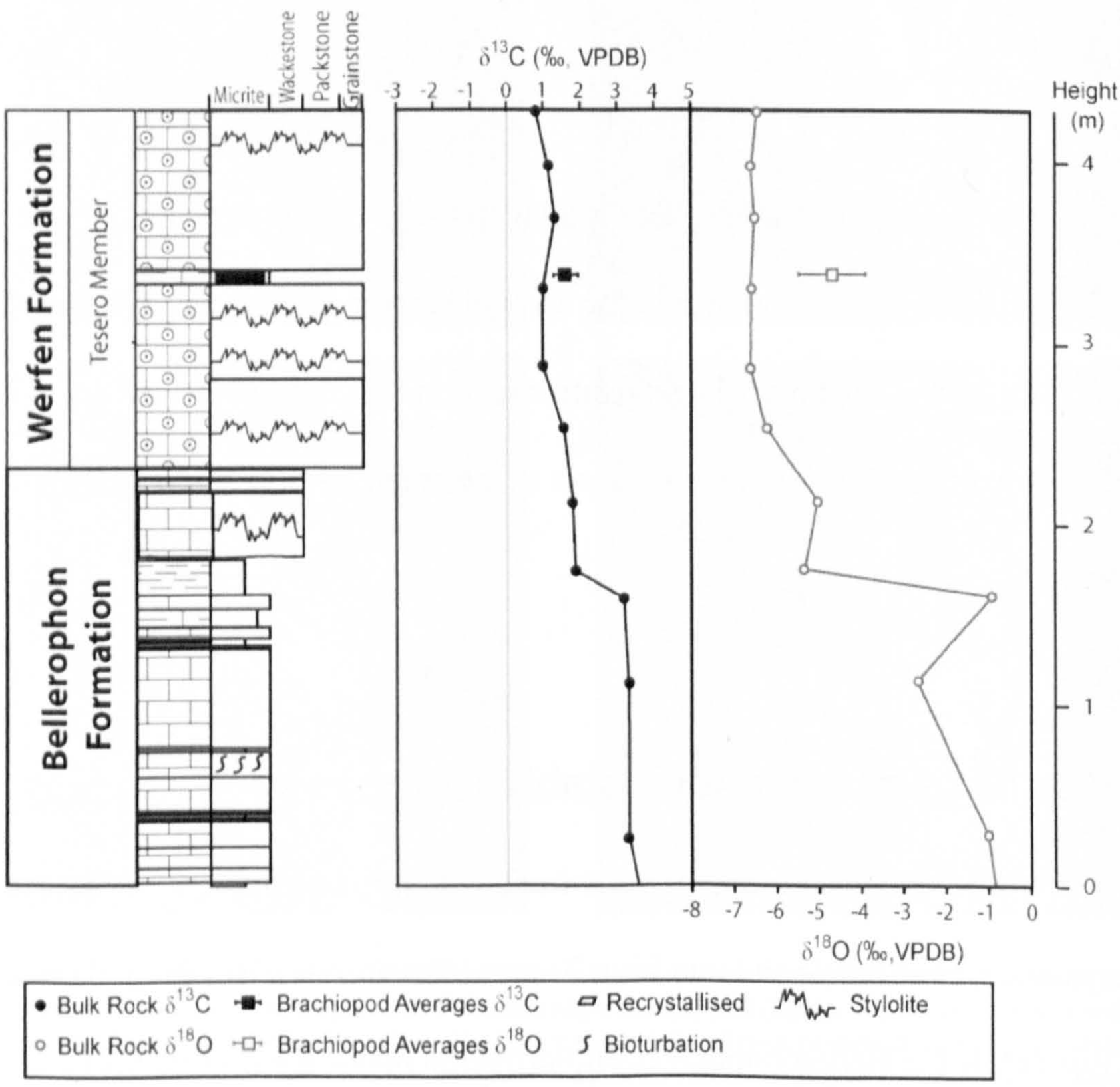


**Figure 6.5 Stable isotope results for both the brachiopods (square) and bulk rock (circles) through the section at Tesero plotted against lithology (bulk rock values from Magaritz *et al.* 1988). The Bellerophon Formation consists of recrystallised and bioturbated wackestones interbedded with micrite and the Tesero Member consists of stylolite-rich oolitic grainstones.**

### 6.4.1 Alteration of brachiopod shells

When using brachiopods to investigate temperature it is essential that the fossil material is not altered (Mii *et al.* 1997; Veizer *et al.* 1999; Korte *et al.* 2005a, b van Geldern *et al.* 2006; Batt *et al.* 2007). When the brachiopods were examined under a petrographic microscope it was possible to discern internal layers (Figure 6.6), analogous to the fibrous secondary layer and prismatic tertiary layer seen in modern brachiopods (Parkinson *et al.* 2005). In some samples a primary layer is also partially preserved, but in most cases this appears to have been removed by abrasion prior to burial (Figure 6.6). In the case of the brachiopod recovered from Tesero (TS1) it appears that both the primary and secondary layers had been removed (Figure 6.7), either by abrasion or prior to burial or in the processing of the fossil (see Chapter 2). All the brachiopods were subjected to Cathodoluminescence (CL) analysis (Appendix A4.1

All the shells are were primarily non-luminescent although all showed some areas of luminescence, which in most cases were concentrated around the umbo and the fibrous layer of the shell (Figure 6.6, Appendix A4.1). One of the 6 shells recovered from Val Brutta one (VB3) extensive luminescent areas to the extent it was impossible to isolate the non-luminescent areas for isotope analysis. Only the non-luminescent (NL, see Chapter 2 for full definitions of the CL classifications) areas were selected for sampling and isotopic analysis to avoid any diagenetic alteration affecting the primary signal. All the shells were significantly less luminescent than altered fossils (mostly foraminifera) in the surrounding matrix.

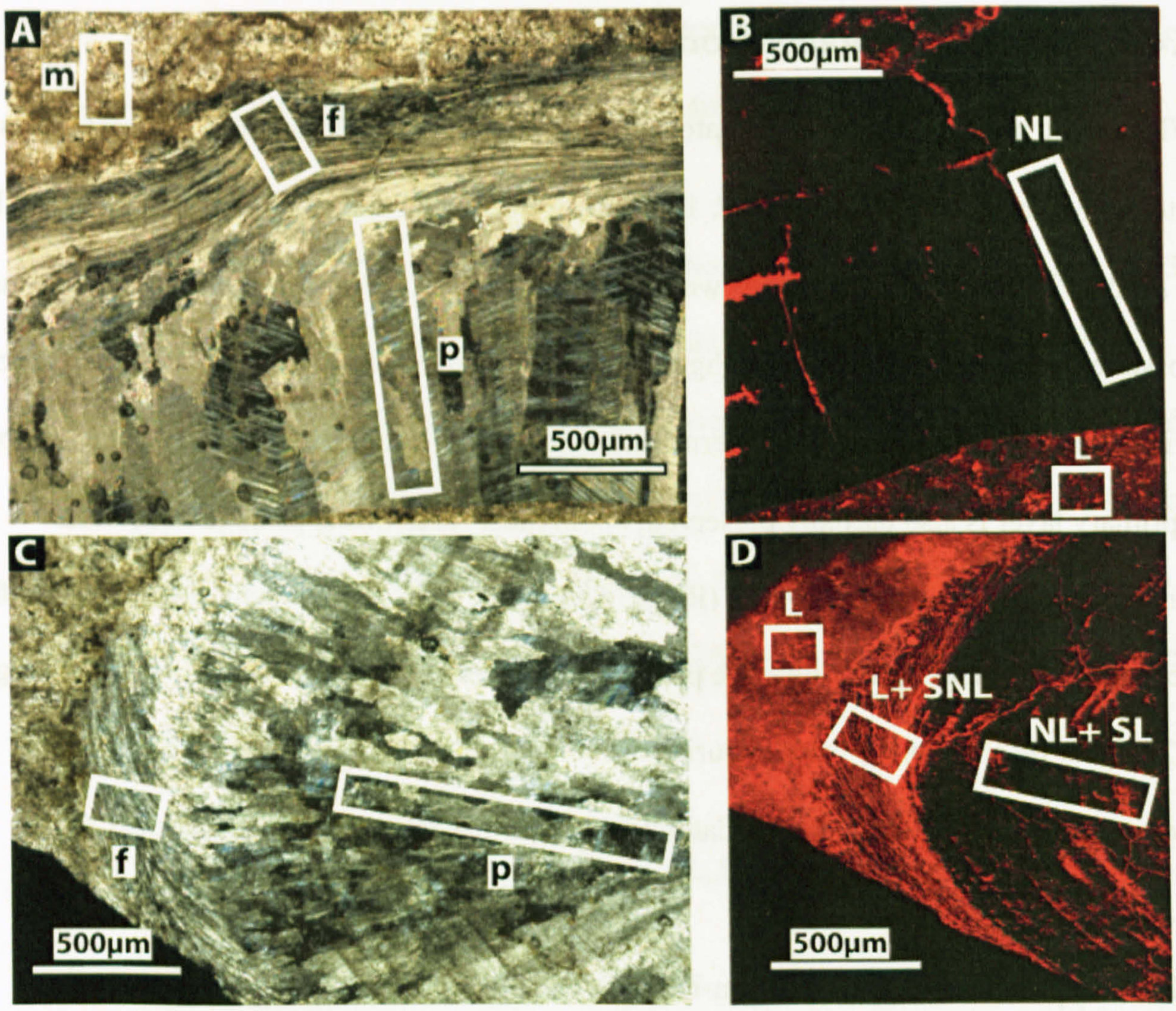


**Figure 6.6 Petrographic and cathodoluminescent images of the brachiopod shells VB2 (A and B) and VB6 (C and D),(A) shows the distinct fibrous (f) and prismatic (p) layers representing the secondary and tertiary shell layers and surrounding bulk rock (m), (B) is the same brachiopod under CL showing the non luminescent (NL) brachiopod shell and the luminescent (L) bulk rock, (C) shows the umbo region of a more altered brachiopod with both fibrous (f) and prismatic (m) layers, (D) is the same brachiopod with the fibrous layer luminesce with slight non luminescence (L+SNL) and the prismatic layer showing non luminescence with slight luminescence (NL+SL).**

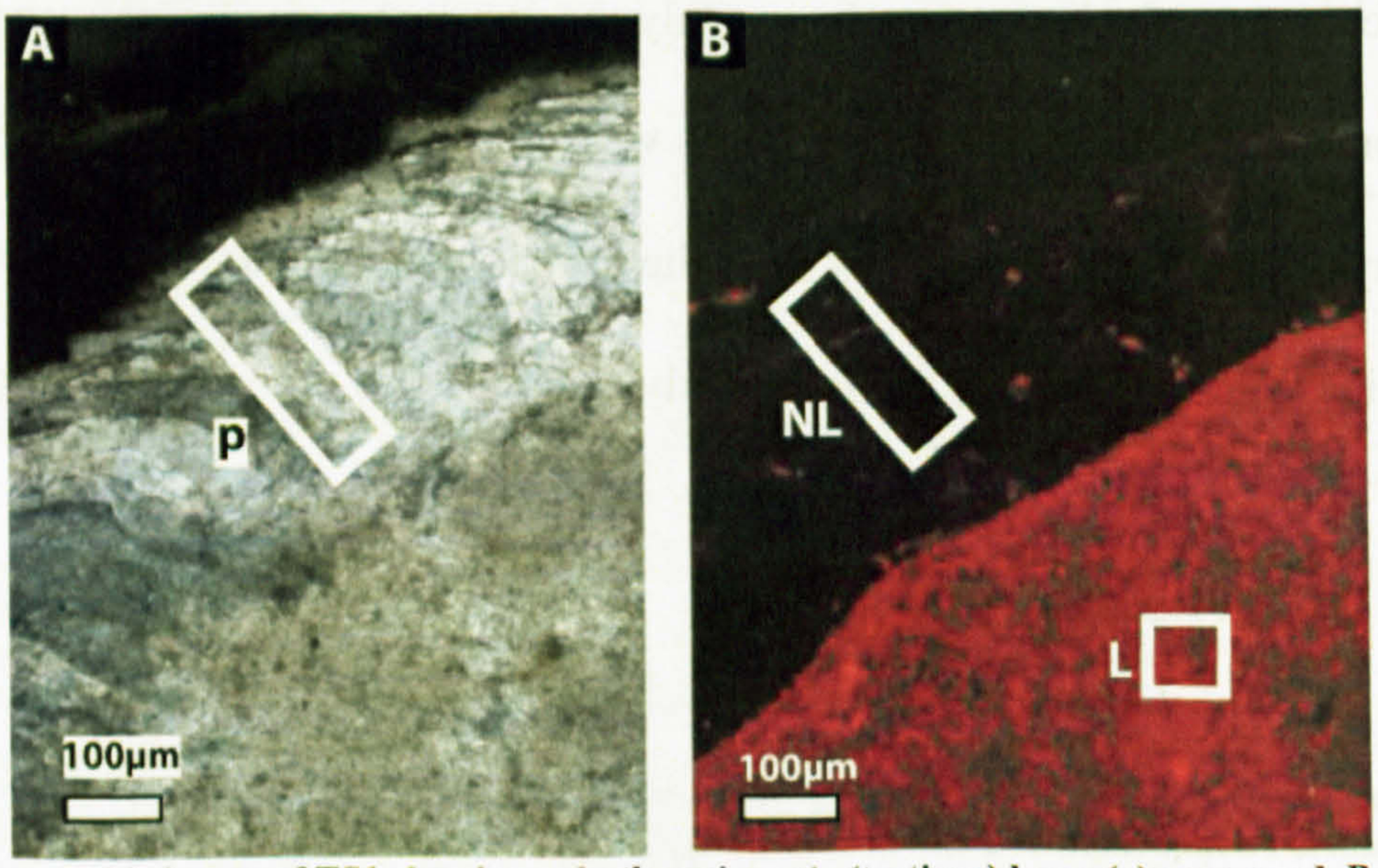


**Figure 6.7 A. Petrographic image of TS1 showing only the prismatic (tertiary) layer (p) preserved. B. A cathodoluminescent image of the same brachiopod showing this layer is luminescent (NL) while the bulk rock is luminescent (L). Image (B) was taken by Nikita Jacobsen (unpublished data).**

| | ppm | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Al** | **Fe** | **Mg** | **Mn** | **Na** | **S** | **Sr** |
| Modern brachiopods (Brand *et al.* 2003)[2] | | <140 | 600-17964 | <80 | | | 450 - 1928 |
| Criteria used by van Geldern *et al.*(2006) | | <400 | | <100 | | | >500 |
| Criteria used by Korte *et al.* (2005a) | | | | <250 | | | >400 |
| Criteria used by Mii *et al.* (1997) | 700 +/- 300 | 270 | 860 +/- 1180 | <190 | 1010 +/- 550 | 4150 +/- 1530 | 960 +/- 210 |

| Specimen name | Species | CL results[1] | Al | Fe | Mg | Mn | Na | S | Sr |
|---|---|---|---|---|---|---|---|---|---|
| VB1 | *Comelicania? sp.* | NL | 35 | 43 | 911 | 25 | 1358 | 2521 | 484 |
| VB1 | *Comelicania? sp.* | NL+SL | 73 | 28 | 654 | 10 | 1279 | 2351 | 481 |
| VB2 | *Janiceps aff.paracuta* | NL | 32 | 104 | 1318 | 23 | 1346 | 1863 | 495 |
| VB2 | *Janiceps aff.paracuta* | NL | 51 | 82 | 1500 | 30 | 1930 | 2189 | 535 |
| VB3 | *Comelicania? sp* | L+SNL | 47 | 26 | 1068 | 8 | 1121 | 1639 | 461 |
| VB3 | *Comelicania? sp* | NL+SL | 36 | 157 | 1356 | 56 | 1242 | 1970 | 473 |
| VB4 | *Comelicania? sp.* | NL+SL | 69 | 115 | 1939 | 4 | 476 | 2442 | 542 |
| VB5 | *Janiceps sp.* | NL+SL | 37 | 64 | 919 | 21 | 878 | 1493 | 440 |
| VB6 | *Comelicania sp.* | NL | 77 | 84 | 1525 | 24 | 1128 | 1792 | 410 |
| **Bulk rock** | | **L** | **349** | **945** | **3750** | **178** | **734** | **852** | **330** |

**Table 6.1 Trace elemental analysis and cathodoluminescence results for the brachiopod fossils and bulk rock, compared against published ranges for modern and unaltered fossil brachiopods. NL – nonluminescent, NL +SL – nonluminescent with slight luminescence (>50% NL by area), L+SNL – luminescent with slight non luminescence (<50% NL by area), L – luminescent. [2] The modern brachiopods described by Brand *et al.* (2003) are from shallow water, mid-low latitudes. TS1 could not be analysed using this method as there was not enough sample to produce an accurate analysis (see Chapter 2) The bold type face highlights those analyses that fall outside the range of modern/unaltered brachiopods.**

The trace element results for the brachiopods show a range of Mn values from 8–56 ppm, with the NL values clustering around a range of 4–56ppm. Fe has a range of between 26–157 ppm, again with the less-luminescent samples clustering closer to the lower values (Table 6.1). These fall within the ranges suggested for unaltered brachiopods (Brand *et al.* 2003; van Geldern *et al.* 2006; Korte *et al.* 2005a; Mii *et al.* 1997). Of all the specimens there is one (VB3) with Fe values above the limit advised by Brand *et al.* (2003) but below that suggested by van Geldern *et al.* (2006). Similarly there are two specimens (VB5 and VB6) with Sr values below that recommended by Brand *et al.* (2003), although still within that suggested by Korte *et al.* (2005a) and van Geldern *et al.* (2006). Both these samples have areas of L+SNL, NL+SL and NL (see Appendix A4.1) and these slightly negative Sr measurements represent both luminescent and non-luminescent areas.

Within individual brachiopods there is a $\delta^{18}O$ variation of between –4.30‰ and –2.33‰ from the outer to the inner part of the shell (Figure 6.8, and Appendix A4.3). This is only recorded in shells which show complete preservation of the fibrous and prismatic layers (VB2 and VB6). Within unaltered, non-luminescent shells the more negative isotope values are associated with the fibrous layers, a situation also observed in modern terebratulid brachiopods (Auclair *et al.* 2003).

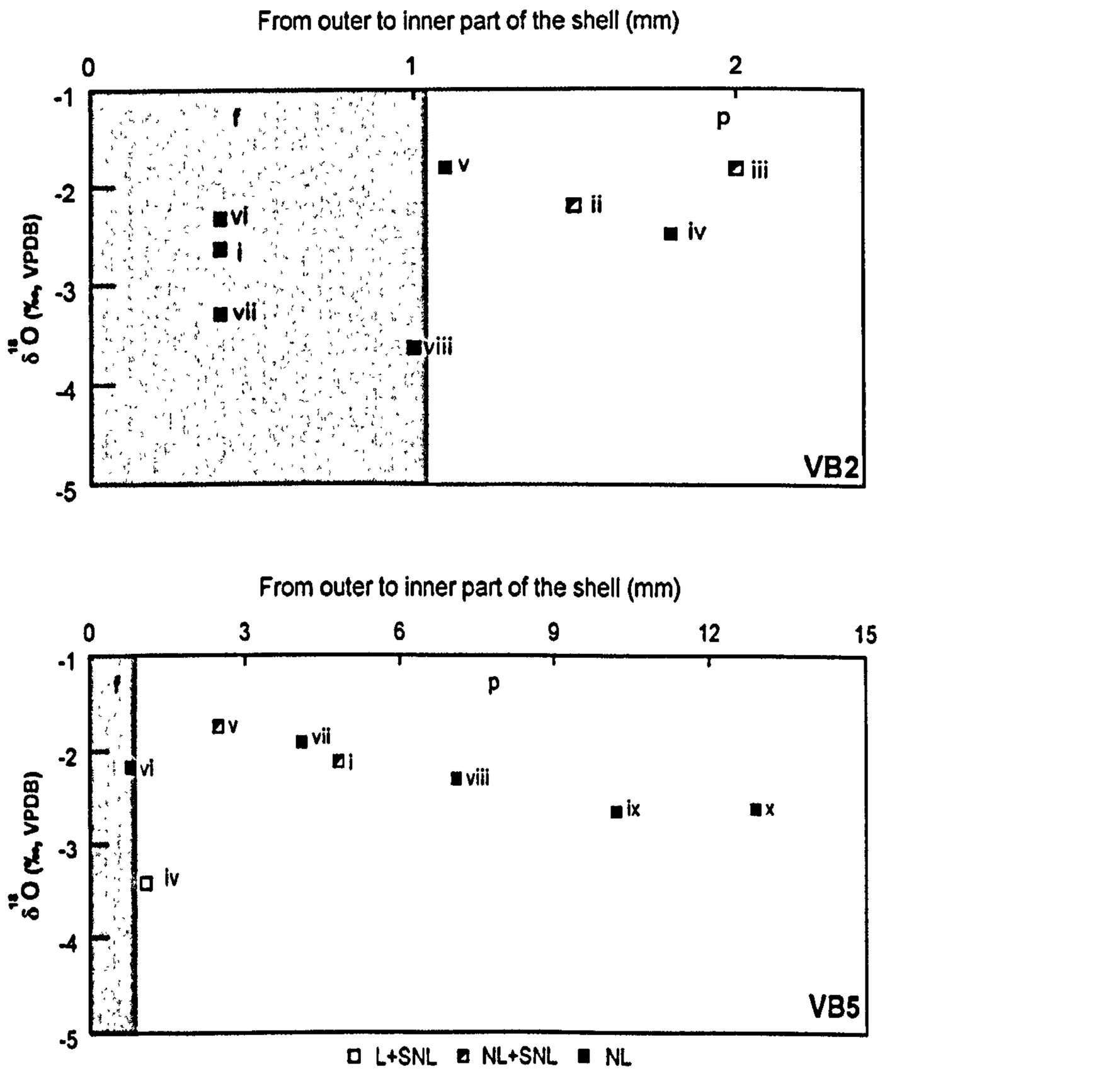


**Figure 6.8 Variation in $\delta^{18}O$ ratios across the fibrous (f, shaded) and prismatic layers (p) within brachiopod fossils VB2 and VB5. The amount of luminescence in each isotope sample is also shown. Note change in scale; see Appendix A1 for positions of isotope samples.**

## 6.5 Discussion

The $\delta^{13}C$ and $\delta^{18}O$ bulk rock excursions recorded at Tesero and Val Brutta have been observed elsewhere in Italy (Magaritz and Holser 1991; Broglio Loriga and Cassinis 1992;

Cirilli *et al.* 1998: Sephton *et al.* 2002; Newton *et al.* 2004; Horacek *et al.* 2007) (Figure 6.9) and globally (Baud *et al.* 1996; Jin *et al.* 2000; Musashi *et al.* 2001; Twitchett *et al.* 2001; Krystyn *et al.* 2003; Payne *et al.* 2004; Krull *et al.* 2004; Algeo *et al.* 2007) suggesting that the excursion is a global event rather than just a local diagenetic artefact (Figure 6.9). The high resolution sampling of the section at Val Brutta has revealed that in the Italian Dolomites the $\delta^{13}C$ and $\delta^{18}O$ excursions are synchronous and occur before the boundary between the Bellerophon and Werfen formation and below the FAD of *H. parvus* in Tesero (Figure 6.2, Figure 6.3)

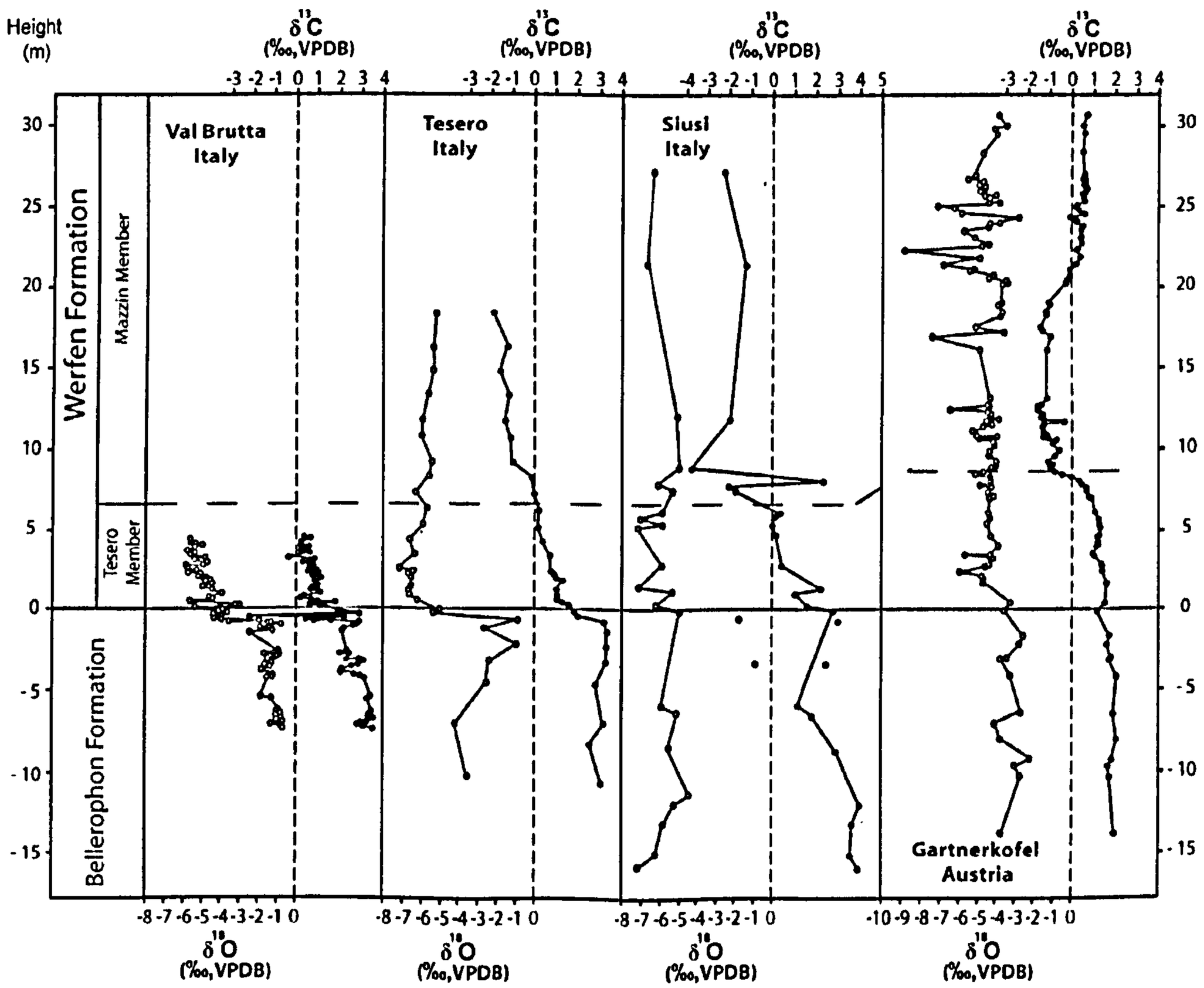


**Figure 6.9 Carbonate isotope variations across the Permian /Triassic boundary in Italy and Austria. The grey open circles are the bulk rock $\delta^{18}O$ values and the filled black circles are the $\delta^{13}C$ values The Val Brutta curve is from this study. Data from Tesero is reproduced from Broglio Loriga and Cassinis (1992), the Siusi section from Newton *et al.* (2004) and the Garnerkofel section from Magaritz and Holser (1991). The two points excluded from both Siusi curves are heavily dolomitised (Newton *et al.* 2004).**

It is generally assumed by many authors (Newton *et al.* 2004; Haas *et al.* 2006; Horacek *et al.* 2007; Algeo *et al.* 2007) that $\delta^{13}C$ values and excursions are unaffected by diagenesis as the carbon reservoir of the rock far outweighs the amount of carbon in a diagenetic fluid, and that alteration is likely to produce a positive excursion rather than a negative (Marshall 1992; Horacek *et al.* 2007). It has been noted that intense alteration of marine carbonates in the presence of meteoric water may lead to lower $\delta^{13}C$ values compared to unaltered carbonate (Haas *et al.* 2006).

Although the Tesero Member is intensely recrystallised there is no evidence of isopachous fringing cements (Figure 6.10) which would be indicative of the influence of meteoric waters (Tucker 2001). Equally those pore-filling cements that have not been completely recrystallised appear have been originally micritic muds which would have limited the ability of any potential meteoric fluids to penetrate the oolite.

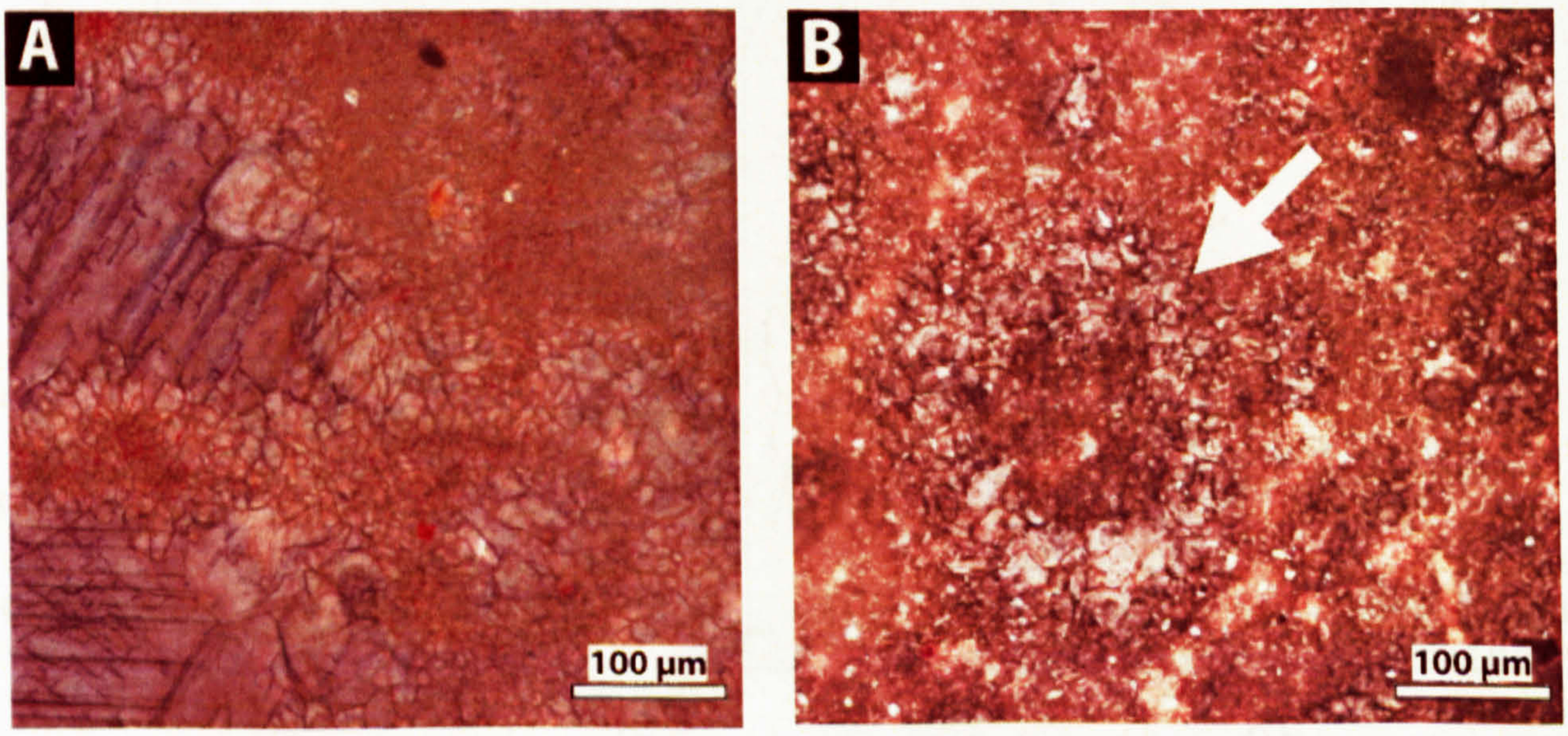


**Figure 6.10 Recrystallisation textures in the Tesero Member. (A) shows a completely recrystallised bed with euhedral crystals filling in the space between ooids. (B) shows the outline of a recrystallised ooid (arrowed). (both slides are from the same stratigraphic height as photomicrograph A in Figure 6.2).**

The petrographic data from the interval around the Bellerophon Formation-Tesero Member boundary at Val Brutta (Figure 6.4) shows that there is alteration present in all the coarse-

grained lithologies; although the amount of dolomite present in different beds varies from 12% to 75% by area. There is one incidence of a large negative point excursion in the $\delta^{13}C$ values of 4‰, 40cm below the Tesero Member (Figure 6.3), which coincides with a level dominated by large recrystallised rhombs (Figure 6.4d) which suggests that recrystallisation may be responsible for some of the changes in the $\delta^{13}C$ values. However, it is very hard to explain a negative excursion in terms of extensive dolomitisation as this produces positive rather than negative excursions (cf. Horacek *et al.* 2007; Algeo *et al.* 2007).

The potential influencing factors controlling the $\delta^{18}O$ values are much more various. Spötl *et al.* (1992) suggest that the $\delta^{18}O$ composition of the bulk rock can be affected by increases in water temperature; sulphate reduction; diagenetic recrystallisation under the influence of higher temperatures; or diagenetic re-equilibrium with fluids depleted in $^{18}O$. It has been suggested that there is a sulphur reducing event associated with the Bellerophon/Tesero Oolite transition in the Italian Dolomites (Newton *et al.* 2004). Equally, the marked increase in recrystallisation in the Tesero Member may suggest the more porous oolites have been more affected by diagenetic fluids than the micrites below them, producing a negative excursion. However, the fact that the $\delta^{13}C$ and $\delta^{18}O$ excursions have been observed globally (cf. Kidder and Worsley 2004; Corsetti *et al.* 2005; Erwin 2006; Gorjan *et al.* 2008) indicate that even though the bulk rock is recrystallised the isotope values are still representative of the primary trends, if not the actual primary isotopic values. Equally, it has been observed that some limestones that have been metamorphosed at temperatures well in excess of 500°C can still preserve their original isotope composition or only partially re-equilibrate to diagenetic/metamorphic fluids (Melezhik *et al.* 2005).

In contrast to the bulk rock record, when all lines of evidence are considered, it seems very probable that all brachiopod shells analysed in this study contain large areas that are unaffected by diagenesis or dolomitisation and at least the non-luminescent areas retain a primary isotope signal. All shells show both the fibrous and prismatic layers (Figure 6.6; Figure 6.7) identical to the secondary and tertiary layers observed in modern brachiopods (cf. Parkinson *et al.* 2005). The trace element results show that all brachiopods have ranges similar to modern and unaltered brachiopods (Table 6.1) Finally the CL analysis (Figure 6.6) shows that although the matrix shows strong luminescence there was sufficient parts of all bar brachiopod VB3 and that did not luminesce to be isotopically sampled (Figure 6.6; Figure 6.7; Appendix 4.1) again indicating that the majority of the brachiopod fossils had not affected by recrystallisation. Only the NL areas of these shells were used in the palaeotemperature and $\delta^{13}C_a$ estimates. Finally, the $\delta^{13}C$ of the non-luminescent parts of the brachiopods fall within the ranges for unaltered samples as suggested by Korte *et al.* (2005a).

### *6.5.1 Disparity between bulk rock and brachiopod values*

In other Permian localities it has been shown that while the bulk rock results show an isotope excursion the isotopic values from unaltered brachiopods from the same locality show no such excursion suggesting that the excursion is purely a diagenetic artefact rather than relating to primary processes (e.g. Mii *et al.* 1997).

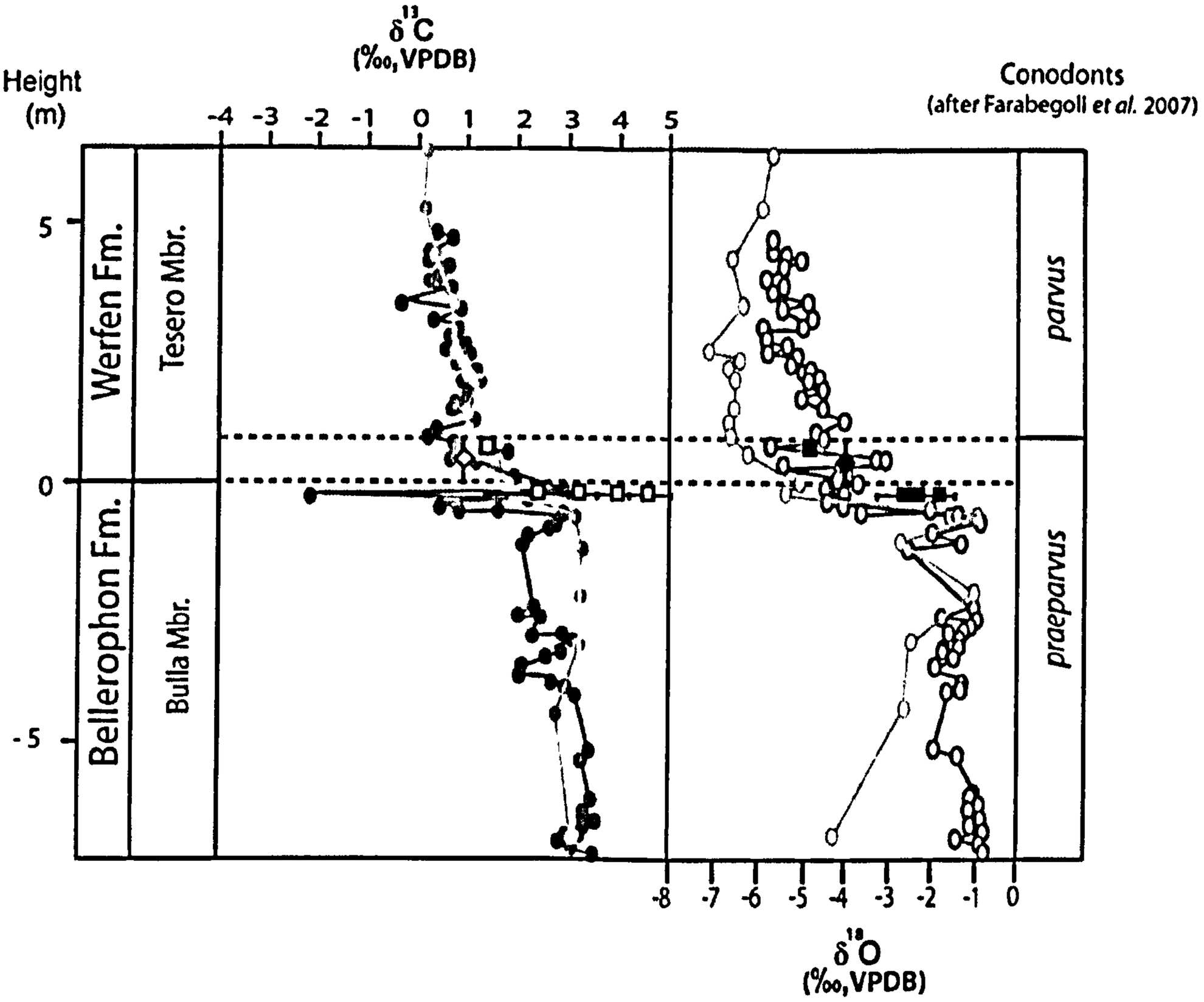


**Figure 6.11 Brachiopod isotopic composition compared to bulk rock values from the Italian Dolomites. The squares are the un-altered isotopic values from brachiopods from this study, the diamonds are brachiopod values from Korte *et al.* (2005a) from Sass de Putia. The dark grey circles are the bulk rock values from Val Brutta while the light grey circles are from the Tesero section from Magaritz *et al.* (1988). The sections are correlated using the correlations of Farabegoli *et al.* (2007).**

In both sections (Val Brutta and Tesero) the brachiopods have an isotopic value which is more positive than that of the bulk rock signal (Figure 6.3; Figure 6.5). The petrographic, CL and trace element evidence seem to indicate the brachiopods are not affected by the recrystallisation event. This may suggest the isotope values of the bulk rock have been altered by the recrystallisation event which has fractionated them relative to the unaltered brachiopods. This is plausible as it is known that early diagenetic stabilisation produces $^{12}C$ enrichment (Batt *et al.* 2007) which could produce a negative shift in values bulk rock. However, both the carbon and oxygen isotope values show a coincident excursion with P/Tr boundary sections worldwide (cf. Baud *et al.* 1989; Retallack and Krull 2006).

A comparison of the bulk rock values from Val Brutta and Tesero with brachiopods from Val Brutta, Tesero (both this study) and unaltered brachiopods from Sass di Putia (Korte *et al.* 2005a) reveal that although the brachiopods have a more positive isotopic value they show the same trend as the bulk rock values (Figure 6.11).

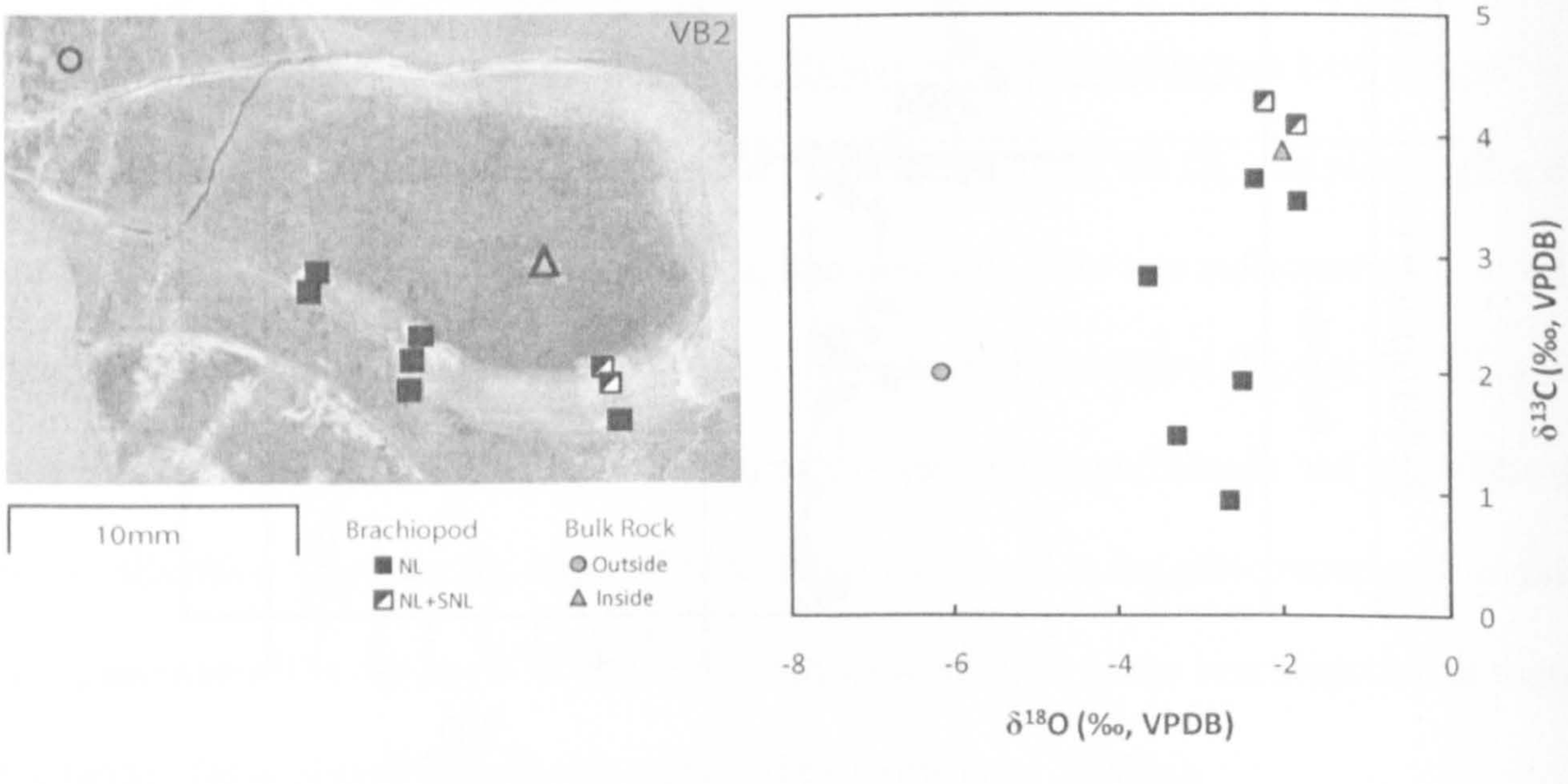


**Figure 6.12 Comparison of the isotopic composition of micritic mud from within an articulated brachiopod and outside it with the isotopic.**

Although all the brachiopods are isotopically more positive than the bulk rock that surrounds the fossils (Figure 6.2, Figure 6.3, Figure 6.5) in one of the articulated brachiopods (VB2), the micritic mudstone sampled from within between the two valves has a similar isotopic composition as the brachiopod shell while the micrite sampled from outside the shell is isotopically more negative (Figure 6.12). This suggests that the micritic muds outside the protection of the brachiopod shell have been slightly altered compared to the micrite protected by the shell. However, slight isotopic depletion seen in the bulk rock signal of micrite from outside the brachiopod, possibly caused by the recrystallisation event, has not been enough to completely overprint the pre-diagenetic/metamorphic signal and thus explaining why the isotopic trends in the brachiopod and bulk rock signal should mirror each other and that

although the bulk rock is still recording primary trends the absolute values are no longer representative of absolute value of palaeo-seawater.

### *6.5.2 Palaeotemperature estimates*

Assuming the isotope ratios of the unaltered brachiopod shells reflect the isotopic composition of palaeo-seawater they can be used to track changes in palaeotemperature (e.g. Lavoie 1993; Mii and Grossman 1994; Grossman *et al.* 1996; Mii *et al.* 1997; Veizer *et al.* 1999; Bojar *et al.* 2004; Korte *et al.* 2005a and 2005b; van Geldern *et al.* 2006). Palaeotemperatures were calculated using the relationship between shell $\delta^{18}O$ calcite precipitation temperature as given by Anderson and Arthur (1983) and modified by Auclair *et al.* (2003) (Equation 6.1) and Parkinson *et al.* (2005) (Equation 6.2).

$$t\,(°C) = 16.9 - 4.14\,(\delta^{18}O_{calcite} - \delta^{18}O_{seawater}) + 0.13(\delta^{18}O_{Calcite} - \delta^{18}O_{seawater})^2 \quad (6.1)$$

$$t\,(°C) = 16.0 - 4.14\,(\delta^{18}O_{calcite} - \delta^{18}O_{seawater}) + 0.13(\delta^{18}O_{calcite} - \delta^{18}O_{seawater})^2 \quad (6.2)$$

$\delta^{18}O_{carb}$ is the oxygen isotope composition of the brachiopod shell calcite with respect to VPDB. $\delta^{18}O_{seawater}$ is the oxygen isotope composition of seawater relative to VSMOW (Standard Mean Ocean Water).

The $\delta^{18}O$ composition of the secondary and tertiary layers of modern Terebratulida form in equilibrium with seawater and thus can be used to estimate palaeotemperature (Parkinson *et al.* 2005). Only the $\delta^{18}O$ data from unaltered, nonluminescent areas of these layers were used to determine palaeotemperature values in this study (see Appendix A4.2). Finally, before a palaeotemperature can be calculated the $\delta^{18}O$ of the seawater from which the brachiopod

shells precipitated must be estimated. Korte *et al.* (2005a, 2005b) assume a $\delta^{18}O_{seawater}$ value of 0‰ for Tethyan tropical open marine basins and large intra-platformal basins in both the Permian and the Triassic.

Ocean salinity also has a direct effect on the $\delta^{18}O$ of seawater (Parkinson *et al.* 2005 and references therein). The rocks at Val Brutta and Tesero were deposited on a tropical subtidal shallow water carbonate ramp (Ghetti and Neri 1983). If surface water salinity is assumed to be 36‰, as seen in modern tropical oceans (Millero 2005), then the $\delta^{18}O_{seawater}$ would be 1.0‰ (cf. Parkinson *et al.* 2005). This also agrees with the lower estimate for the value of Hay *et al.* (2006) for the Early Triassic, ice free world of 37.32‰ which equal a salinity of 1.66‰ (method after Parkinson *et al.* 2005). Finally, there is no evidence of permanent ice sheets in the Late Permian and Early Triassic (Chumkov and Zharkov 2003; Kidder and Woresley 2004). In such an ice–free world it has been argued that $\delta^{18}O_{seawater}$ would be as low as -1‰ (Joachimski *et al.* 2006; Grossmann *et al.* 2008).

Using these three different estimates of $\delta^{18}O_{seawater}$, 0‰, 1‰ and –1‰ produces three different temperature estimates. Assuming a $\delta^{18}O_{seawater}$ of 0‰ and using the equation 6.1 produces average palaeotemperature estimate of 28°C (±3, 1σ std) across all the brachiopods at Val Brutta(see Table 6.2). The brachiopod from Tesero produces an average palaeotemperature estimate of 36°C (±2, 1σ std) (Table 6.2). Equation 6.2 produces an estimate of 27°C (±3, 1σ std) at Val Brutta and 35°C (±2, 1σ std) at Tesero, suggesting an 8°C rise in temperature across the excursion event. Assuming a $\delta^{18}O_{seawater}$ of 1‰ increases the temperature estimates by 5°C although the increase in temperature across the excursion event is still 8°C (Table 6.2). However, a using $\delta^{18}O_{seawater}$ of –1‰ produces estimates of 24°C (±3,

1σ std) at Val Brutta and 31°C (±2, 1σ std) at Tesero using equation 6.1 and equation 6.2 produces an estimate of 23°C (±3, 1σ std) at Val Brutta and 30°C (±2, 1σ std) at Tesero

| Brachiopod | MAT (°C) $\delta^{18}O_{seawater}$ = 0‰ | | MAT (°C) $\delta^{18}O_{seawater}$ = 1‰ | | MAT (°C) $\delta^{18}O_{seawater}$ = -1‰ | |
|---|---|---|---|---|---|---|
| | Equ. 6.1 | Equ. 6.2 | Equ. 6.1 | Equ. 6.2 | Equ. 6.1 | Equ. 6.2 |
| VB1 | 29 (±4) | 29 (±4) | 34 (±5) | 33 (±5) | 25 (±4) | 24 (±4) |
| VB2 | 29 (±3) | 28 (±3) | 34 (±3) | 33 (±3) | 24 (±3) | 23 (±3) |
| VB5 | 27 (±2) | 26 (±2) | 32 (±2) | 31 (±2) | 23 (±1) | 22 (±1d) |
| VB6 | 27 (±3) | 26 (±3) | 32 (±3) | 31 (±3) | 22 (±3) | 21 (±3) |
| TS1 | 36 (±2) | 35 (±2) | 41 (±3) | 40 (±3) | 31 (±2) | 30 (±2) |

**Table 6.2 Palaeotemperature estimates from unaltered brachiopods at different salinity and thus $\delta^{18}O$ seawater compositions. Brachiopods VB3 and VB4 did not have large enough NL areas to be isotopically sampled. Errors given to 1σ std.**

There is some independent corroboration which can be used to test which of these different $\delta^{18}O_{seawater}$ values is likely to be correct. Eighty kilometres to the north, at Sass di Putia (Figure 4.1), there is extensive gypsum precipitation in the Bellerophon Formation (Broglio Loriga *et al.* 1986; T.K. field observations). Gypsum forms in a temperature range of between 25-27°C in modern lagoon environments (Morris and Dickey 1957) and this correlates closest with the palaeotemperature estimate produced in this study with a $\delta^{18}O_{seawater}$ of 0‰. This palaeotemperature estimate also broadly agrees with that predicted by climate models of the late Permian and P/Tr boundary interval, which predict a temperature of 28-33°C for this palaeolatitude (e.g. Gibbs *et al.* 2002; Kiehl and Shields 2005; Winguth and Maier-Reimer 2005).

In contrast, the model of Kidder and Worsley (2004) assumed an equatorial ocean temperature of 35°C. From the isotope results from the brachiopods, the only way to generate a temperature of 35°C is to have much higher levels of salinity. Kidder and Worsley (2004), however, inferred a surface ocean water salinity of just 32‰. If this salinity is used to

generate a palaeotemperature estimate using the brachiopod isotope data, an temperature estimate of between 18-22°C is generated. This value is far cooler than the 35°C predicted by Kidder and Worsley (2004), and also cooler than predictions from other climate models (e.g. Gibbs *et al.* 2002; Kiehl and Shields 2005), suggesting that the surface salinity was not as low as 32‰ as they predict.

### 6.5.3 $\delta^{13}C$ of the Permian atmosphere

The $\delta^{13}C$ composition of brachiopod shells has been utilised by many studies to investigate changes in the isotopic composition of seawater (Veizer *et al.* 1999; Korte *et al.* 2005a, b; Batt *et al.* 2007; Jaffrés *et al.* 2007). It has been suggested that there is an −8‰ fractionation from marine seawater values to atmospheric $\delta^{13}C$ values (Ekart *et al.* 1999). This fractionation factor was derived by Ekart *et al.* (1999) based on the isotopic composition of pre-industrial carbon dioxide and contemporaneous values for surface ocean carbonates from the study of biogenic carbonate by Veizer *et al.* (1999). As such, this fractionation should be applicable to brachiopods as they were an integral part of the Veizer *et al.* (1999) dataset.

Korte *et al.* (2005a) note a rapid negative shift in brachiopod $\delta^{13}C$ values in the Changhsingian which they link to the negative excursion observed at the P/Tr boundary. They suggest (in Korte *et al.* 2005b) that this excursion culminated in the basal Triassic (base of the *Hindeodus parvus* zone and into the lower *Isarcicella isarcica* zone). This is recorded in both the brachiopod and bulk rock data from Val Brutta and Tesero. However, some of the mechanisms proposed as a cause of such an anomaly, such as influx of organic matter or ocean turnover, would have the effect of producing a negative anomaly in organic carbon without significant change in atmospheric $\delta^{13}C$ (cf. Sephton *et al.* 2005; Algeo *et al.* 2007). Using the fractionation factor suggested by Ekart *et al.* (1999) and the NL brachiopod values

produces and estimate of atmospheric $\delta^{13}C$ of –4.56‰ (±1.06, 1σ std) before the excursion, from Val Brutta, and –6.56‰ (±0.26, 1σ std) at Tesero, suggesting a –2‰ in atmospheric $\delta^{13}C$ values across the event. This is similar to the atmospheric change observed by others (e.g. Retallack and Jahren 2008).

It has been observed that although the $\delta^{18}O$ values from unaltered brachiopods may be in equilibrium with seawater, the $\delta^{13}C$ values maybe controlled by metabolic effects rather than simple equilibrium (Parkinson *et al.* 2005). Thus, it seems prudent to be cautious even of unaltered brachiopod $\delta^{13}C$ values when they show a different trend to the bulk rock values. However, as both follow the same trend in this study the use of the $\delta^{13}C$ composition of brachiopod shells as a proxy for atmospheric $\delta^{13}C$ is valid.

## 6.6 Summary

Detailed study of the bulk rock and brachiopod isotope compositions from Val Brutta and Tesero in the Italian dolomites has revealed that both the bulk rock and brachiopods record both the $\delta^{13}C$ and $\delta^{18}O$ excursion across the Permian/Triassic boundary. From this it is possible to conclude that:

1. Both the bulk rock and the brachiopods are recording the primary carbon and oxygen isotopic signals, although the bulk rock values may be depleted by the recrystallisation of these rocks;
2. The brachiopods from Val Brutta yield a palaeotemperature estimate of between 26-29°C, which is realistic for an equatorial seaway and agrees with other palaeotemperature estimates for this period. Although the method described by

Parkinson *et al.* (2005) assumes the $\delta^{18}O$ isotopic composition of the brachiopod shells were only controlled by temperature and there is no influence of vital affects;

3. The temperature, as recorded from the fossil brachiopods, rose by ~8°C across the bulk rock isotope excursion seen at the base of the Tesero Member. This is similar to the 5-6°C predicted from the bulk rock signal by Magaritz and Holser (1991). Also it is similar (within error) to that predicted at the P/Tr boundary in Russia (excursion P4, see chapter 6);
4. Although the palaeotemperature estimate agrees with modelled temperatures for this palaeolatitude, the reduced salinity values proposed for equatorial surface ocean waters by Kidder and Worsley (2004) are not supported by these results;
5. The $\delta^{13}C$ values of bulk rock, while undoubtedly recording changes in the global carbon cycle across the P/Tr boundary, may represent a fractionation of equilibrium seawater values. Thus, the use of bulk rock values to calculate absolute values for $\delta^{13}C$ of the atmosphere may lead to erroneous results and thus, the use of bulk rock values in models, such as for $pCO_2$ values from pedogenic carbonate (cf. Ekart *et al.* 1999), must be treated with caution and brachiopods provide a more realistic estimate of such values.

# Chapter 7. Atmospheric carbon dioxide and the $\delta^{13}C$ composition of pedogenic carbonate

One of the principal factors in controlling the $\delta^{13}C$ signature of primary pedogenic soil carbonate is the partial pressure of carbon dioxide in the atmosphere ($pCO_2$) (Cerling 1991; Cerling and Quade 1993; Ekart *et al.* 1999). This relationship has been described by Cerling (1991) and modified by Ekart *et al.* (1999) and there are many examples where this has been successfully applied to paleosols (Mora *et al.* 1991; Ekart *et al.* 1999; Arens and Jahren 2000; Ghosh *et al.* 2001; Robinson *et al.* 2002; Prochnow 2006).

## 7.1 The model

As well as $pCO_2$ there are many other factors that can control the isotopic composition of pedogenic carbonate. These are all described in the $pCO_2$ equation as created by Cerling (1991) and modified by Ekart *et al.* (1999) based on modern-day relationships:

$$Ca = S_{(z)} \frac{(\delta^{13}C_s - 1.0044\ \delta^{13}C_\Phi - 4.4)}{\delta^{13}C_a - \delta^{13}C_s} \tag{7.1}$$

where $Ca$ is atmospheric $pCO_2$ (ppmV); $S_{(z)}$ is the $CO_2$ contributed by soil respiration as a function of depth (ppmV); $\delta^{13}C_a$ is the isotopic composition of the atmosphere (‰); $\delta^{13}C_\Phi$ is the isotopic composition of respired soil $CO_2$ from plant matter in the soil (‰) and $\delta^{13}C_s$ is the isotopic composition of the soil water (‰).

### 7.1.1 Generating the variables

Today it is possible to measure each of these variables directly from the soil and atmosphere. However, when dealing with paleosols many of these variables must be generated from other proxies or estimated using modern analogues. All of these variables can bring levels of uncertainty into the estimates of $pCO_2$ which must be kept in mind when interpreting the results.

#### $S_{(z)}$ – Soil respiration

$S_{(z)}$ refers to the difference in concentration between the soil $CO_2$ and atmospheric $CO_2$ and depends on waterlogging, soil porosity, respiration rates and depth of $CO_2$ production (Ekart *et al.* 1999; Ghosh *et al.* 2001). It has been suggested that this may be calculated from rooting structures and depths, but at present no such model has been created (Ghosh *et al.* 2001). Most authors (Mora *et al.* 1991; Ekart *et al.* 1999, Arens and Jahren 2000, Ghosh *et al.* 2001; Robinson *et al.* 2002; Prochnow *et al.* 2006) use estimates based on measurements from modern soils in similar environments as the paleosols under study to generate this parameter. It has been suggested that desert soils have a range less than 3000ppmV (Ghosh *et al.* 2001), arid to semi-arid soils have a value of 4000ppmV; subhumid soils have a value of 5000ppmV (Prochnow *et al.* 2006) and waterlogged soils have a value of 10000ppmV (Robinson *et al.* 2002). Based on the arid to semi-arid environment suggested by the paleosols in this study (Chapter 3), the range between 3000ppmV and 4000ppmV was chosen as the best representative of the environment in the Southern Urals of Russia in the Permian-Triassic.

#### $\delta^{13}C_a$ – isotopic composition of the atmosphere

The isotopic carbon concentration of the atmosphere ($\delta^{13}C_a$) is another variable which cannot be directly measured from paleosols. There are two methods proposed for

estimating this variable, the first is using marine brachiopods or inorganic carbonate (Mora *et al.* 1996; Ekart *et al.* 1999); the second uses organic carbon in the paleosol (Ghosh *et al.* 2001). The first method assumes either a –8‰ fractionation from marine inorganic carbonate to atmospheric carbonate (Robertson *et al.* 2002; Cerling 1999; Ekart *et al.* 1999) or a –7‰ fractionation between shallow benthic marine inorganic carbonate and atmospheric carbonate (Driese and Mora 2002; Prochnow *et al.* 2006). It has been suggested that brachiopods could be used instead of marine inorganic carbonate (Mora *et al.* 1996; Ghosh *et al.* 2001). Brachiopods are likely to provide a better proxy for the isotope composition of sea water as it is easier to assess if they have been affected by alteration (Chapter 6). It has been shown that recent brachiopods secrete calcite in carbon isotopic equilibrium with ambient seawater (e.g. van Geldern *et al.* 2006, Lee and Wan 2000). In this study the isotopic compositions of brachiopods closest to the age of the relevant paleosols were used (Table 7.1).

| | Age | Locality | $\delta^{13}C$ brachiopod shell (‰) | | Source |
|---|---|---|---|---|---|
| | | | Brachiopod | Ave. | |
| **Permian** | Changhsingian *Janiceps* and *Comelicania*, | Val Brutta | 3.44 | | Chapter 6 |
| | Changhsingian (251.72) | Sass di Putia | 0.86 | | Korte *et al.* (2005a) |
| | Changhsingian (252 37) | Meishan D | 2.47 | | Korte *et al.*(2005a) |
| | Changhsingian (252 76) | Meishan D | 4.51 | **2.83** | Korte *et al.* (2005a) |
| **Triassic** | Induan *(Crurithyris sp.)* | Italy (Tesero) | 1.44 | **1.44** | Chapter 6 |
| | Olenekian | Pietra del Saracini | 4.2 | | Korte *et al.* (2005b) |
| | Olenekian | Pietra del Saracini | 0.33 | **2.27** | Korte *et al.* (2005b) |

**Table 7.1 $\delta^{13}C$ values of unaltered brachiopods from before and after the P/Tr boundary from published data and field data (see chapter 3). Species names listed where known. The bold values are the average of the brachiopod isotopic values from the same time period.**

Using the averages for the Permian and Triassic brachiopod values this would produce $\delta^{13}C_a$ for the Permian of –5.17‰ (±1.55‰) and Triassic values of –6.56‰ (±0.26‰)

for the Induan and −5.74‰ (±2.74‰) for the Olenekian using a fractionation of −8‰ (Cerling 1999; Ekart *et al.* 1999; Robertson *et al.* 2002).

The second method for calculating $\delta^{13}C_a$ is to use the organic matter present in the paleosols. $C_3$ vegetation is depleted by an average of 21‰ from the atmospheric $\delta^{13}C$, thus adding this fractionation to the isotopic composition of organic carbon found in the soil will give an estimate of $\delta^{13}C_a$ (Ghosh *et al.* 2001). Using the organic carbon values found at Sambullak (Table 7.2) and using the fractionation factor described above (Ghosh *et al.* 2001) produces an estimate for $\delta^{13}C_a = -2.03‰ (\pm 1.55‰)$ which is two permil more positive than the estimate derived by the brachiopod fractionation method.

| Sample | Height from based of section (m) | % Carbon | $\delta^{13}C_{org}$ (‰ VPDB) |
|---|---|---|---|
| 06.7.21c | 117.83 | 0.44 | -22.11 |
| 06.7.20a | 122.70 | 2.88 | -22.45 |
| 06.7.20c | 123.48 | 2.90 | -24.55 |

**Table 7.2 Values for organic carbon recovered from Sambullak.**

The relationship between $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ has been modelled by Arens *et al.* (2000) in equation (7.2). Using the organic carbon values found at Sambullak (Table 7.2) produces an estimate for $\delta^{13}C_a$ of −3.97‰ (±1.20‰ 1σ std).

$$\delta^{13}C_a = \frac{(\delta^{13}C_\phi + 18.67)}{1.10} \qquad (7.2)$$

*$\delta^{13}C_\Phi$ – isotopic composition of soil organic matter*

To estimate $pCO_2$ using equation 7.1 the isotopic composition of respired soil $CO_2$ from organic matter in the soil ($\delta^{13}C_\Phi$) also has be calculated. As with $\delta^{13}C_a$, there are two methods to calculate $\delta^{13}C_\Phi$. The first is by using the isotopic value of organic carbon found in the soil (e.g. Table 7.1). It is suggested that this can be used as a proxy for $\delta^{13}C_\Phi$ (Driese and Mora 2002; Ghosh *et al.* 2001). Organic carbon was recovered from

three carbon-rich beds at Sambullak (Table 7.2) which yield an average of –23.03‰ (± 1.32‰ 1σ std). This is well within the range of modern $C_3$ vegetation (Arens *et al.* 2000). However, no organic carbon was recovered from Boyevaya Gora in either the Permian or Triassic.

A second method to calculate $\delta^{13}C_\Phi$ has been proposed for sections where not enough organic carbon has been preserved which can be used for those parts of the sections where organic carbon has not been recovered, such as the Triassic in Russia. This method assumes a fractionation between $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ (Cerling *et al.* 1999; Ekart *et al.* 1999; Robinson *et al.* 2002; Prochnow *et al.* 2006). Some authors assume a simple –18‰ fractionation between $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ (Cerling *et al.* 1999; Ekart *et al.* 1999; Robinson *et al.* 2002). Prochnow *et al.* (2006) use the equation (7.2) and solving it for $\delta^{13}C_\Phi$. When both these techniques are applied to the $\delta^{13}C_a$ calculated from oceanic brachiopods (Table 7.1) estimates of $\delta^{13}C_\Phi = -23.17$ ‰, for the Permian, and $\delta^{13}C_\Phi = -25.71$ ‰, for the Triassic, are produced using the simple fractionation model of –18‰. While using equation (7.2) yields estimates of $\delta^{13}C_\Phi = -23.28$ ‰, for the Permian, and $\delta^{13}C_\Phi = -26.05$ ‰, for the Triassic. The Permian values produced by these techniques (–23.17 ‰, –23.28 ‰) produce values very close to the average value of organic matter from Sambullak (–23.03‰) this suggests that there is no contamination of younger organic matter.

### *$\delta^{13}C_s$ – isotopic composition of soil water*

The final variable to be generated is the isotopic composition of the soil water ($\delta^{13}C_s$). This is directly measured from the isotopic composition of the pedogenic carbonate found in the soil which forms in equilibrium with such fluids (Cerling 1991; Cerling and Quade 1993; Ekart *et al.* 1999). There is a fractionation between the soil water and

pedogenic carbonate which varies with temperature (Ekart *et al.* 1999; Ghosh *et al.* 2001; Robinson *et al.* 2002; Prochnow *et al.* 2006). To account for this the temperature-dependent fractionation factor described by Romanek *et al.* (1992) (equation 7.3) is used to calculate the fractionation factor between the soil water and pedogenic carbonate.

$$\varepsilon_{cl\text{-}CO_2}=11.98(\pm0.13)-0.12(\pm0.01)T \quad (7.3)$$

where $\varepsilon_{cl-CO_2}$ is the fractionation factor (‰) and $T$ is temperature of precipitation (°C). Many authors use an average soil temperature of between 20 and 25°C, based on modern analogues (Ekart *et al.* 1999; Ghosh *et al.* 2001; Robinson *et al.* 2002). However, this could produce erroneous results if there is a major change in surface temperature. It has been shown that although there is much as 5°C difference between temperature at depth in a soil and surface air temperature within a year, interannual temperature averages are the same at depth as at the surface (Zhang *et al.* 2001; Smerdon *et al.* 2003). Prochnow *et al.* (2006) utilise the mean annual temperatures produced by equation (5.8a) to calculate their fractionation factor.

Ekart *et al.* (1999) suggest that only nodular (i.e. stage II) carbonates from Aridisols, Alfisols and Mollisols are suitable to be used for $\delta^{13}C_s$, although equation (7.1) has also been successfully applied to Vertisols (Prochnow *et al.* 2006; Ghosh *et al.* 2001). Ekart *et al.* (1999) also suggest a soil must be not formed in anaerobic or waterlogged conditions; be deeper than 20cm in the soil profile and not contain morphologies associated with burial diagenesis or groundwater origin.

The $\delta^{13}C$ values of a pedogenic carbonate can be controlled by both the atmospheric $\delta^{13}C$ and the $\delta^{13}C$ produced by in situ oxidation of organic matter (Cerling 1991), as described in equation (7.1). Tabor *et al.* (2007) argue that in the Karoo Basin across the P/Tr boundary the calcitic isotopic values only represent oxidation of biological matter and have no input from atmospheric carbon dioxide thus rendering them useless as an indicator of $pCO_2$. This is because the $\delta^{13}C$ of the pedogenic calcite is within +14.8‰ of the isotopic composition organic matter found at the section. This fractionation factor is derived from the 4.4‰ enrichment between carbonate and biologically derived $CO_2$ and additional 10.4‰ enrichment between the gas and carbonates (Tabor *et al.* 2007). It has been shown elsewhere that the theoretical minimum difference can be less than 4.4‰ if the difference between the biologically derived $CO_2$ and atmospheric $CO_2$ is small (Davidson 1995).

| Age | | | $\delta^{13}C_{\Phi}$ (‰, VPDB) | $\delta^{13}C_{calcite}$ (‰, VPDB) |
|---|---|---|---|---|
| Permian | Changhsingian | Method 1 | -23.17 | -8.37 |
| | | Method 2 | -23.26 | -8.46 |
| | | Method 3 | -23.03 | -8.23 |
| Triassic | Induan | Method 1 | -25.71 | -10.91 |
| | | Method 2 | -26.05 | -11.25 |
| | Olenekian | Method 1 | -23.36 | -8.56 |
| | | Method 2 | -23.50 | -8.70 |

**Table 7.3 Calculated values of $\delta^{13}C$ calcite if only formed from $CO_2$ produced from organic carbon present in the soil.**

Although there is very little evidence of the intensive gleys associated with waterlogging, except at perhaps Mescheryakovka (see Chapter 3), Table 7.3 shows the theoretical values of pedogenic carbonate if it was only formed from biologically derived $CO_2$.

Based on these conditions only the isotope results which could be demonstrated to have passed all the screening criteria described in Chapter 4, Table 4.2, were used to calculate $pCO_2$ estimates (see Chapter 4, Table 4.2). The pedogenic dolomite is also

problematic, although it is possible that these represent the $\delta^{13}C$ of the active soil, because the $\delta^{18}O$ values are possibly fractionated (Land 1980). Quast *et al.* (2006) suggest that it not clear if $^{13}C$-values of dolomites represent $^{13}C$-values of soil $CO_2$ at higher soil levels. Those nodules that show a microcrystalline texture are also problematic as they may be formed by groundwaters (Quast *et al.* 2006). However, the overlap with those nodules that were of unaltered cryptocrystalline micrite (see chapter 4) suggests that those nodules are also pedogenic, so they were included in the palaeotemperature estimates but only where they are similar to unaltered vadose pedogenic carbonate values from the same paleosol. As only Boyevaya Gora, Sambullak and Mescheryakovka have isotopic values that are definitely unaltered pedogenic calcite; these were used to calculate $pCO_2$ estimates.

## 7.2 Application and results from Russia

As discussed in the previous section there are many ways of estimating the variables in equation 7.1. These different approaches all yield different $pCO_2$ estimates so they have been summed up in three different methods all of which were applied to the $\delta^{13}C_{carb}$ values from the Russian sections (Table 7.4). Method 1 is based on an approach used by Robinson *et al.* (2002) which calculates $\delta^{13}C_a$ from brachiopods using a fractionation factor of −8‰ and $\delta^{13}C_\Phi$ from a fractionation of −18‰ of $\delta^{13}C_a$. Method 2 is based on the approach of Prochnow *et al.* (2006) calculating $\delta^{13}C_a$ from brachiopods using a fractionation of −7‰ and $\delta^{13}C_\Phi$ from $\delta^{13}C_a$ using equation (7.2). Finally, Method 3 is based on the approach of Ghosh *et al.* (2001) who use organic carbon found in the soil to generate $\delta^{13}C_\Phi$ and $\delta^{13}C_a$ from a fractionation of 21‰ from $\delta^{13}C_\Phi$. Because no organic carbon was recovered from the Triassic, method 3 cannot be applied to the Triassic sections in Russia. It may be possible to estimate $\delta^{13}C_\Phi$ from other terrestrial sections in the Earliest Triassic. The Earliest Triassic is typified by many $\delta^{13}C_{org}$ organic

excursions (cf. Retallack and Krull 2006). As there are no extreme excursions in the Triassic at Boyevaya Gora it may be assumed that these excursions fall between or before the paleosols in the section.

| Variable | Method 1 | Method 2 | Method 3 |
|---|---|---|---|
| $S_{(z)}$ | 3000 – 4000ppmV | 3000 – 4000ppmV | 3000 – 4000ppmV |
| $\delta^{13}C_a$ | Permian –5.17‰<br>Induan –6.56‰<br>Olenekian –5.74‰ | Permian –4.17‰<br>Induan –5.56‰<br>Olenekian –4.74‰ | Permian –2.03‰ |
| $\delta^{13}C_\Phi$ | Permian –23.17‰<br>Induan –24.17‰<br>Olenekian –23.74‰ | Permian –23.26‰<br>Induan –24.79‰<br>Olenekian -23.88‰ | Permian –23.03‰ |
| $\delta^{13}C_s$ | From $\delta^{13}C$ of pedogenic carbonate using equ.(8) | From $\delta^{13}C$ of pedogenic carbonate using equ.(8) | From $\delta^{13}C$ of pedogenic carbonate using equ.(8) |

**Table 7.4 The variables used in the three different methods used for generating the $pCO_2$ estimates. See text for details.**

With all three methods, $\delta^{13}C_s$ was calculated from the screened unaltered pedogenic carbonate results using the temperature-controlled fractionation factor proposed by Romanek *et al.* (1992) (equation 7.3). The temperature estimates used in this equation were those generated from the $\delta^{18}O_{carb}$ results using equation (5.10) (Chapter 5). Although, as stated previously, there are potential issues with this equation (i.e. the low $R^2$ value of the underlying relationship), it represents the temperature estimate which fits closest to both the pedological evidence and the predicted values for the latest Permian (cf. Kiehl and Shields 2005) and successfully models the temperature rise of 7-8°C just prior to the P/Tr boundary observed in the Italian brachiopods (Chapter 6). For the pedogenic dolomites averaged estimated temperatures from calcite paleosols in the same magnetochron from both Boyevaya Gora and Sambullak were used to generate the fractionation factor.

## 7.2.1 Results

| Section | $\delta^{13}C_{carb}$ (‰) | MAT °C (eq5) | $pCO_2$ estimate (ppmV) Method 1 ($S_z$) 3000 ppmV | Method 1 ($S_z$) 4000 ppmV | Method 2 ($S_z$) 3000 ppmV | Method 2 ($S_z$) 4000 ppmV | Method 3 ($S_z$) 3000 ppmV | Method 3 ($S_z$) 4000 ppmV |
|---|---|---|---|---|---|---|---|---|
| **Permian** | | | | | | | | |
| *Boyevaya Gora* | −6.76 (± 3.08) | 38 (±5) | 3503 (± 2031) | 4670 (± 2708) | 2807 (± 1721) | 2444 (± 1948) | 1904 (± 1826) | 2539 (± 2333) |
| *Sambullak* | −5.56 (± 1.02) | 40 (±4) | 2800 (± 955) | 3733 (± 1274) | 2530 (± 784) | 3374 (± 1045) | 1915 (± 535) | 2554 (± 713) |
| **Triassic** | | | | | | | | |
| *Boyevaya Gora* | −3.52 (± 2.59) | 43 (±1) | 13463 (±17162) | 17951 (± 22883) | 8200 (± 7049) | 10933 (± 9398) | – | – |
| *Mescheryakovka* | −8.50 (± 0.81) | 47 (±8) | 1330 (±302) | 1774 (± 403) | 1271 (± 269) | 1694 (±358) | – | – |

**Table 7.5 Summary of average atmospheric carbon dioxide calculations are based on stable carbon isotopes in pedogenic carbonate using the three different methods summarised in Table 3. Sz is soil $CO_2$ concentration (ppmv), $\delta^{13}C_{carb}$ is the isotopic measurement from the pedogenic carbonate (‰), and the average MAT is mean annual temperature (°C) calculated from $\delta^{18}O_{carb}$ using equation (10) (for full results see Appendix A3.3).**

All $pCO_2$ estimates show a dramatic rise from the Permian in to the Triassic (Table 7.5).

There is also a large variation in the $pCO_2$ estimates between the three methods, for instance with the same input variables (Permian at Boyevaya Gora, with an $S_{(z)}$ of 3000ppmV) there is a difference of between 2766ppmV between the highest and lowest estimates (Table 7.5) although the variation between methods is not bigger than the increase in $pCO_2$ seen across the P/Tr boundary. Also there is a lot of variation both within the time-averaged estimates and within the horizons themselves (Figure 7.1). The variation in $pCO_2$ estimates within the Permian is as much as ±2333ppmV (1σ std). However, the overall trends are the same between the three methods.

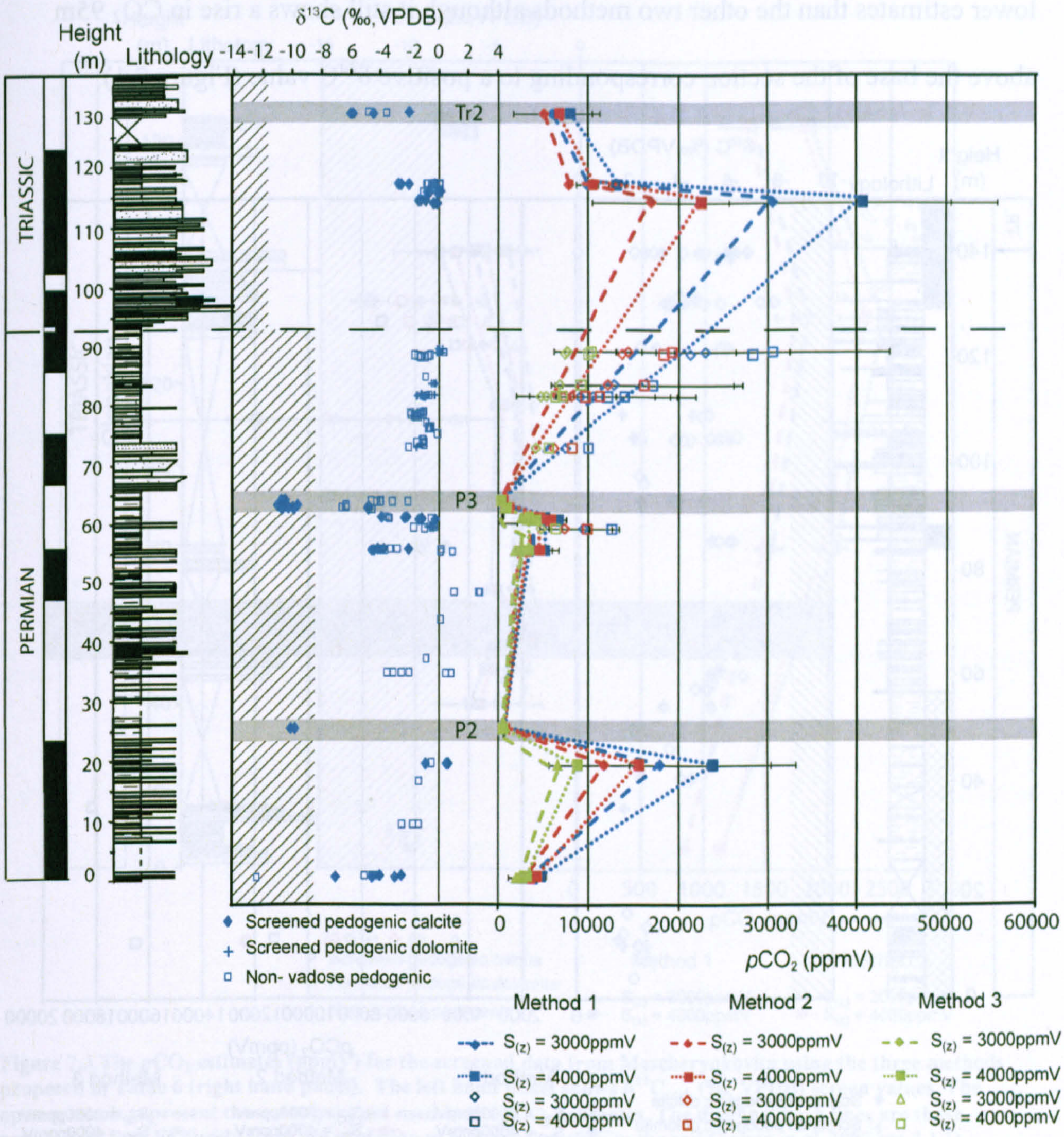


**Figure 7.1 The $pCO_2$ estimates (ppmV) for the screened data from Boyevaya Gora using the three methods proposed in table 6 (right hand panel). The open symbols are those estimates from pedogenic dolomite nodules. The left hand panel shows $\delta^{13}C_{carb}$ (‰, VPDB) screen values the open symbols represent those analyses not used in the $pCO_2$ estimates and the crosses are pedogenic dolomite values. The diagonal hash lines mark the field in which the isotopic composition can be explained purely by the oxidation of biological matter in the soil (Tabor *et al.* 2007 see Section 7.1.1). The grey horizontal lines highlight the positions of the excursions that may not give accurate estimates if the system is out of equilibrium (Ekart *et al* 1999, see Section 7.3.2).**

The estimates from Boyevaya Gora (Figure 7.1) show extreme variation in values, especially in the Triassic where Method 1 predicts values as high at 30000ppmV which is over 100 times greater than pre-industrial levels (Pre- industrial levels 280-380ppmV; Royer 2006). Method 3 (which can only be applied to the Permian) gives significantly

lower estimates than the other two methods although it still shows a rise in $CO_2$ 95m above the base of the section corresponding to a positive $\delta^{13}C$ value (Figure 7.1).

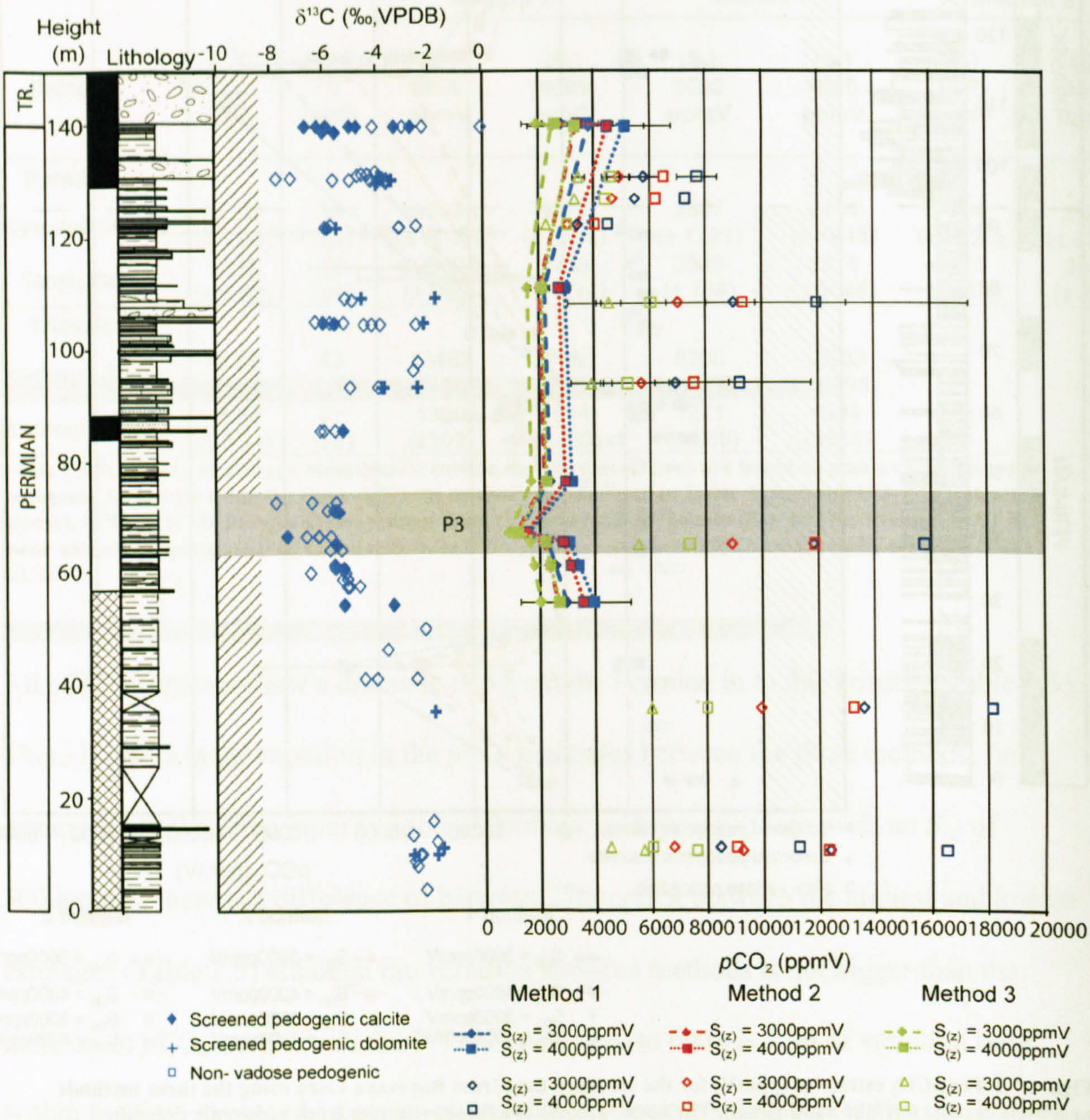


**Figure 7.2 The $pCO_2$ estimates (ppmV) for the screened data from Sambullak using the three methods proposed in Table 6 . The open symbols are those estimates from pedogenic dolomite nodules. The left hand panel shows $\delta^{13}C_{carb}$ (‰, VPDB) screen values the open symbols represent those analyses not uses in the $pCO_2$ estimates and the crosses are pedogenic dolomite values The diagonal hash lines mark the field in which the isotopic composition can be explained purely by the oxidation of biological matter in the soil (Tabor *et al.* 2007 see Section 7.1.1). The grey horizontal lines highlight the positions of the excursions that may not give accurate estimates if the system is out of equilibrium (Ekart *et al* 1999, see 7.3.2).**

The paleosols at Sambullak show much less variation (Figure 7.2) with the average within-paleosol variation being ± 541ppmV (1σ std) for all three methods (Method 1, ± 644ppmV 1σ std; Method 2, ± 539ppmV 1σ std; Method 3 ± 377ppmV 1σ std). Also, the $pCO_2$ estimates are all much reduced, being between 6 and 11 times pre-industrial levels (Pre industrial levels 280-380ppmV; Royer 2006) depending on the method used.

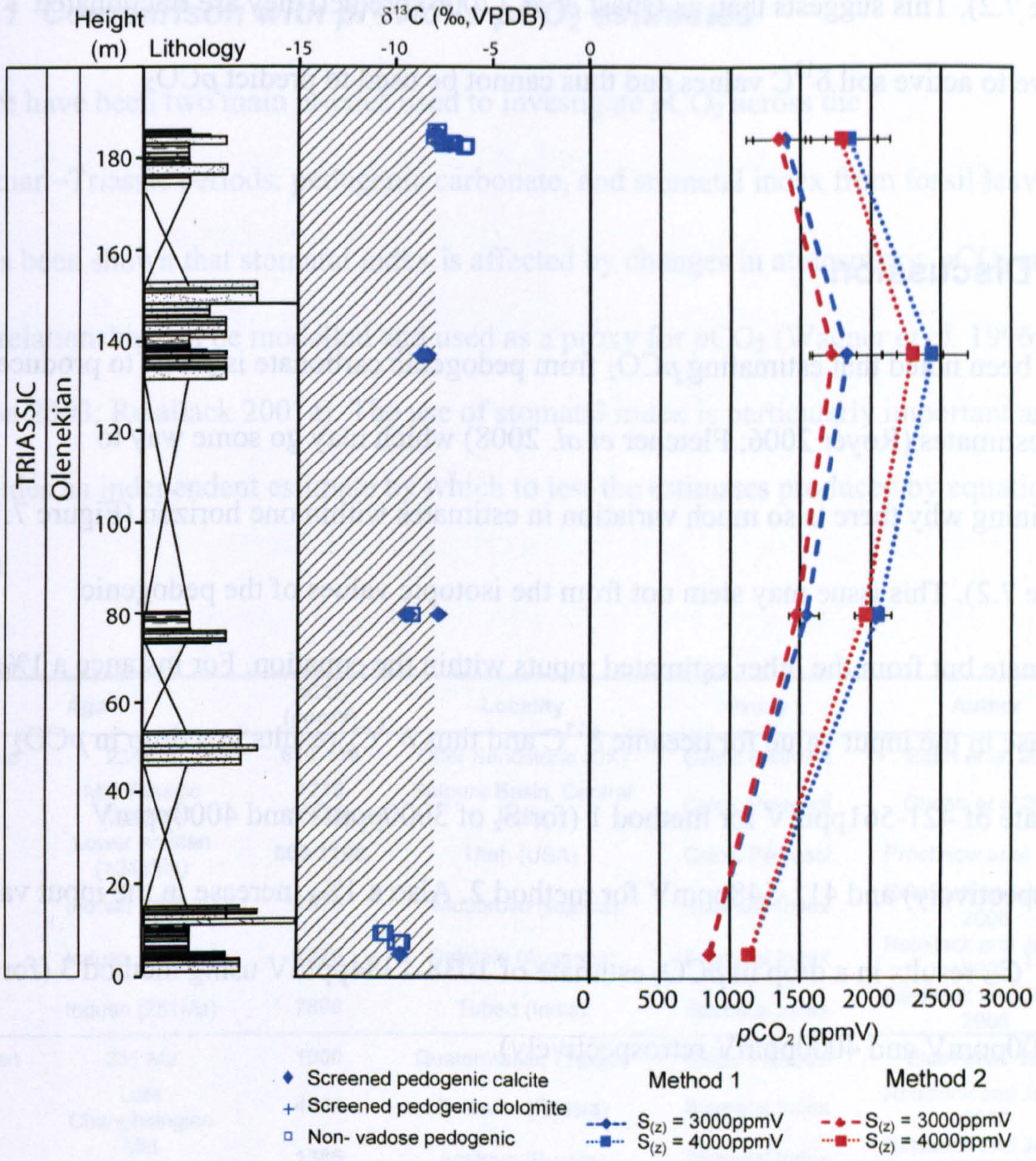


**Figure 7.3 The $pCO_2$ estimates (ppmV) for the screened data from Mescheryakovka using the three methods proposed in Table 6 (right hand panel). The left hand panel shows $\delta^{13}C_{carb}$ (‰, VPDB) screen values. The open symbols represent those analyses not used in the $pCO_2$ estimates. The diagonal hash lines are those results that may be purely from the oxidation of biological matter in the soil (Tabor *et al.* 2007 see 7.1.1).**

The values and within paleosol variation from Mescheryakovka (Figure 7.3) are much reduced compared to the Triassic values at Boyevaya Gora (Figure 7.1, Table 7.5).. However, many of the values could be explained purely by oxidation of biological matter (Figure 7.3) rather than atmospheric values.

The pedogenic dolomite values appear to produce significantly elevated $pCO_2$ estimates compared to the pedogenic calcite values from a similar stratigraphic level (Figure 7.1,

Figure 7.2). This suggests that, as Quast *et al.* (2006) predict, they are fractionated relative to active soil $\delta^{13}C$ values and thus cannot be used to predict $pCO_2$.

## 7.3 Discussion

It has been noted that estimating $pCO_2$ from pedogenic carbonate is prone to produce over-estimates (Royer 2006; Fletcher *et al.* 2008) which may go some way to explaining why there is so much variation in estimates within one horizon (Figure 7.1, Figure 7.2). This issue may stem not from the isotopic values of the pedogenic carbonate but from the other estimated inputs within the equation. For instance a 1‰ increase in the input value for oceanic $\delta^{13}C$ and thus $\delta^{13}C_a$ results in a drop in $pCO_2$ estimate of 421-561ppmV for method 1 (for $S_z$ of 3000ppmV and 4000ppmV retrospectively) and 411-548ppmV for method 2. Also a 1‰ increase in the input value for $\delta^{13}C_\Phi$ results in a drop in $pCO_2$ estimate of 1038-1384ppmV using method 3 (for $S_z$ of 3000ppmV and 4000ppmV retrospectively).

In comparison a 1‰ rise in $\delta^{13}C_s$ only produces a rise of 350-520ppmV across all three methods. This means that the input variables that are not measured from paleosols directly have an equal or greater control over the final $pCO_2$ estimate than those which were analytically measured. Equally, all three methods assume that the external variables are constant through the Permian and then change in the earliest Triassic. If there are changes in $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ within the Permian or Triassic periods these can produce erroneous estimates. For example, if a negative excursion in $\delta^{13}C_s$ is caused by both a rise in $pCO_2$ and a fall in either $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ it would make it impossible to estimate the $pCO_2$ values without some independent measure in the change in $\delta^{13}C_a$ and $\delta^{13}C_\Phi$ (see section 5.3.2).

### 7.3.1 Comparison with previous $pCO_2$ estimates

There have been two main proxies used to investigate $pCO_2$ across the Permian–Triassic periods: pedogenic carbonate, and stomatal index from fossil leaves. It has been shown that stomatal index is affected by changes in atmospheric $pCO_2$ and this relationship can be modelled and used as a proxy for $pCO_2$ (Wagner *et al.* 1996; Wynn 2003; Retallack 2001a). The use of stomatal index is particularly important as it provides an independent estimate by which to test the estimates produced by equation (7.1).

| | Age | $pCO_2$ (ppmV) | Locality | Proxy | Author |
|---|---|---|---|---|---|
| Triassic | 234 Ma | **610-710** | Otter Sandstone (UK) | Calcic Paleosol | Ekart *et al.* 2000 |
| | Mid Triassic (240Ma) | **1210 (±424)** | Satpura Basin, Central India | Calcic Paleosol | Ghosh *et al.*2001 |
| | Lower Anisian (>242Ma) | **600-1160** | Utah (USA) | Calcic Paleosol | Prochnow *et al.* 2006 |
| | Induan (251Ma) | **7876** | Nedubrovo (Russia) | Stomatal Index | Retallack and Jahren 2008 |
| | Induan (251Ma) | **7876** | Oakdale (Australia) | Stomatal Index | Retallack and Jahren 2008 |
| | Induan (251Ma) | **7876** | Tubed (India) | Stomatal Index | Retallack and Jahren 2008 |
| Permian | 251 Ma | **1000** | Quatermaster (Texas) | Calcic Paleosol | Ekart *et al.* 1999 |
| | Late Changhsingian | **4264** | Sokovka (Russia) | Stomatal Index | Retallack and Jahren 2008 |
| | Mid Changhsingian | **1385** | Aristovo (Russia) | Stomatal Index | Retallack and Jahren 2008 |
| | Early Changhsingian | **1034** | Aristovo (Russia) | Stomatal Index | Retallack and Jahren 2008 |
| | mid Permian (260Ma) | **715 (±241)** | Satpura Basin, Central India | Calcic Paleosol | Ghosh *et al.*2001 |
| | Early Permian (270Ma) | **300-1500** | Texas | Calcretes and Goethite | Tarbor *et al.* 2004 |

**Table 7.6 Published $pCO_2$ estimates using both calcic paleosols (as in this study) and stomatal indexes across the Permian –Triassic period.**

Table 7.6 shows $pCO_2$ estimates from other studies using both stomatal and pedogenic carbonate proxies. As Sambullak is Changhsingian in age and Boyevaya Gora spans the Changhsingian and earliest Induan (Chapter 3) these estimates are the most relevant to evaluate the results from this study. The published data shows a rise from 1385ppmV in the lower part of the Changhsingian to 4264ppmV in the Late Changhsingian and a dramatic rise of 7876ppmV in the lowest Triassic (Table 7.6). The estimates generated by method 3 are closest to those estimates predicted by other authors (Table 7.5, Figure

7.1 and Figure 7.2). This suggests that using locally derived values for $\delta^{13}C_{\Phi}$, rather than those derived from a fractionation of global averaged $\delta^{13}C_a$ values (as in methods 1 and 2), produce the most consistent results with the stomatal proxy estimates. This implies that knowledge of local soil conditions (e.g. soil organic matter) is imperative in $pCO_2$ estimates. Also that an $S_{(z)}$ of 3000ppmV produces values that are closer to those values predicted by others (Table 7.6).

Unfortunately method 3 cannot be applied to the Triassic of Boyevaya Gora as no organic carbon was recovered from this locality. However, the average values for the Earliest Triassic using method 2 and a $S_{(z)}$ of 3000ppmV produce an average of 8200ppmV (±7049), close to the 7876ppmV predicted by Retallack and Jahren (2008) for the earliest Triassic (Figure 7.4). This agreement between the pedogenic carbonate and stomatal proxies suggests that there indeed was rise in atmospheric $pCO_2$ in the earliest Triassic. The Russian data seems to show a minor rise in the mid to late Changhsingian to 4000ppmV, which is in agreement the stomatal data (Retallack and Jahren 2008, Retallack, www.uoregon.edu 2008) The paleosols then suggests a subsequent reduction before the massive increase in the early Triassic (Figure 7.4). There is one apparently anomalous estimate in the Permian from paleosol KOR 27, which gives an average of 7711ppmV (±6402) (method 3, $Sz$ = 3000 ppmV). Such an anomaly cannot be explained by be explained by oxidation of biomass in the soil as this would cause a negative shift (cf. Tabor *et al.* 2007). Another way of explaining a positive $\delta^{13}C_{carb}$ shift is by increasing the amount of $CO_2$ in the soil by a change in grain size.

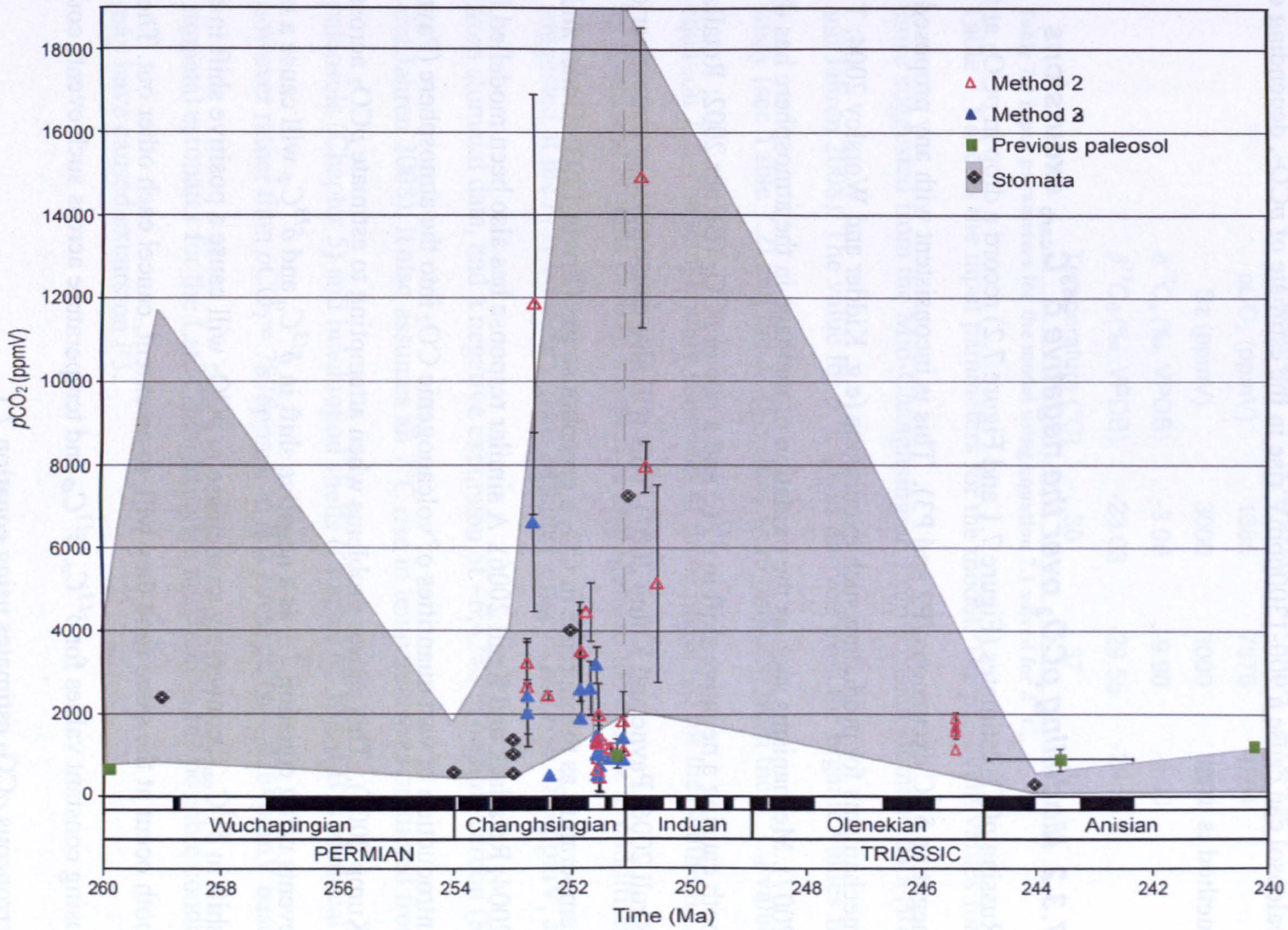


**Figure 7.4 The *p*CO2 estimates from this study compared to previously published data. i) is stomatal records (Retallack and Jahren 2008, Retallack www.uoregon.edu 2008). (ii) other pedogenic carbonate estimates (Ekart *et al.*1999; Ghosh *et al.* 2001 and Prochnow *et al.* 2006). The open triangles are estimates using method 2 (Sz=3000ppmV) and the closed are using method 3 (Sz=3000ppmV). The data from this study is are stratigraphically arranged based on magnetic reversals (based on Taylor *et al.* 2009) apart from those in the Olenekian which are based on biostratigraphy (see Chapter 3).**

However, KOR27 and those of the Triassic at Boyevaya Gora which contains the positive values are all the same siltstone grain size as the paleosols in the rest of the section (see Chapter 3, 4 and Appendix A2.1). More likely it may be due to local variation in organic matter in that paleosol as a –2‰ shift in the $\delta^{13}C_{\Phi}$ value in the paleosol can cause a 900-1300ppmV rise in the estimate of $pCO_2$, depending on which method is used.

### 7.3.2 Modelling $pCO_2$ over the negative $\delta^{13}C_{carb}$ excursions

Russian $pCO_2$ estimates (Figure 7.1 and Figure 7.2) record a drop in $pCO_2$ at the negative $\delta^{13}C$ excursions (P2 and P3). This is inconsistent with any proposed mechanisms for producing such excursions (e.g. Kidder and Worsley 2004; Twitchett 2007). Mechanisms such as the oxidation of methane in the atmosphere has the effect of both causing a negative shift in $\delta^{13}C_a$ and a rise in $pCO_2$ (Berner 2002; Retallack and Krull 2006; Payne and Kump 2007). This will also cause a rise in atmospheric temperature as the increase in $CO_2$ a greenhouse gas (Erwin 1993; Kidder and Worsley 2004; Retallack and Krull 2006). A similar response has also been modelled for the introduction of vast quantities of volcanogenic $CO_2$ into the atmosphere (Payne and Kump 2007). This causes problems when attempting to estimate $pCO_2$ across such events using equation 7.1 as a negative shift in $\delta^{13}C_a$ and $\delta^{13}C_{\Phi}$ will cause a negative shift in $\delta^{13}C_{carb}$, conversely an increase in $pCO_2$ will cause a positive shift in $\delta^{13}C_{carb}$. If both occur at the same time they will, to an extent, cancel each other out. Therefore using constant values for $\delta^{13}C_a$, $\delta^{13}C_{\Phi}$ and temperature across such events could lead to erroneous $pCO_2$ estimates using equation 7.1.

It is possible to theoretically model the pedogenic isotope signal of such an event in a paleosol by solving equation 7.1 for $\delta^{13}C_s$ and inputting $pCO_2$ values from stomatal data

whilst using $\delta^{13}C_{org}$ values to model the change in $\delta^{13}C_{\Phi}$, and thus $\delta^{13}C_a$ (using equation 7.2). The results from this model then can be compared to the real $\delta^{13}C_{carb}$ paleosol signal to see if it explains the variation seen.

| Parameter | Pre event | Event A | Event B |
|---|---|---|---|
| $pCO_2$ (ppmV) | 1385 | 7876 | 4264 |
| Sz (ppmV) | 3000 | 3000 | 3000 |
| $\delta^{13}C_a$ (‰, VPDB) | -3.96 | -9.90 | -9.90 |
| $\delta^{13}C_\Phi$ (‰, VPDB) | -23.03 | -29.55 | -29.55 |
| Temperature (°C) | 30 | 37 | 37 |

**Table 7.7 Input parameters for the model using equation 7.1 solved for $\delta^{13}C_r$.**

Table 7.7 shows the input parameters for the model. The pre-event values for $pCO_2$ those suggested from the Mid-Changhsingian from Russian stomatal data (Retallack and Jahren 2008). The value for $\delta^{13}C_\Phi$ was derived from the organic values from this study (see Table 7.2) and the $\delta^{13}C_a$ values were obtained from the $\delta^{13}C_\Phi$ values using equation 7.2. The temperature estimates at those predicted for the Southern Urals area by Kiehl and Shields (2005). Event A is analogous to the change in conditions suggested at the P/Tr boundary. This assumes a rise in $pCO_2$ to 7876ppmV, as observed from stomatal data, and a negative excursion of –6.42‰ in organic carbon (Retallack and Jahren 2008). It also assumes an 7°C rise in temperature as predicted from the paleosols (Chapter 5) and brachiopod shells (Chapter 6). Event B is identical to Event A however rather than $pCO_2$ = 7876ppmV at this event $pCO_2$ = 4264ppmV based on stomatal estimates for the Late Changhsingian and models the possible conditions that may have caused excursion P3.

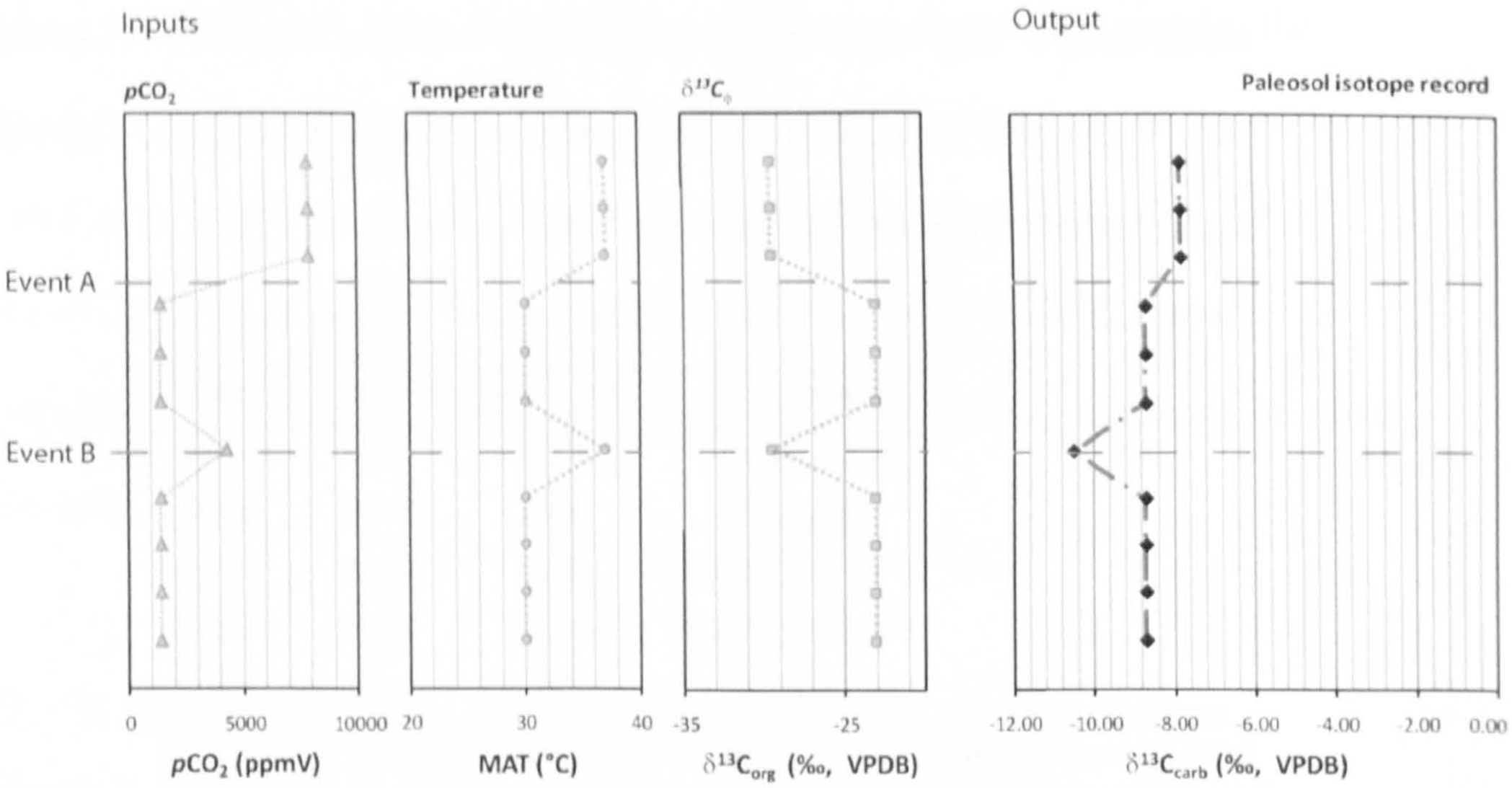


**Figure 7.5 Results from the scenario described in Table 7.7. The pCO2, Temperature and $\delta^{13}C_\Phi$ graphs show how those variables change through both events. The output graph predicts how the $\delta^{13}C$ of pedogenic carbonate would vary through both events based using equation 7.1.**

Figure 7.5 shows the results of this model. Event A, even though it includes a negative shift in $\delta^{13}C_\Phi$ and $\delta^{13}C_a$, does not produce a negative excursion in pedogenic carbonate values. Instead the massive increase in $pCO_2$ offsets this, producing a slight positive excursion of +2‰. This appears counter intuitive, but can be explained by the nature of the two component mixing model proposed by Cerling (1991) which underlies equation 7.1. This suggests there are two primary controls on the isotopic composition of pedogenic carbonate, $\delta^{13}C_\Phi$ and $\delta^{13}C_a$; as atmospheric $pCO_2$ increases there is a switch between $\delta^{13}C_\Phi$ and $\delta^{13}C_a$ being the dominant control on soil waters and thus pedogenic carbonate. In the modern world and at low $pCO_2$ values $\delta^{13}C_\Phi$ is the dominant control on the isotopic composition of soil water, but at times of extreme increases in $pCO_2$ this swaps over and thus the less negative $\delta^{13}C_a$ values dominate, producing a slight positive excursion in soil carbonates (Figure 7.6). The threshold between $\delta^{13}C_\Phi$ and $\delta^{13}C_a$ dominating, in the scenario describes in this model (Table 7.7 and Figure 7.5), is $pCO_2$ = ~6000ppmV and this explains why Event B, due to lower $pCO_2$ values (4264ppmV) shows a negative excursion rather than a positive one. In this case because $\delta^{13}C_\Phi$ is

dominating the composition of the soil water and thus the change in isotopic composition of the atmosphere is being recorded in the pedogenic carbonate.

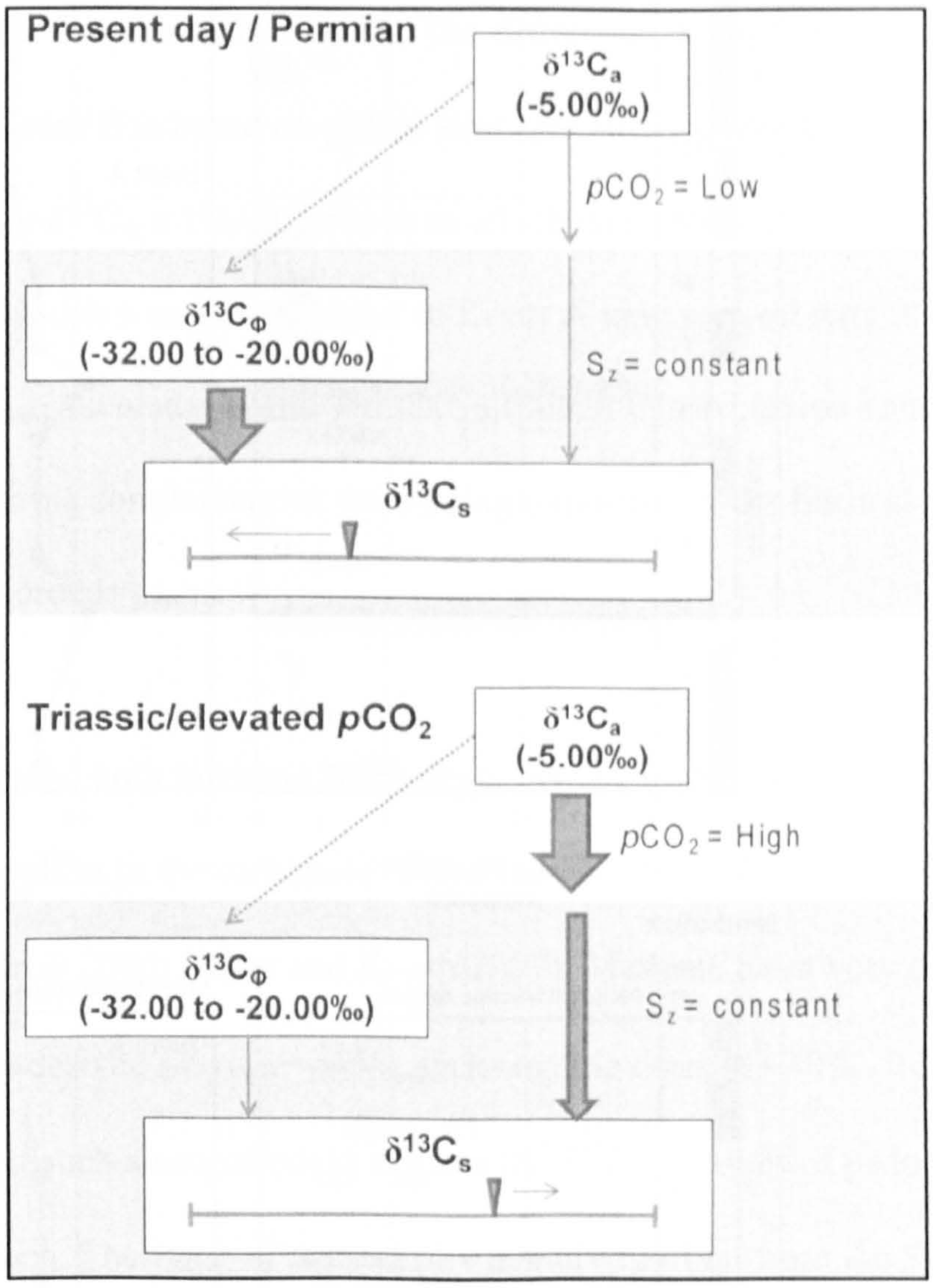


**Figure 7.6 The dominance of the two component mixing model described by Cerling (1991) and Ekart *et al.*(1999). In present day/Permian conditions (top panel) $\delta^{13}C_{\Phi}$ has dominant control over $\delta^{13}C_s$ and because $\delta^{13}C_{\Phi}$ and $\delta^{13}C_a$ are linked negative excursions in $\delta^{13}C_a$ are recorded. However, in elevated $pCO_2$ conditions $\delta^{13}C_a$ is dominant and because it is isotopically more positive than $\delta^{13}C_{\Phi}$ it appears to produce a positive shift when switching between the control of $\delta^{13}C_{\Phi}$ and $\delta^{13}C_a$.**

Like Event A (which is analogous to the P/Tr boundary), at Event B the value for the change in $\delta^{13}C_{\Phi}$ was assumed to be –6.42‰, however there is no experimental data to support this as there was no organic carbon recovered from the excursion P3 or any global values from elsewhere from which to model this event. It is equally possible to produce such results as modelled in Event B by the input of the same amount of $CO_2$ but a more isotopically negative source for that $CO_2$.

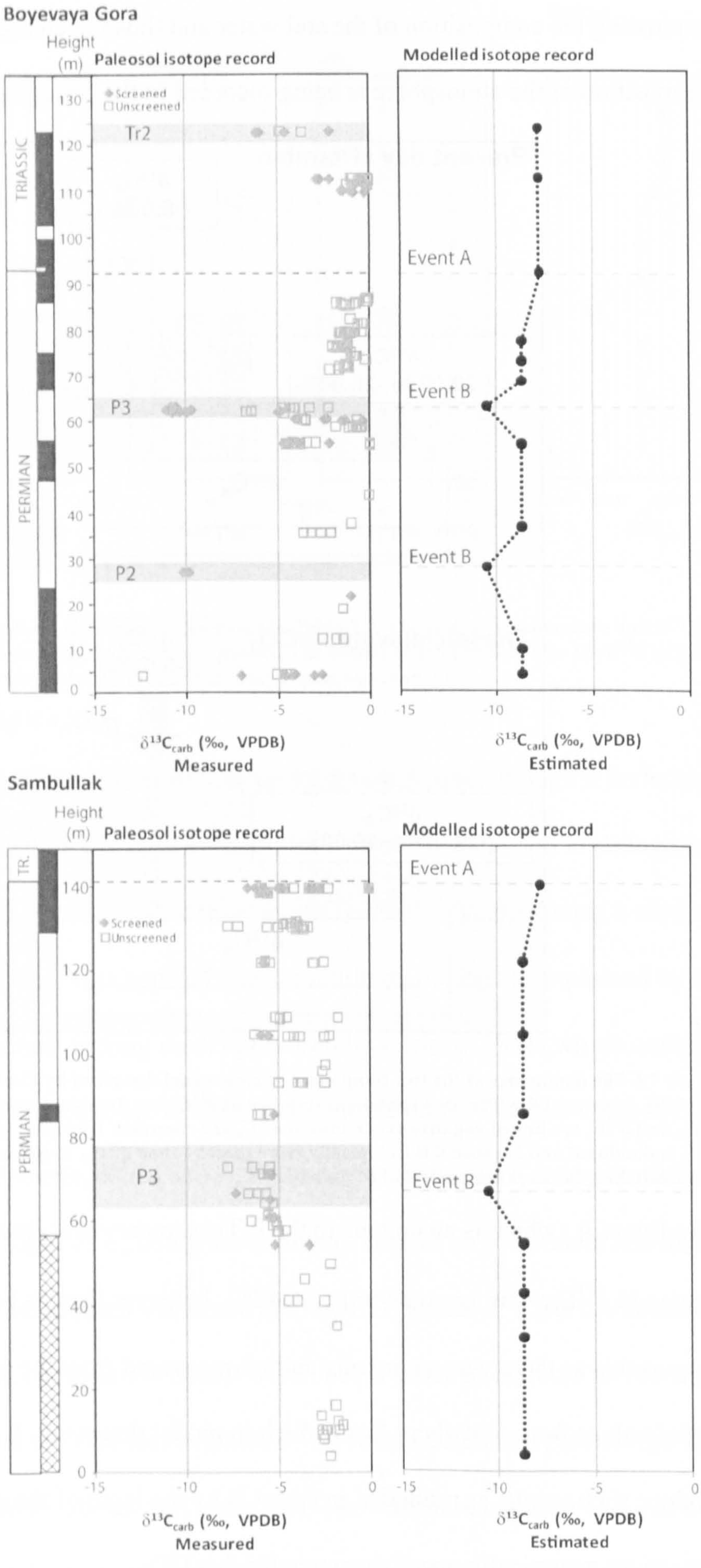


**Figure 7.7 Comparison of modelled $\delta^{13}C_{carb}$ values using the parameters in Table 7.7 with recorded $\delta^{13}C_{carb}$ values from Boyevaya Gora and Sambullak. The change across the P/Tr boundary was modelled as an Event A while P2 and P3 were modelled as Event B excursions. Note excursions P4 and Tr1 are not shown as they are only recorded in the $\delta^{18}O_{carb}$ values.**

Comparing these modelled values with the measured isotope record from the Russian sections (Figure 7.7) suggests that a scenario similar to that suggested in Event B may be responsible for excursions P2 and P3. The difference in absolute values may be due to the fact that Event B is based on global averages and does not take in to account local variations in $S_z$ or $\delta^{13}C_{\Phi,}$ a 1‰ difference in which can alter the predicted $\delta^{13}C_{carb}$ value by ~1‰. Equally, this a scenario similar to Event A may suggest why there is no prominent $\delta^{13}C_{carb}$ excursion in the Triassic, although this excursion could occurred at the same time as the conglomerates were being deposited in the Earliest Triassic and thus was not recorded.

As previously stated both methane and volcanogenic $CO_2$ have been proposed as causes of negative anomalies in the carbonate record (Erwin 1993; Kidder and Woresley 2004; Retallack and Krull 2006; Payne and Kump 2007). Methane has a very negative $\delta^{13}C$ value (clathrates derived average –60‰; thermogenic derived –40‰, Retallack and Jahren 2008) and such a source could explain the $\delta^{13}C_{carb}$ values of pedogenic carbonate observed in Russia. The input of isotopically negative carbon from the Siberian Traps has also been postulated as a cause of the negative anomalies (e.g. Payne and Kump 2007) However, others have argued that volcanogenic emissions have an isotopic value of –5‰, which is close to the predicted atmospheric values of the Permian atmosphere (Retallack and Jahren 2008, Table 7.4). Thus, however much volcanic $CO_2$ is introduced into the atmosphere, it could not have caused the negative shift in atmospheric isotopic values (Retallack and Jahren 2008). This value of –5‰ is based on data collected from highly fractionated fumaroles at Mauna Loa in Hawaii in the 1950s (Faure 1986; Hansen 2006 and references therein). Hansen (2006) argues that $CO_2$ sampled directly from lava flows has a value of –24‰ ±2‰ and carbon recovered from lava flows, including the Deccan Traps from $CO_2$ in the lava, has values of between

−24.1‰ and −27.8‰. These more negative values could also be responsible for a negative excursion in $\delta^{13}C_{\Phi}$ of −6.42‰ assuming enough $CO_2$ is released.

The modelling of the isotope signal (Table 7.7 and Figure 7.5) shows that it is possible to explain why a dramatic rise in $pCO_2$ caused by input of isotopically negative $CO_2$ may not produce a negative excursion in the $\delta^{13}C_{carb}$ values of pedogenic carbonate. Also it suggests that the negative excursions seen in the pedogenic carbonate record in, such as P2 and P3 relate to either lesser inputs of $CO_2$ in to the atmosphere than at the P/Tr boundary, or they were caused by a different source which was more isotopically negative than that the source which caused the rise in $pCO_2$ observed at the P/Tr boundary.

## 7.4 Summary

There is much variation even between methods of generating the variables in the $pCO_2$ equation (7.1) and between and within individual paleosols. This variability must be considered when interpreting and using the $pCO_2$ estimates, as they are exactly that – estimates. With this consideration in mind there are several conclusions that can be drawn from the $\delta^{13}C_{carb}$ and $pCO_2$ modelling of the data from Boyevaya Gora and Sambullak.

1) There appears to be a dramatic rise in $pCO_2$ in the earliest Triassic which appears to be consistent with stomatal records of a similar age from Russia (Retallack and Jahren 2008). Although the extreme variation seen between methods may suggest the environment was not in equilibrium or that one of the other factors in the equation are not being accurately modelled.

2) The negative excursions (P2 and P3) observed at Boyevaya Gora and, to a lesser extent Sambullak, could be explained by a rise in $pCO_2$, but only if there is a

corresponding drop in the isotopic composition of organic carbon ($\delta^{13}C_{\Phi}$) at the same point in time.

3) A negative $\delta^{13}C$ excursion in the atmosphere will not necessarily cause a negative excursion in the $\delta^{13}C_{carb}$ record of pedogenic carbonate if it coincides with a dramatic rise in $pCO_2$ which is big enough to change the dominant control on the isotopic composition of pedogenic carbonate.

# Chapter 8. Global comparisons

## 8.1 Introduction

In recent years there has been a move to correlate the various isotope records from around the globe across the Permian/Triassic boundary with a view to understanding how these events may have related to the mass extinction (deWit *et al.* 2002; Kidder and Worsley 2004; Erwin *et al.* 2006). There have also been attempts to map these anomalies, especially the $\delta^{13}C$ anomaly, to understand how the isotope excursions vary globally (Retallack and Krull 2006; Retallack and Jahren 2008). It has been suggested that the carbon isotope excursion is greater on land than in the sea (Retallack and Krull 2006; Retallack and Jahren 2008) and is more pronounced at high latitude than at low latitude (Krull *et al.* 2000; Krull *et al.* 2004; Retallack and Krull 2006; Retallack and Jahren 2008). It is important to understand how the new results from Russia and the Italian Dolomites fit into this emerging global picture.

It has been proposed that the mechanism which records the isotope signature in the material being analysed may also control the distribution or reason for the isotope anomaly. For instance marine carbonate values represent time averaging over millennia (Retallack and Jahren 2008); and paleosol carbonate nodules are thought to re-equilibrate isotopically through the time that a paleosol is active (Liu *et al.* 1996) and thus also represent an averaged signal. Organic carbon from terrestrial sections, on the other hand, records local annual–decadal values (Retallack and Krull 2006; Retallack and Jahren 2008). The same is true for carbonate isotope values recovered from vertebrate teeth and tusks (MacLeod *et al.* 2001).

The mechanisms that have been cited as causing the isotopic anomalies are different in different facies and sections. Marine carbonate and marine fossils are influenced by inputs of

organic carbon from land and influxes of anoxic bottom waters, along with direct changes in atmospheric chemistry (Hallam and Wignall 1997; Foster *et al.* 1997; Sephton *et al.* 2005; Algeo *et al.* 2007). Similarly, pedogenic carbonate can be influenced by changes in waterlogging (Tarbor *et al.* 2007), groundcover and meteoric source (Quast *et al.* 2006, see Chapter 5) as well as atmospheric changes. Even organic carbon, although thought to relate directly to the $\delta^{13}C$ composition of the atmosphere (Arens *et al.* 2000), can also be affected by changes in plant productivity, amount of wood and physiology (Foster *et al.* 1997; Krull and Retallack 2000; Retallack and Krull 2006).

With such varied potential influences controlling the isotope signal, knowing the relative timing of anomalies is imperative to understand and test proposed extinction mechanisms. For instance, if the marine $\delta^{13}C$ excursion is controlled by input of terrestrial organic material into the sediment caused by a die-off of land plants due to the terrestrial extinction (Foster *et al.*1997; Visscher *et al.* 2004; Sephton *et al.* 2005) then it must post-date the terrestrial $\delta^{13}C$ excursions as these are more likely to have been directly caused by changes in the atmospheric chemistry or plant cover. However, relative durations and sedimentation rates may make excursions appear synchronous without comprehensive stratigraphic control.

There is also debate over whether the excursion comes before or after the mass extinction event (Gorjan *et al.* 2008). In some localities, such as Jameson Land in Greenland, the $\delta^{13}C$ excursion occurs after the mass extinction (Looy *et al.* 2001; Twitchett *et al.* 2001) and is due either to changes caused by the mass extinction (as discussed in Chapter 7) or a mechanism which had little or no affect on the biotic crisis (Twitchett *et al.* 2001). However, there are other examples (e.g. Musashi *et al.* 2001; Dolenec *et al.* 2001; Krull *et al.* 2004) where the

extinction postdates the $\delta^{13}C$ excursion, suggesting that the excursion itself is linked to the cause of the mass extinction rather than the consequence.

Finally, there have been other $\delta^{13}C$ excursions observed below the excursion coincident with the P/Tr boundary. In northern Xinjiang in China two episodes of $\delta^{13}C$ depletion have been observed in the organic carbon in terrestrial and marine sequences (Cao *et al.* 2008; Hansen 2000). These have also been observed in Nelben in Germany 1 metre below the P/Tr excursion which has been correlated with the lower excursion seen at Xinjiang (Hansen *et al.* 2006). These excursions pre-date the P/Tr boundary excursions and are thought to be caused by onset of the latest Permian environmental stress linked to changes in the isotopic composition of the atmosphere (Cao *et al.* 2008). It must be remembered, however, that at the Global Stratotype Section and Point (GSSP) in Meishan the extinction occurs below the P/Tr boundary as defined by the FAD of *Hindeodus parvus*. There have also been $\delta^{13}C$ excursions observed in terrestrial and marine, organic and carbonate records coincident with the end-Guadalupian event (Retallack *et al.* 2005; Retallack *et al.* 2006). These have been observed in Karoo, Antarctica, Australia, Greece, and Slovenia and are thought to be caused by a mass methane release similar to the P/Tr boundary event (Retallack *et al.* 2006).

It is important to determine how the data from the Russian paleosols and Italian brachiopods fit within this global framework, especially with reference to how the isotope excursion observed in the mid-Changhsingian in Russia relates to the other global sections. Also, to track the changes in the environmental conditions, mean annual precipitation (MAP) and other climatic proxies will be compared to other paleosol sections from Antarctica (Retallack and Krull 1999), Australia (Retallack 1999) and the Karoo basin (Retallack *et al.* 2003). These will be used to test how the Russian excursions correlate with others and with the

Siberian Traps which are a proposed mechanism for the mass extinction (Erwin 1993; Kamo *et al.* 2003; Grard *et al.* 2005; Beerling *et al.* 2007; Payne and Kump 2007).

## 8.2 P/Tr Global correlations and stratigraphy

There are three main methods used to correlate between different Permian/Triassic sections: biostratigraphy (including conodonts, ammonoids, vertebrates and palynomorphs, see Gradstein and Ogg 2004), chemostratigraphy (matching the carbon isotope records, e.g. Retallack and Krull 2006; Retallack *et al.* 2006; Retallack and Jahren 2008) and magnetostratigraphy (e.g. Jin *et al.* 2000; Steiner 2006). Each technique has its own advantages and drawbacks, especially at times of mass extinction when fossil geographical ranges can change dramatically before they go extinct; isotope excursions can be caused by either the effects or the causes of the extinction, and erosion caused by facies changes associated with the extinctions (e.g. Ward *et al.* 2000; Benton *et al.* 2004) can remove magnetochrons.

The first appearance datum (FAD) of the conodont *Hindeodus parvus* was agreed as the marker for the base of the Triassic (Paull and Paull 1994; Yin *et al.* 2001) due to its global occurrence in both shallow and deep water facies (Yin *et al.* 2001). The GSSP was defined as the first appearance of the conodont *H. parvus* in bed 27c at Meishan section D in Changxing County in South China where the boundary is sandwiched between ash layers which can be used to date it at 251.0±0.4 Ma (Bowing *et al.* 1998; Gradstein *et al.* 2004). Since the definition of the GSSP newer U/Pb dates for the boundary at Meishan and terrestrial sections at Chahe (Guizhou Province in China) date main pulse of the extinction at 252.6 ±0.2 Ma and 252.6 ±2.8 Ma (Mundil *et al.* 2004; Yu *et al.* 2008). It was proposed that the $\delta^{13}C$ excursion

could act as an auxiliary marker for the P/Tr Boundary (Yin *et al.* 2001), although the excursion occurs below the FAD of *H. parvus* (Gradstein *et al.* 2004).

In terrestrial sediments, however, *Hindeodus parvus* cannot be used. As a result correlating terrestrial P/Tr stratigraphy with both marine sections and other global terrestrial sections is still problematic. As with the marine sections the extinction event appears to occur at dramatic a facies change. This manifests as a change from fluvial meandering rivers to coarse braided rivers which have been observed in the Southern Urals (Newell *et al.*1999; Benton *et al.* 2004), in the Karoo in South Africa (Ward *et al.* 2000), in Antarctica (Retallack 2005a; Retallack *et al.*2006; Retallack *et al.*2007) and Australia (Michaelsen 2002) (see Chapter1, Figure1.1 for palaeogeographical locations). There is also a global hiatus in coal formation and preservation at the P/Tr representing a dramatic change in the environment (Faure *et al* 1995, Retallack and Krull 2006). Although these changes are all attributed to be results of the extinction mechanism, it is hard to say whether these facies changes all occurred at one time or are diachronous and thus if the extinction influenced different latitudes and localities at different times.

Unlike the marine sections there is no global biomarker for terrestrial sections, thus correlations are far more complicated. The boundary is often defined by the last occurrence of the Permian zonal index fossil *Dicynodon* and the first occurrence of the vertebrate *Lystrosaurus* (Ward *et al.* 2005, Retallack *et al* 2005). However, Ward *et al.* (2005) have identified that, in the Karoo Basin in South Africa, *Lystrosaurus* is found in the *Dicynodon* zone. They explain this by suggesting that Triassic vertebrate fauna may have pre-dated the main Permian extinction pulse, similar to the pattern of mammalian radiation after the Cretaceous–Palaeogene extinction. An alternative hypothesis is that there was a migration of

the reptilian and amphibian fauna from South Africa to Antarctica in the Early Triassic (Collinson *et al.* 2006). Either way, this overlap causes great problems for correlative purposes as it is not seen in other world sections such as Antarctica (Collinson *et al.* 2006). Also, to date, *Lystrosaurus* has not been found in the Southern Urals (Russia) or in Australia (Retallack *et al.* 2005, Benton *et al.* 2004). Also, the use of *Dicynodon* as Late Permian zone fossil has been questioned due to its confusing taxonomic history and possible polyphyletic nature of the clade (Angielczyk and Kurkin 2003).

The other issue with using terrestrial vertebrates is that within terrestrial sedimentary sequences fossils can be scarce. For instance, at Boyevaya Gora in Russia, the first Triassic tetrapods are found within the basal strata of the Triassic as defined by magnetostratigraphy (Taylor *et al.* 2009), while the last Permian tetrapods and fishes are 22 metres below this point (Taylor *et al.* 2009). This can cause large areas of uncertainty and compound any issues resulting from extinction-induced migrations and localised extinction.

Palynology has also been used to correlate Indian and Madagascan terrestrial sections across the P/Tr boundary. However, in both these cases the pollen could only be used to identify the extinction within a basin rather than correlating between basins (de Wit *et al.* 2002). *Protohaploxypinus microcorpus* was used by Morante (1996) to define the P/Tr boundary in Australia. It has also been found in sections in Antarctica where it also occurs one metre above the last occurrence of *Glossopteris* fossils, which have been used locally to define the top of the Permian (Collinson *et al.* 2006, Retallack *et al.* 2005). In the Karoo Basin the top of the *P. microcorpus* biozone occurs over 20 metres above the major faunal extinction, just before the 'fungal spike' (Ward *et al.* 2005, Steiner *et al.* 2003).

The use of the $\delta^{13}C$ excursion itself as a chemostratigraphic marker has also been suggested as a global correlative tool between marine and terrestrial sections because the surface ocean mixes on a $10^4$yr cycle and is in dynamic equilibrium with the atmosphere (MacLeod *et al.* 2000; Yin *et al* .2000). Thus, a global $\delta^{13}C$ excursion should be geologically simultaneous in terrestrial and marine sections (MacLeod *et al.* 2000). This technique has been used globally to correlate both marine and terrestrial sections (Retallack *et al.* 2006; Retallack and Krull 2006; Retallack and Jahren 2008).

However, this technique too has its drawbacks. Firstly, as with biostratigraphy, it assumes that the major extinction event occurred at the same time globally and that the excursion is geologically instantaneous. It has been observed that globally the excursion occurs both before and after the extinction event depending on locality (Gorjan *et al.* 2008) suggesting that at least one of these events is diachronous. Secondly, it only provides a datum on which to hang sections and gives little control over how time varies through a section. It has been suggested that there is a negative $\delta^{13}C$ excursion related to the end Guadalupian and this may be used as a lower correlative tool (Retallack *et al.* 2006). Finally, it has been suggested that some negative excursions are due to local factors and not global atmospheric changes (Tabor *et al.* 2007). Also, chemostratigraphy only works if both the marine and terrestrial $\delta^{13}C$ excursions are caused by the same mechanism (e.g. mass methane release or a volcanic eruption), or if the marine excursion is caused by influx of terrestrial organic matter (Foster *et al.* 1997; Visscher *et al.* 2004; Sephton *et al.* 2005).

All the techniques mentioned thus far are either biological or environmental, so are likely to be affected by an extinction event in different ways, such as migration of ranges and changes in facies. Magnetostratigraphy, however, reflects the changes in the polarity of the Earth's

magnetic field and thus should not be affected by the mass extinction event so providing an unbiased correlative tool. Equally, as reversals in polarity are typically less than 5000 years and are potentially recorded simultaneously globally, this is the most precise method available for global correlation (Ogg and Smith 2004). There have been several interbasinal magnetostratigraphic correlations between marine and terrestrial sections across the Permian/Triassic boundary (e.g. Szurlies *et al.* 2003; Molostovskii 2005; Szurlies 2007; Hounslow *et al.* 2008) and global correlations (e.g. Jin *et al.* 2000; Kozur and Bachmann 2005; Steiner 2006). Therefore, magnetostratigraphy should be a primary candidate for correlating between terrestrial sections and marine sections.

There are, however, issues with using magnetostratigraphy. Firstly, major terrestrial sections, such as Antarctica, do not have a reliable magnetostratigraphic record because of heating of the rocks by Jurassic diabase sills (Collinson *et al.* 2006). Likewise, it is suggested that the Karoo basin magnetostratigraphic record may have been affected by later diagenetic fluids and magmatic intrusions (de Wit *et al* 2002). Secondly, without corroborating fossil data it is possible to produce very different interpretations of magnetostratigraphic correlations such as for the Siberian Traps (compare Steiner 2006 and Dobretsov *et al.* 2007).

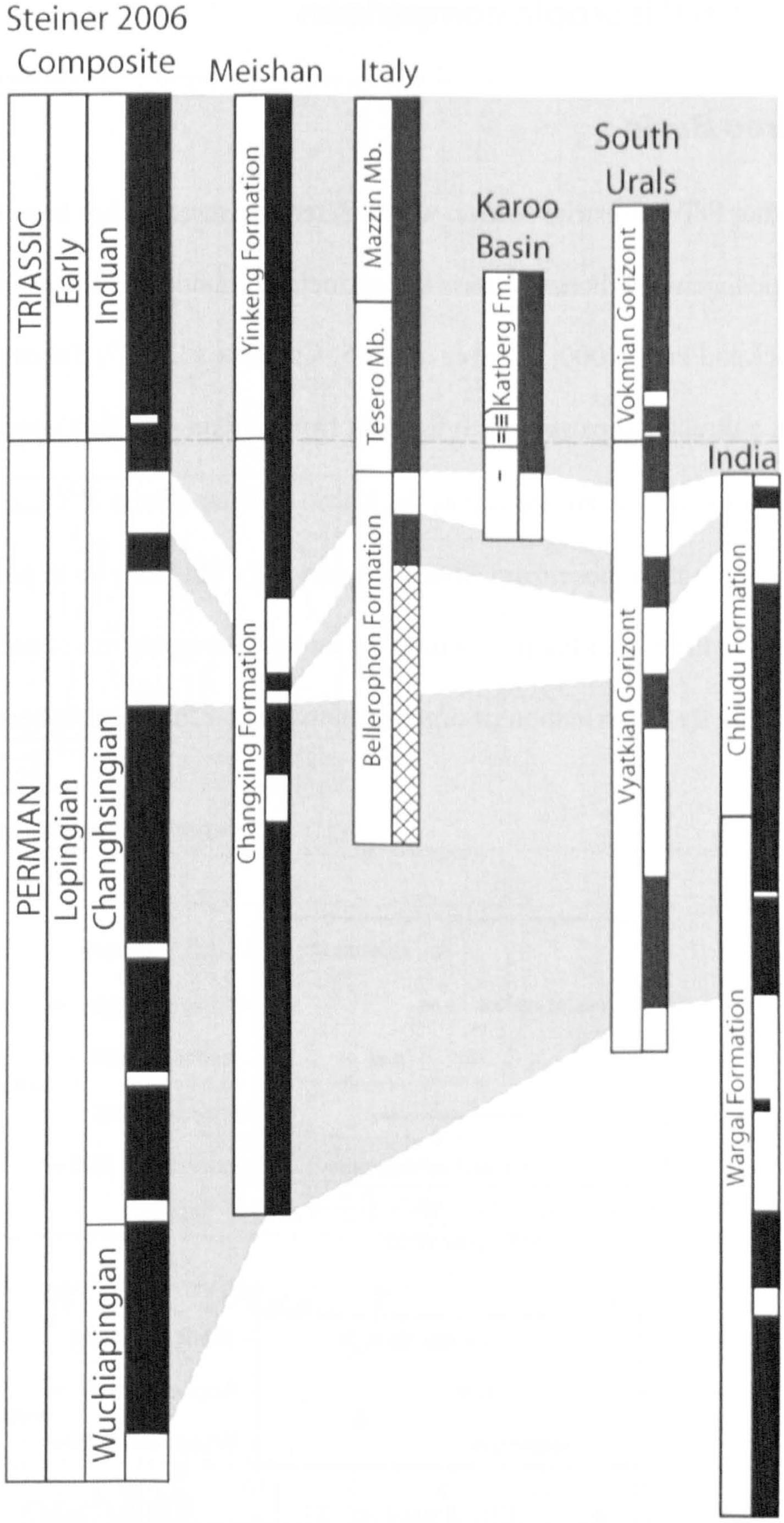


**Figure 8.1 Magnetostratigraphic correlations used in this study. Correlations between sections from Steiner 2006 apart from the South Urals which was based on the correlation of Taylor *et al.* (2009) to Steiner's composite.**

## 8.3 Terrestrial isotopic comparison

### *8.3.1 Karoo Basin*

The only other P/Tr terrestrial section where extensive research has been undertaken in relation to pedogenic carbonate across the extinction boundary is the Karoo Basin in South Africa (MacLeod *et al.* 2000; Ward *et al* 2005; Coney *et al.* 2007; Tabor *et al.* 2007) and thus can provide a direct comparison with the data from Russia. The first observation that can be made from these isotope studies is that the Karoo nodular calcite $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values are more negative than those from Russia (Figure 8.2). This may be in part due to waterlogging in the Karoo Basin in which the isotopic composition of carbonate nodules is controlled more by the oxidation of organic matter rather than atmospheric changes (Tabor *et al.* 2007).

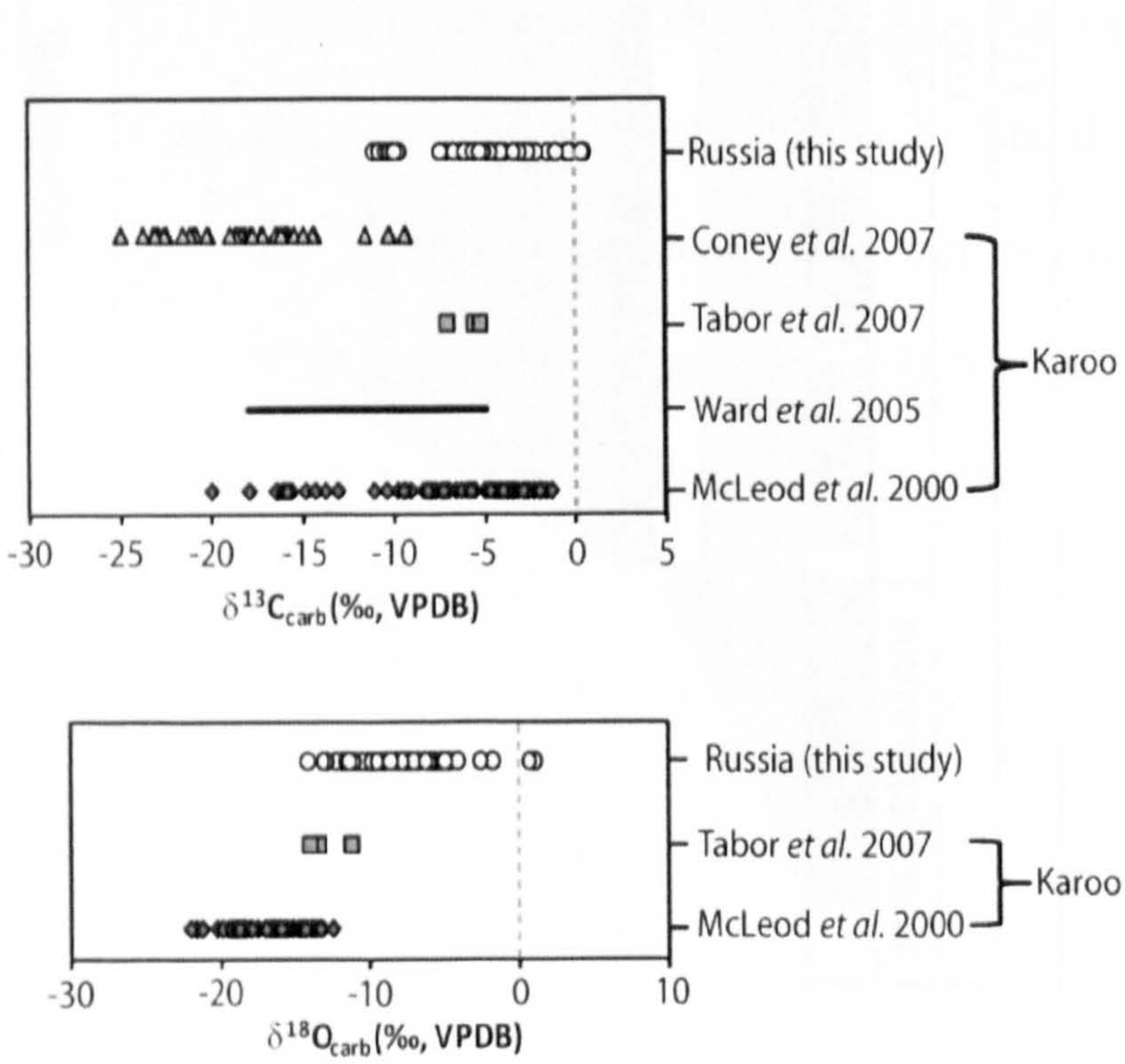


**Figure 8.2 The ranges of other pedogenic carbonate studies across the Permian-Triassic boundary from the Karoo basin. Note the bar representing the values from Ward *et al.* (2005) is the range of values rather than the exact data points as these were not published. All the other values refer are those described as being 'primary and unaltered' by the papers from which the data are from.**

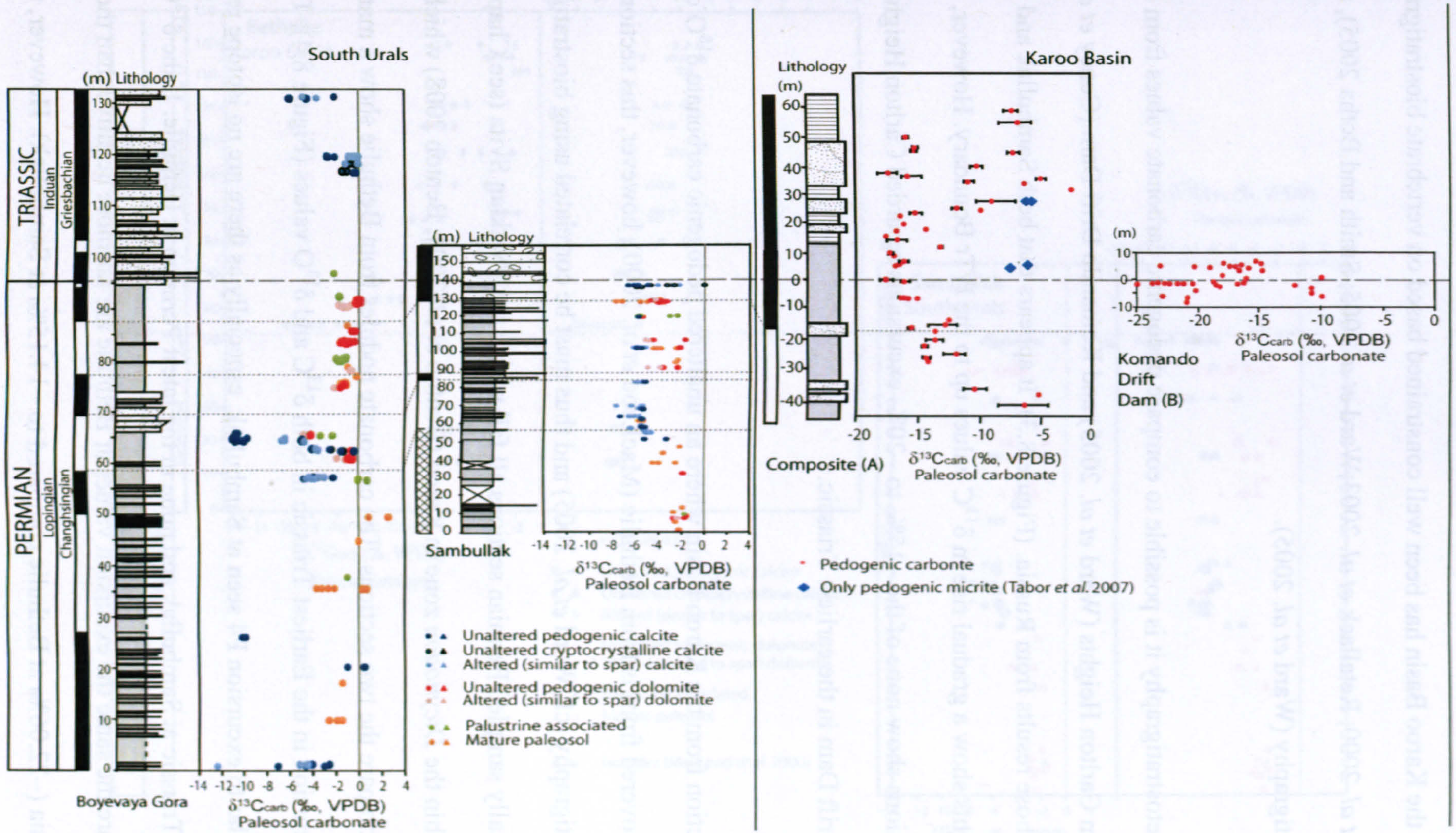


**Figure 8.3 Pedogenic carbonate nodules from Russia (this study) and the Karoo basin (South Africa) correlated using magnetostratigraphic data (correlation based on Steiner 2006). A is the composite carbonate record of Ward *et al.* (2005) and their magnetostratigraphic data. Super imposed on this are micritic nodule values from Tabor *et al.* (2007) (blue diamonds) from Carlton heights. B are data from Komando Drift Dam recorded by Coney *et al.* (2007) correlated using magnetostratigraphic data from Ward *et al.* (2005).**

When comparing the different isotope patterns observed in the Karoo region with Russia it is essential to understand how far in to the Permian the Karoo sections extend. The P/Tr boundary in the Karoo Basin has been well constrained based on vertebrate biostratigraphy (MacLeod *et al.* 2000; Retallack *et al.* 2003;Ward *et al* 2005; Smith and Botha 2005), and magnetostratigraphy (Ward *et al.* 2005).

Using magnetostratigraphy it is possible to compare pedogenic carbonate values from the sections from Carlton Heights (Ward *et al.* 2005) and Komando Drift Dam (Coney *et al.* 2007) with those results from Russia. (Figure 8.3). It appears that both Sambullak and Carlton heights show a gradual rise in $\delta^{13}C$ values up to the P/Tr Boundary. However, the Russian sections show none of the –15‰ to –20‰ excursions recorded Carlton Heights and Komando Drift Dam in the earliest Triassic.

The only section from the Karoo Basin where an unaltered pedogenic carbonate $\delta^{18}O$ curve has been recovered from is from Bethulie (MacLeod *et al.* 2000), however, this section lacks magnetostratigraphy (cf. Ward *et al.* 2005) and thus must be correlated using biostratigraphy. The isotopically sampled Permian sections all fall within the Vyatkian Svita (see Chapter 3) which is within the *Dicynodon* zone in Karoo (Benton *et al.* 2004; Benton 2008) which can be used to compare the two sections  The carbonate nodules from Bethulie show a marked negative excursion in the Earliest Triassic in both $\delta^{13}C$ and $\delta^{18}O$ values (Figure 8.4). This may be similar to excursion P4 seen at Sambullak, especially as there are no isotope results in the Earliest Triassic at Sambullak and none in the latest Permian at Bethulie. If the $\delta^{18}O$ excursions are the same the excursion values at Bethulie are far more negative than those seen in Russia (–22.06‰ at Bethulie compared to –14.15‰ at Sambullak). However, the excursion at Sambullak (–6.76‰) is greater than that recorded at Bethulie (–4.98‰).

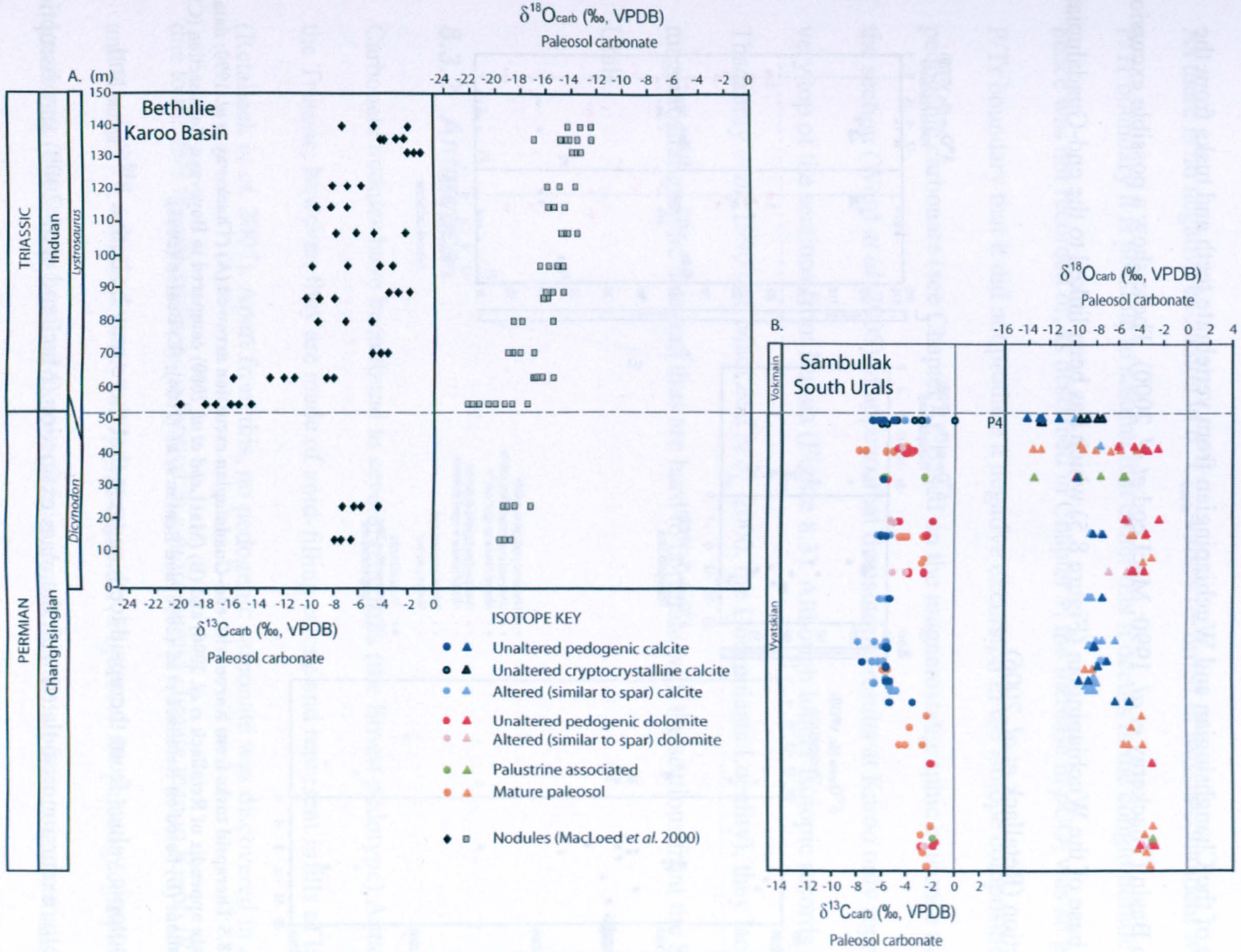


**Figure 8.4 Pedogenic nodules from Bethulie section from the Karoo Basin (MacLeod *et al.* 2000) and Sambullak from the Southern Urals.**

None of the sections which have had pedogenic carbonate analysis results extend far down into the Permian and thus are unlikely to contain the mid-Changhsingian excursion (P3) observed at Boyevaya Gora and Sambullak. There are, however, isotopic records spanning the whole of the Changhsingian and Wuchiapingian from vertebrate teeth and tusks from the Karoo Basin (Thackeray *et al.* 1990; MacLeod *et al.* 2000). These show a possible excursion at the base of the Wuchiapingian (Figure 8.5) which has been linked to the end-Guadalupian extinction (Retallack *et al.* 2006). .

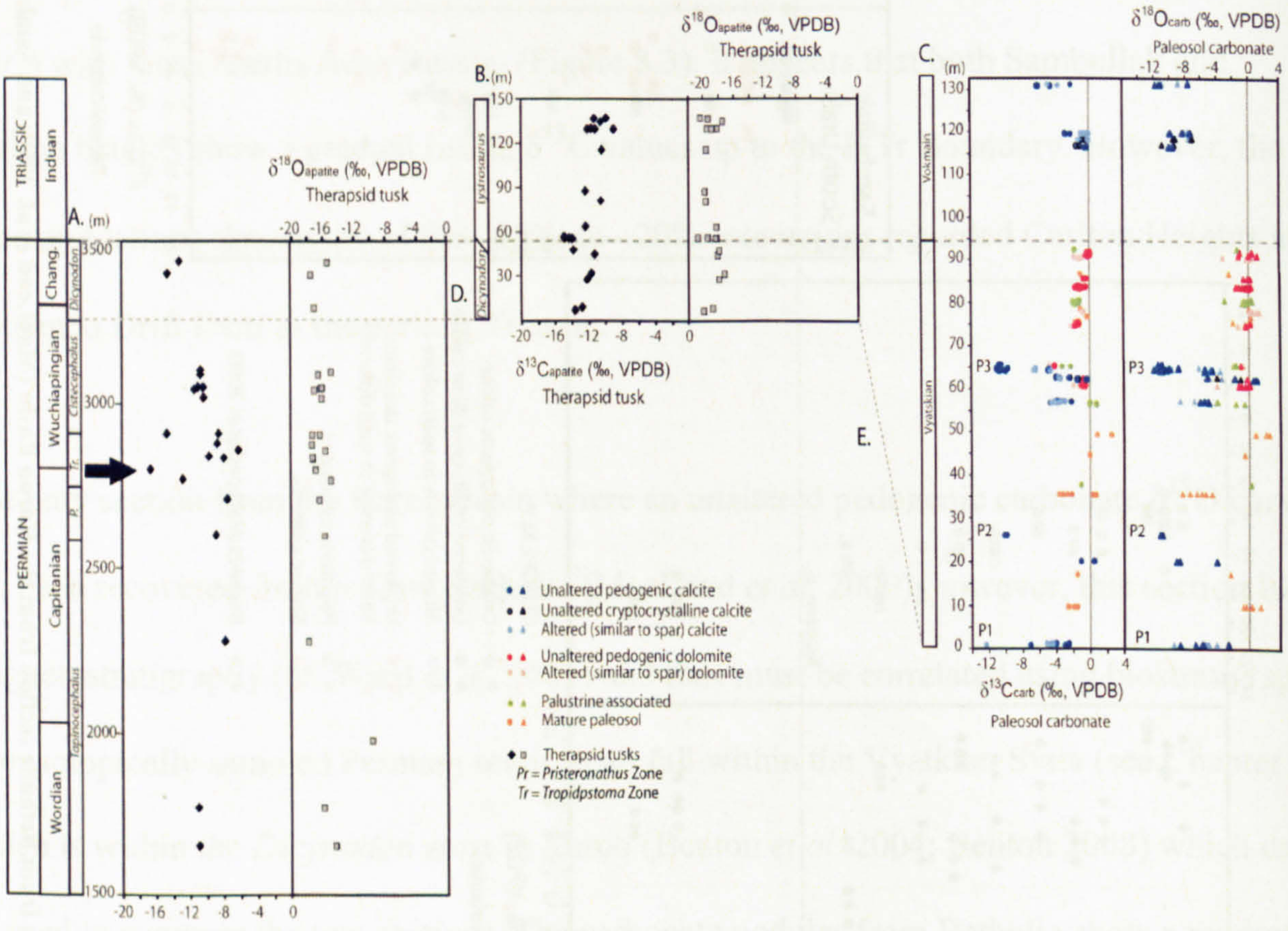


**Figure 8.5 Therapsid tusks from Karoo with end-Guadalupian excursion arrowed (A) (Thackeray *et al.* 1990; data from data appendix of Retallack *et al.* 2006) and (B) (MacLeod *et al.* 2000) compared to Boyevaya Gora section (C). Correlations (D) based on Retallack *et al.* (2006) and Benton *et al.* (2004); (E) Benton (2008).**

The isotopic values from therapsid teeth suggest that there may be both a $\delta^{13}C_{apatite}$ and $\delta^{18}O_{apatite}$ excursion associated with the mass extinction (MacLeod *et al.* 2000) and disruption in the $\delta^{13}C$ values throughout the *Dicynodon* zone (Thackeray *et al.* 1990). However, there is no evidence of any excursions in the Changhsingian to correspond with those seen in Russia, although there are only 10 analyses for this interval (Figure 8.5). Equally it is evident that the

negative $\delta^{13}C$ and $\delta^{18}O$ anomaly associated with the end-Guadalupian (Retallack *et al.* 2006) event is below the base of the Russian sections.

As there is no negative excursion in $\delta^{13}C_{carb}$ values recorded in Russia coincident with the P/Tr boundary it is possible to assume that either this it occurs in the conglomeratic units and hence was not recorded or, as described in Chapter 7, the increase in $pCO_2$ was so great at the P/Tr boundary that it did not produce a negative excursion in the isotope composition of the pedogenic carbonate (see Chapter 4). Based on the magnetostatigraphic evidence available for the section (Ward *et al.* 2005), it appears that the isotopic results at Karoo only represent the very top of the sections from Russia (Figure 8.3). Although longer isotopic records exist (e.g. Thackeray *et al.* 1990 and MacLeod *et al.* 2000, the Doornplaats Locality), they lack magnetostratigraphic data and thus are hard to correlate with the sections from the Southern Urals.

### *8.3.2 Antarctica*

Carbonate nodules have been found in several paleosols (the Ernest pedotype) Antarctica in the Triassic; however, they are made of void-filling calcite and represent infills of large vugs (Retallack *et al.* 2007). Apart from this, no pedogenic carbonate was discovered in Antarctica due to the fact the paleosols were formed in a more humid climate than in Karoo (Retallack and Krull 1991; Retallack *et al.* 2007) (see Chapter1, Figure1.1 for palaeogeographical locations). The isotopic values recovered from Antarctica are all from organic matter contained in the paleosol (Krull and Retallack 2000; Retallack *et al.* 2005; Retallack and Krull 2006; Retallack *et al.* 2006 Retallack *et al.* 2007, see Chapter1, Figure1.1) and thus cannot be directly compared to those from Russia. The organic carbon recovered from Sambullak (Chapter 7) has an average of $\delta^{13}C_{org}$ –23.03‰ (±1.32, 1σ std), which is similar to the organic

carbon values observed in the Permian in Antarctica (Krull and Retallack 2000; Retallack *et al.* 2005; Retallack and Krull 2006; Retallack *et al.* 2006 Retallack *et al.* 2007).

The $\delta^{13}C_{org}$ record from Antarctica is marked by a dramatic isotope anomaly just before the P/Tr boundary (as defined by Collinson *et al.* 2006) of values as negative as –46.2‰ in the Graphite Peak section (Krull and Retallack 2001). This marks the start of a period of negative excursions in the earliest Triassic which last for about 10ky (Krull and Retallack 2000; Retallack *et al.* 2006; Retallack and Jahren 2008). There is also evidence of a Permian $\delta^{13}C_{org}$ isotope anomaly of up to –16‰ in several of the sections in Antarctica which has been related to an atmospheric disturbance related to the end-Guadalupian mass extinction event (Krull and Retallack 2000; Retallack and Krull 2006; Retallack *et al.* 2006, Figure 8.6).

These variations in $\delta^{13}C_{org}$ values from the paleosols are greater than anything that could be caused by either waterlogging or plant variation (cf. Arens *et al.* 2000). It is assumed that they must be documenting atmospheric $\delta^{13}C$ values or the reaction of methanotrophic bacteria (Krull and Retallack 2000). As discussed earlier, it is thought that the isotopic composition of $C_3$ organic matter from soils is directly related to the isotopic composition of the atmosphere rather than the influence of physiological or local factors (Arens *et al.* 2000). Therefore, as the $\delta^{13}C_{org}$ values in Antarctica are reacting to changes in atmospheric carbon, as are the $\delta^{13}C_{carb}$ values of pedogenic carbonates from Russia, it should be possible to compare the excursions between the two sections.

As previously stated there are no magnetostratigraphic data available for Antarctica (Collinson *et al.* 2006) so precise comparison of the Antarctic results with those from Russia is difficult.

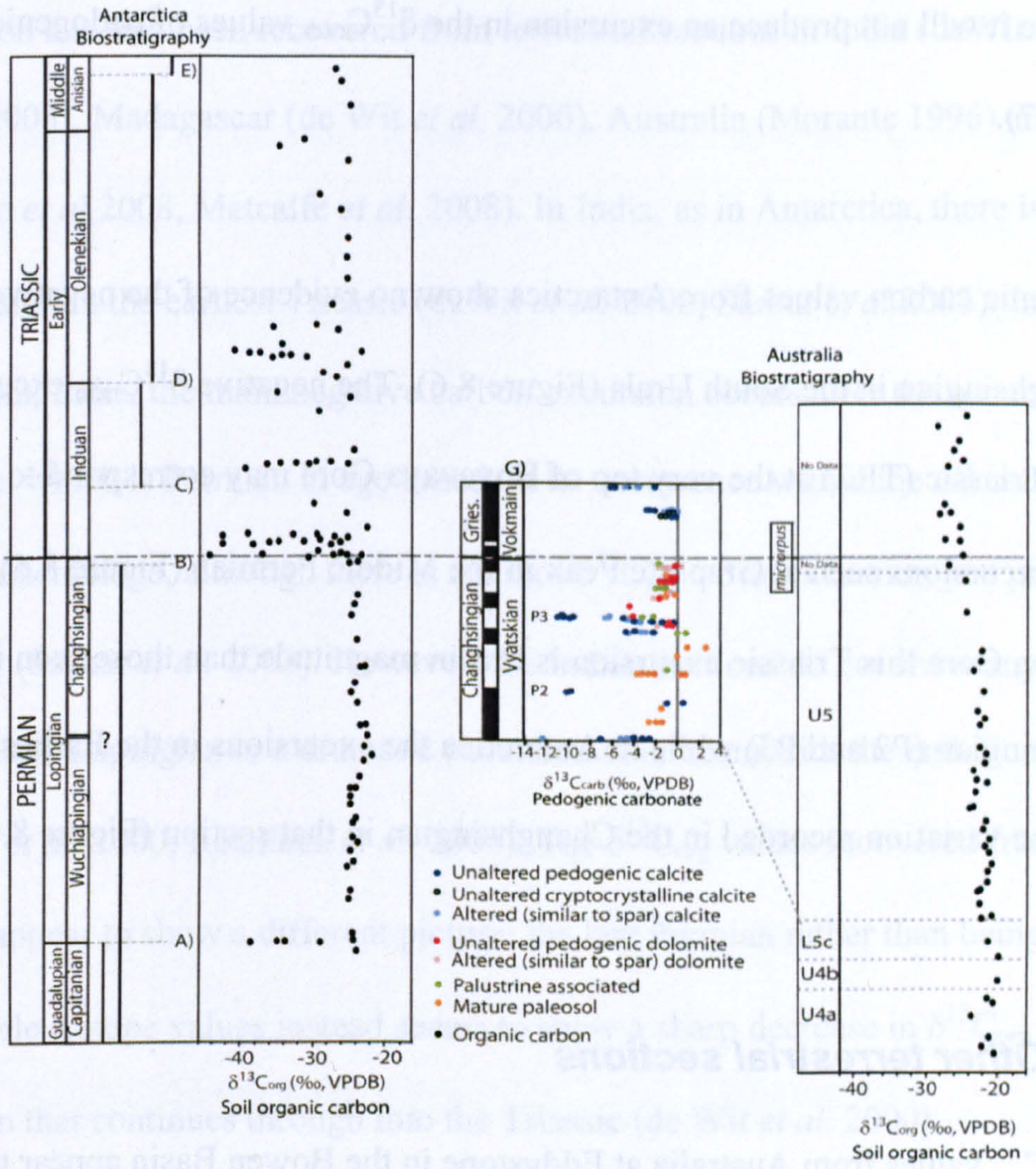


**Figure 8.6 Organic carbon values from Graphite peak in Antarctica (Krull and Retallack 2001, left panel) and Eddystone Australia (Morante 1996) compared to Boyevaya Gora in Russia. Antarctica Biostratigraphy: A) Last occurrence of *Gangamopteris cyclopteroides* and *Palaeovittaria kurtz*i (Retallack and Jahren 2008), B) Last occurrence of *Glossopteris* and *Vertebraria* (Krull and Retallack 2000) C) Last occurrence of *Lystrosaurus* (Krull and Retallack 2000) D) First occurrence of *Dicroidium zuberi* (Krull and Retallack 2000). E) First occurrence of *Dicroidium odontopteroides* (Krull and Retallack 2000). The Russian stratigraphy is based on Surkov *et al.* 2007 (G). The correlation between the palynological zone U5 in Australia and the Vyatkian is based on Morante (1996) who correlates U5 to the *Dicynodon* zone in South Africa which is linked to Vyatkian Gorizont (Benton 2007).**

The multiple negative $\delta^{13}C_{org}$ excursions observed in the earliest Triassic in Antarctica are not recorded in the Triassic at Boyevaya Gora (Figure 8.6). However, the Triassic paleosols from Boyevaya Gora have more positive $\delta^{13}C_{carb}$ values, possibly reflecting a rise in atmospheric $pCO_2$ (see Chapter 7). This may reflect the time averaging of the different materials, as organic matter is likely to record the $^{12}C$ release into the atmosphere (Retallack and Jahren 2008) while the paleosols if the $^{12}C$ release coincides with a dramatic rise in $pCO_2$ which is big enough to change the dominant control on the isotopic composition of pedogenic

carbonate it will not produce an excursion in the $\delta^{13}C_{carb}$ values of pedogenic carbonate (see Chapter 7).

The organic carbon values from Antarctica show no evidence of the negative excursions seen in Changhsingian in the South Urals (Figure 8.6). The negative $\delta^{13}C_{carb}$ excursion seen in the earliest Triassic (TR2) at the very top of Boyevaya Gora may correspond to the negative $\delta^{13}C_{org}$ excursions seen at Graphite Peak in the Middle Permian (Figure 8.6). However, at Boyevaya Gora this Triassic excursion is less in magnitude than those seen in the Changhsingian (P2 and P3) while in Antarctica the excursions in the Earliest Triassic dwarf any of the variation recorded in the Changhsingian in that section (Figure 8.6).

### *8.3.3 Other terrestrial sections*

The $\delta^{13}C_{org}$ values from Australia at Eddystone in the Bowen Basin appear to show minor isotope anomalies before the P/Tr boundary and in to the Early Triassic (Morante 1996) (Figure 8.6). The P/Tr boundary is defined as being very near or at the base of the *Protohaploxypinus microcorpus* zone (Morante 1996). The lower excursions have been correlated with the first P/Tr excursion at Graphite Peak in Antarctica (Retallack *et al.* 2006). It has been observed that Upper Stage 5 which contains *Glossopteris* up to 25cm below the hiatus in the section (Morante 1996) and thus can be correlated with the *Dicynodon* zone in Karoo (Retallack *et al.* 2006) and thus the Vyatkian of Russia. Like Antarctica, there are no corresponding anomalies to those recorded in Russia in the Changhsingian. Unfortunately no comprehensive magnetostratigraphic data exist for Australia (cf. Steiner 2006) so it is impossible to test this correlation.

Organic carbon has also been recovered from terrestrial sections in India (deWit *et al.* 2000; Sarkar *et al.*2003), Madagascar (de Wit *et al.* 2000), Australia (Morante 1996) and Xinjiang in China (Cao *et al.*2008, Metcalfe *et al.* 2008). In India, as in Antarctica, there is a marked $\delta^{13}C_{org}$ excursion in the earliest Triassic (deWit *et al.* 2000; Sarkar *et al.*2003). In the Raniganj Basin, India, the main negative carbon excursion occurs after the occurrence of the conglomerate, which is Permian in age based on its occurrence within the *Glossopteris–Vertebraria* assemblage, although there is a minor $\delta^{13}C_{org}$ –3‰ excursion just prior to this conglomerate (Sarkar *et al.* 2003). However, the Indian sections do not show any dramatic excursions in the Lopingian or a dramatic excursion coincident with the end-Guadalupian event (deWit *et al.* 2000; Retallack *et al.* 2006). The $\delta^{13}C_{org}$ values recovered from Madagascar appear to show a different picture: the late Permian rather than being a period of relatively stable isotope values instead seems to show a sharp decrease in $\delta^{13}C_{org}$ values in the latest Permian that continues through into the Triassic (de Wit *et al.* 2000).

$\delta^{13}C_{org}$ values recovered from sections in the Tian Shan in Xinjiang Province, China appear to show two episodes of $^{13}C$ depletion (Cao *et al.* 2008). The lower of these is below the extinction horizon and is interpreted as an onset of environmental stress before the end-Permian mass extinction began (Cao *et al.* 2008). Global correlations using palynology, vertebrates, and conchostracans, place the sections from Tian Shan within the last reversal of the Permian and the P/Tr boundary normal (Metcalfe *et al.* 2008). This would mean that this lower $^{13}C$ depletion seen in Tian Shan does not correlate to the excursion (P3) seen in Russia. Furthermore, Metcalfe *et al.* (2008) argue that in their results they do not see two episodes of $^{13}C$ depletion, but rather multiple $\delta^{13}C_{org}$ negative excursions which they ascribe to multiple atmospheric perturbations.

## 8.4 Marine $\delta^{13}C$ comparisons

Comparing marine and terrestrial sections is notoriously difficult (cf. Retallack and Jahren 2008). Although some marine sections have terrestrial palynomorphs (e.g. Twitchett *et al.* 2001; Foster and Afonin 2005) which can be used to compare terrestrial sections, these data do not exist for the GSSP record at Meishan (Metcalfe *et al.* 2008). Correlating between terrestrial sequences and the GSSP record at Meishan is most accurately accomplished using magnetostratigraphy (Steiner 2006; Metcalfe *et al.* 2008).

The major boundary anomalies seen at Meishan occur within the normal polarity containing the P/Tr boundary (Yin *et al.* 2001; Metcalfe *et al.* 2008). Longer $\delta^{13}C_{carb}$ sections have been published by Jin *et al.* 2000 and correlating these with the magnetostratigraphy published in Yin *et al.* (2001), using the correlations of Steiner (2006), it is possible to compare these values with the Russian sections (Figure 8.7).

There is a suggestion that there is a very minor negative carbon anomaly concurrent with excursion (P3) at Meishan (Figure 8.7, arrowed). However, this correlation is debatable as there is evidence that some of the reversals, including the very brief reversal concurrent with the P/Tr (Figure 8.7), are actually remagnetised overprints (cf. Kozur and Bachmann 2005; Steiner 2006; Metcalfe *et al.* 2008). What is evident from the Meishan record is that there are negative, albeit noisy, $\delta^{13}C_{carb}$ excursions in the base of the section. These are Changhsingian in age as the base of the Changhsingian is defined as the first occurrence of *Clarkina wangi* in Bed 4 at Meishan D section (Jin *et al.* 2006) and these may be comparable with the excursions seen at the base of Boyevaya Gora (such as P2).

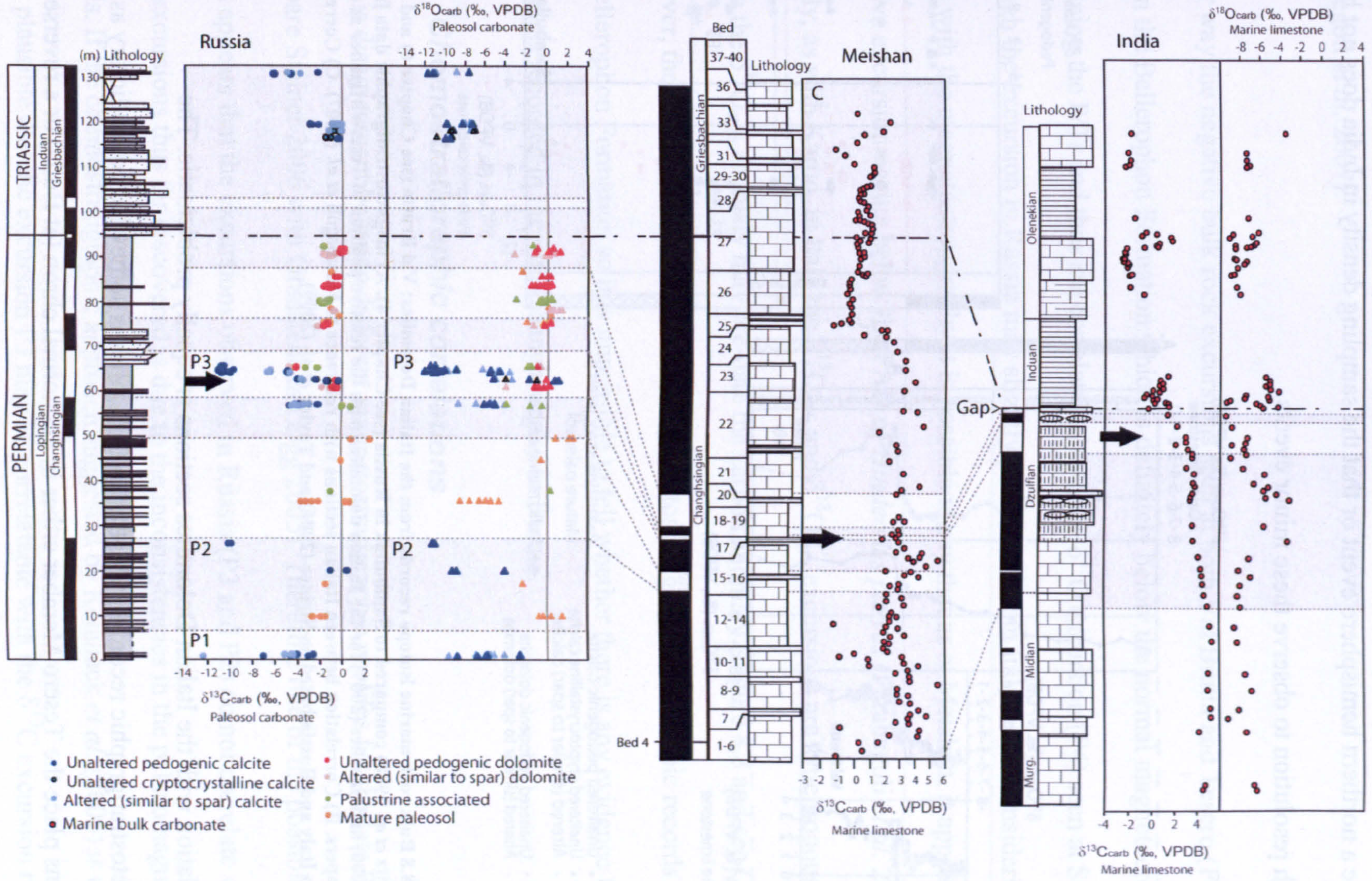


**Figure 8.7 Russian section at Boyevaya Gora correlated with marine sections at Meishan (Jin *et al.* 2000, Yin *et al.* 2001) and India (Baud *et al.* 1996). Correlated using Steiner (2006). The arrow marks the level of excursion P3 at Boyevaya Gora. Bed 4 at Meishan is the base of the Changhsingian (Jin *et al.* 2006).**

These lower excursions at Meishan are, however, not recorded globally. In northern India marine carbonate sections show none of this noise (see Baud *et al.* 1996), suggesting that it may be a northern hemisphere event or that the sampling density in India does not have enough resolution to observe these minor events.

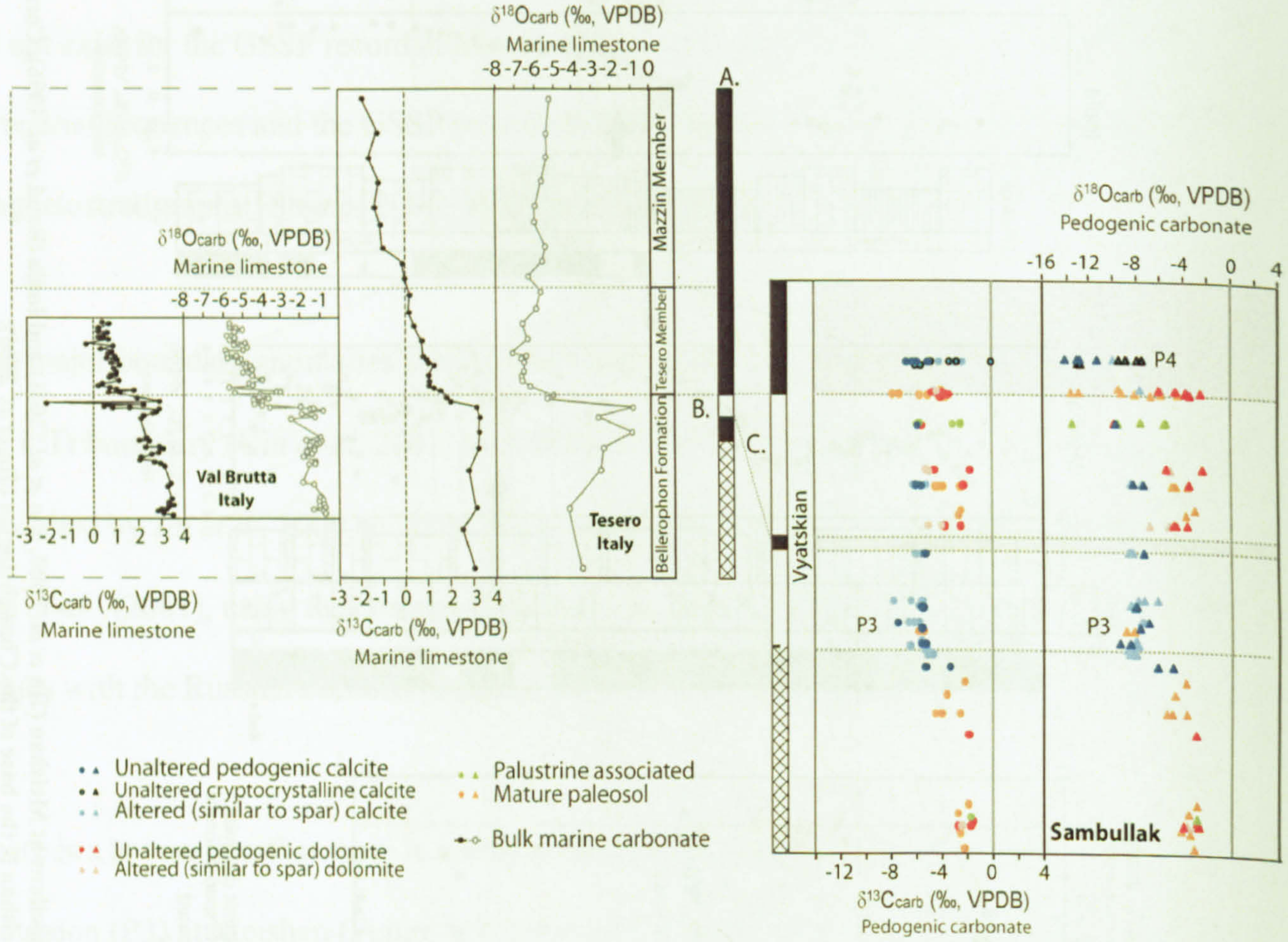


**Figure 8.8 Bulk rock marine isotope records from the Italian Dolomites; Val Brutta (see Chapter 6) and Tesero (Magaritz *et al.* 1988) compared to Sambullak in Russia (see Chapter 4). A) magnetostratigraphic data from Scholger *et al.* (2000) and Szurlies (2007) for the Italian dolomites with the relative position of Tesero Member as described in those papers. B) Correlation between Italian sections with reference to Farabegoli *et al.* (2007). C) Correlation between Italy and Russia based on Steiner (2006) and Taylor *et al.* (2009).**

Correlation with the Italian Dolomites sections is equally problematic. The magnetostratigraphic record for the Italian Dolomites is somewhat contradictory as different sections place the Tesero Member either in the normal chron (at Bulla) or a reversed chron (at Siusi) polarity (Scholger *et al.* 2000). Steiner (2006) suggests that some of the strata at Siusi are missing as the distinctive reversed polarity of the Late Changhsingian is not present and concludes that the Tesero Member is within the boundary normal event. Another explanation

for this is that the Tesero Member is a transgressive unit and thus is a different age in different parts of the basin at it transgressed from west to east (Broglio Loriga and Cassinis 1992; Farabegoli *et al.* 2007).

Either way the negative bulk rock excursions seen at both Val Brutta and Tesero (Figure 8.8) start in the Bellerophon Formation which is definitely below the normal magnetocron containing the P/Tr and thus are correlatable with the $\delta^{18}O$ excursion (P4) seen at Sambullak although the excursion in Russia may slightly post date that in Italy. Even considering these issues with the magnetostratigraphy it is possible to say that as at Meishan, it appears that the negative excursion occurs below the FAD of *Hindeodus parvus* (Farabegoli *et al.* 2007). Equally, as with Karoo, in Italy the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ excursions are synchronous while in Russia the $\delta^{18}O_{carb}$ anomaly may pre-date the carbon anomaly (Figure 8.8 and see Chapter 5). However, the sections in Italy do not have magnetostratigraphic or isotopic records far in to the Bellerophon Formation so it is impossible to tell whether there is any evidence for the excursions recorded in the mid-Changhsingian in Russia.

### *8.4.1 Chemostratigraphic correlations*

There is disagreement between different magnetostratigraphic profiles for the late Permian (compare Steiner 2006 with Gradstein and Ogg 2005). Therefore one of the possible reasons why it appears that the excursions observed in Russia (P3 and P2) do not correlate with any other excursions thus far discovered is due to the inconsistencies in the palaeomagnetic records. If the chemostratigraphic approach suggested by Retallack *et al.* (2006) is used it seems plausible that the excursion P3 may be correlatable with the $\delta^{13}C$ excursion recorded in bed 25 at Meishan (Figure 8.7) as it is known that the Meishan section is highly condensed (Prof. G.J. Retallack *pers. comm.*).

## 8.5 $\delta^{18}O$ and temperature

Understanding the correlation between $\delta^{18}O$ values and temperature globally is complicated. Many authors still contest that the $\delta^{18}O$ values from both marine carbonates and brachiopods do not represent variation in temperature (Spötl *et al.* 1992; Heydari *et al.* 2001; Batt *et al.* 2007). Equally, the $\delta^{18}O$ values of pedogenic carbonate in Russia could be explained by changes in seasonality rather than changes in temperature (see Chapter 5). This being said there is independent sedimentological evidence to suggest that there was a temperature rise up to the P/Tr, such as the increase in the number of Vertic paleosols and the prevalence of Type A dolomite (see Chapters 3 and 4). There is also global evidence for an increase in temperature across the P/Tr boundary, such as the migration of thermophilic plants into both the high latitudes of the northern and southern hemispheres (Retallack 1999, 2002, Retallack and Krull 1999 Looy 2001; Retallack and Krull 2006).

The oft-quoted temperature rise across the P/Tr boundary is 5–6°C (e.g. Erwin 1993; Benton and Twitchett 2003; Kidder and Worsley 2004) which is based on bulk rock analysis of the Gartnerkofel-1 core from Austria (Magaritz and Holser 1991). However, as discussed in Chapter 6, many authors have reservations about this estimate (e.g. Twitchett 2007). Negative excursions in $\delta^{18}O$ bulk rock values have been observed in China, Iran, Italy, Austria and India (Magaritz *et al.* 1988; Magaritz and Holser 1991; Baud *et al.* 1996; Dolenec *et al* 1999; Heydari *et al.* 2001).

The temperature rise predicted from the brachiopods at Val Brutta and Tesero suggest a rise of ~8°C just before the P/Tr boundary (Chapter 6). There is a marked $\delta^{18}O$ anomaly excursion in pedogenic carbonate just prior to the P/Tr boundary in Russia at Sambullak (P4, Chapter 4) which, assuming that the $\delta^{18}O$ values are not being controlled by changes in seasonality and

thus the influence of the amount effect, corresponds to a rise in MAT of ~7°C (see Chapter 5). Bearing in mind the potential issues with the Italian magnetostratigraphy (cf. Steiner 2006), it is possible to correlate the Italian brachiopod values with the boundary excursion at Sambullak (Figure 8.9). Both records seem to show an increase in temperature of 7-8°C just before the boundary. Comparing the Russian records also suggests a step-wise warming, culminating at the P/Tr boundary and then decreasing slightly into the Triassic (Figure 8.9). This being said, the $\delta^{18}O$ record in even unaltered pedogenic carbonate is a product of many factors, strongest among them being the isotopic composition of rainwater (see Chapter 5). Therefore, as with $\delta^{13}C$ values, global records need to be compiled to compare different basins and latitudes.

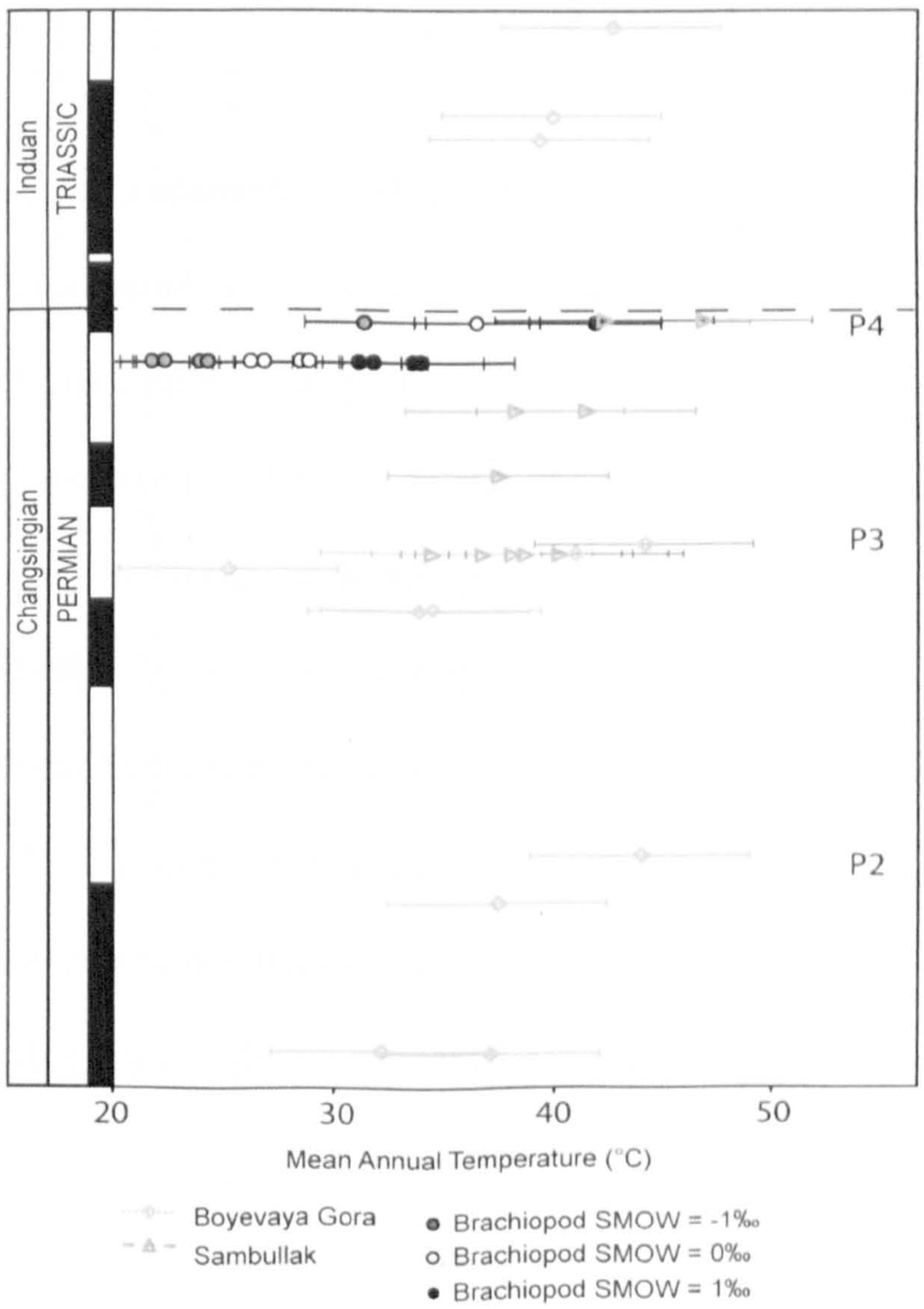


**Figure 8.9 Temperature estimates from the Italian Brachiopods (Chapter 6) with the estimates for Boyevaya Gora and Sambullak using equation 5.10 (Chapter 5). Correlated using the magnetostratigraphic data from Scholger *et al.* (2000) and Szurlies (2007) and Steiner (2006) and Taylor *et al.* (2009).**

## 8.6 Paleosol climate record

The P/Tr boundary has been linked to dramatic changes in terrestrial landscapes and paleosols in Antarctica (Retallack *et al.* 1998; Retallack and Krull 1999; Retallack *et al.* 2005; Retallack *et al.* 2007), Australia (Retallack 1999; Michaelsen 2002); and the Karoo Basin in South Africa (Ward *et al* 2000; Retallack *et al.* 2003). This study (see Chapter 3 and 5) and others conducted in the Southern Urals (Newell *et al.* 1999; Tverdokhlebov *et al.* 2005) have observed a similar dramatic shift in change in environment and paleosol type. Table 8.1 summarises the different changes in climate and paleosols across the P/Tr boundary in these four latitudinally different localities.

While it is evident that all of these localities show a dramatic change across the boundary, the type of change is not always the same. For instance, both Antarctica and Karoo show an increase in precipitation across the P/Tr boundary while Russia and Australia show a decrease. However, in Russia, the fact that all the earliest Triassic paleosols are capped by erosive sands which could have eroded and foreshortened the depth to Bk horizon creating an underestimate of MAP (Table 8.1). Therefore, this may suggest that the drop in precipitation observed is an underestimate. Also Russian paleosols from the Olenekian show a rise in MAP relative to the Permian and increase in seasonality (see Chapter 5). The paleosols from Antarctica, Karoo and Russia all show a change in soil colour across the boundary, although not in Australia (Table 8.1). This is probably due simply to locally distinct changes in environment and thus soil type across the boundary.

| | | Australia (65-85°S) | Antarctica (65-77°S) | Karoo (South Africa) (50-60°S) | Russia (30-35°N) |
|---|---|---|---|---|---|
| **Triassic** | | | | | |
| | Soil colour | 5Y to 5GY | 5Y to 10R | 2.5YR | 5GY |
| | MAP (mm) | 800 to 1200 | 853(±175) -1159(±175) | 732 (±141) | 185(±48) - 180(±6) |
| | Nodule horizons | n/a | n/a | Deep well focused | Shallow poorly developed |
| | Climate regime | Cold temperate | Cold temperate (but warmer) | Semi-arid | Arid |
| | Inferred environment | Broad leaf and conifer forest | Conifer forest | Open woodland | Braided river flood plain |
| Thickness of boundary conglomerate/breccia (m) | | 0.3-1 | 0.7 | 5 to 10 | 5 to 20 |
| **Permian** | | | | | |
| | Soil colour | 5Y | 5Y to 5bg | 10R | 10R |
| | MAP (mm) | 1000 to 1300 (overlapping into earliest Triassic ) | 596(±175) -926(±175) | 346 (±141) | 392(±158) - 242(±72) |
| | Nodule horizons | n/a | n/a | Diffuse and shallow | Diffuse and shallow |
| | Climate regime | Cold temperate and marginally frigid | Cold temperate | Arid | Semi-arid /sub-humid |
| | Inferred environment | Swamp land | Broad leaf deciduous swap | Open shrub land/riparian woodland | Open shrub land/steppe |

**Table 8.1 Paleosol and palaeoclimate changes across the P/Tr boundary in terrestrial environments. Data for Australia is from Retallack (1999) and Michaelsen (2002); Karoo is from Ward *et al.* (2000), Retallack *et al* (2003); Antarctica is from Retallack and Krull (1999), Retallack *et al.* (2007). The data for Russia comes from this study (Chapter 3 and 5) and Newell *et al* 1990; Taylor *et al.* (2009).**

Pedogenic carbonate nodules are only found in Russia and Karoo, and while they both show diffuse and shallow nodule horizons in the Permian suggesting monsoonal climates (cf. Retallack 2005b), in the Triassic nodule horizons in the Karoo basin become deep and well focused while in Russia they stay shallow but are poorly developed. Part of this change may be explained by the dramatic conglomerate fans seen in Russia (Newell *et al.* 1999; Benton *et al.* 2004) which mean that paleosols did not have time to form.

The inferred environments and climate regimes all show a shift to more active, less stable environments across the P/Tr boundary (Table 8.1). All the paleosols show a general warming of climate across the boundary (Retallack 1999; Retallack and Krull 1999; Retallack *et al.* 2003; Chapter 3 and 5). However, in Antarctica and Karoo the climate becomes wetter in the earliest Triassic. It is worth noting that both Karoo and Russia are thought to have an arid climate which suggest that arid zones extend to at least 50-60°S and 30-35°N at the present day these latitudes are dominated by temperate climate (cf. Peel *et al.* 2007). This probably reflects the extensive nature of dry continental interior related to the Pangaea landmass (Roscher and Schneider 2006; Deroin 2008).

The paleosols from Russia mirror the climatic and environmental changes inferred globally across the P/Tr boundary. The only area where Russia appears to show a difference from the trends in the southern hemisphere is that it does not show the increase in precipitation in the Triassic. However, the fact that no pedogenic dolomite is found in the Triassic soils suggests a higher moisture content in the soil and therefore a greater amount of water present in the fluvial system (Chapter 4 and 5). Also it appears that only in Russia is there evidence of changes in climate prior to the P/Tr boundary linked with isotope anomalies).

## 8.7 Siberian Trap correlation

Given the close proximity of the South Urals sections to the Siberian Traps, especially with the discovery that the Traps extend in to the Western Siberian basin under younger sediment cover (Figure 8.10; Reichnow *et al.* 2005; Saunders and Reichnow 2009), it would be expected that there should be some direct environmental impacts of the eruptions on the Russian sections. The Siberian Traps have often been linked to the mass extinction (Erwin 1993; Kamo *et al.* 2003; Grard *et al.* 2005; Beerling *et al.* 2007; Payne and Kump 2007), however, it has also been argued that the link to the mass extinction is purely on temporal relation (Heydari *et al.* 2008).

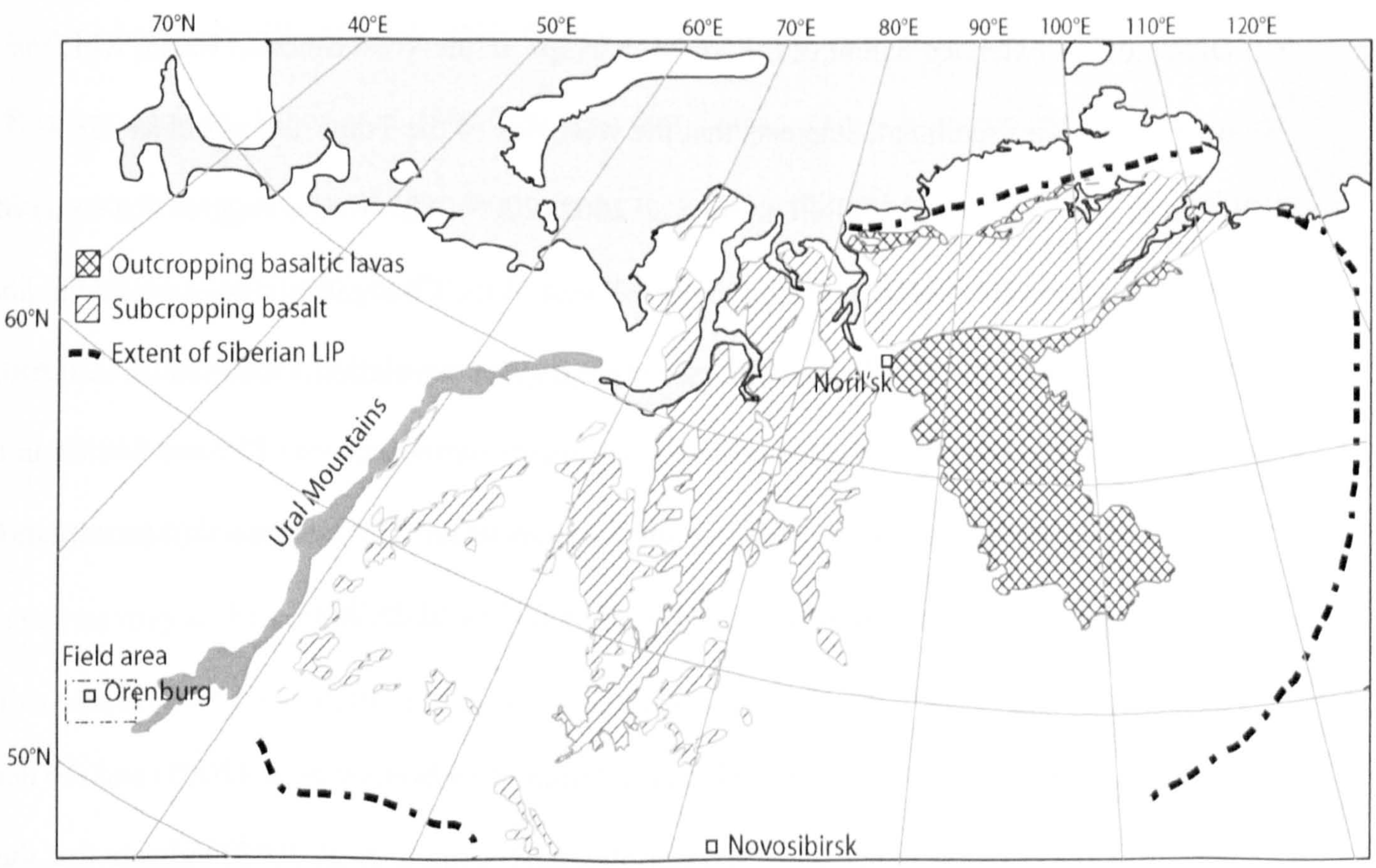


**Figure 8.10 The extent of the Siberian large igneous province (LIP) in both surface outcrop and subcrop (adapted from Saunders and Reichnow 2009) and the field area of this study (see figure 3.2 localities of individual sections).**

The precise timing of the Siberian Traps with reference to the P/Tr boundary is still an area of debate (cf. Reichnow *et al.* 2002 Kamo *et al.* 2003; Mundil *et al.* 2004 Steiner 2006;

Dobretsov *et al.* 2008 ). Steiner (2006) in her correlation uses the summary of $^{40}Ar/^{39}Ar$ results (from Kamo *et al.* 1996) and the patterns of reversals in the different palaeomagnetic sections from across the Siberian Traps to suggest that the volcanics were a long-lived event spanning much of the Lopingian and Induan. However, U-Pb dating from the Noril'sk section suggests the middle of this section to be 251.2±0.3 Ma in age and that the base of the section is no older that 251.7±0.3 Ma (Kamo *et al.* 2003). Kamo *et al.* (2003) argue that the main phase of the traps is coincident with the P/Tr boundary. However, more recent closed-system U/Pb dating of the P/Tr boundary by Mundil *et al.* (2005) has suggested an older date of 252.6 ±0.2Ma for the extinction but they still claim this is synchronous with the Siberian flood volcanism, and it occurred within the quoted uncertainty.

Dating of the extended extent of the Siberian Traps in the West Siberian Basin, which is overlain by later sediment, suggests that the west side of the Traps are as old as 253.4 ±0.3Ma and 252.4 ±1.5Ma (Reichnow *et al.*2002; 2005). This would suggest that some of the traps were active in the Changhsingian as the base of the Changhsingian is assigned to about 254Ma (Jin *et al.* 2006). In their magnetostratigraphic correlation, Dobretsov *et al.* (2008) suggest that the majority of the trap-based volcanism started between 251 and 248Ma in the Siberian Platform, West Siberian Basin and Kuzbass areas. They suggest that precursors to the main phase began in these areas from between 255 and 252Ma.

Based on both the magnetostratigraphic correlation of Dobretsov *et al.* (2008) and the dates proposed for the traps in the West Siberian Basin (Reichnow *et al.* 2002) indicate that there was active volcanism in the Siberian region in the Changhsingian. This may suggest that the negative excursion (P3) seen in both the $\delta^{13}C$ and $\delta^{18}O$ pedogenic carbonate records at Boyevaya Gora and Sambullak, and the time dominated by Type A dolomite in the South

Urals basin (Chapter 4 and 5) prior to the P/Tr boundary, are time equivalent to this initial stage of trap activity described by Reichnow *et al.* (2002; 2005) and that the main facies break at the P/Tr boundary is related to the onset of the main trap volcanism. This being said, the lack of agreement between different magnetostratigraphic correlations may cast doubt on this precise correlation.

## 8.8 Discussion

The Russian results indicate that the climatic changes in the terrestrial northern hemisphere were in some ways quite different from those seen in the southern hemisphere. Comparing the nodular carbonate isotopic values it is evident that the negative 10–15‰ $\delta^{13}C_{carb}$ anomaly recorded at Karoo (Ward *et al.* 2005; Coney *et al.* 2007). However, this is not recorded in the Russian sections. Tabor *et al.* (2007) suggest that $\delta^{13}C_{carb}$ values in Karoo are only recording the isotopic composition of organic matter as they fall within the range of calcite formed from $CO_2$ derived purely from organic matter. If this was an anoxic closed system, as they suggest, then it is isolated from the atmosphere and is not recording the variation the atmospheric $\delta^{13}C$ values. However, it has been shown that some plant matter (such as leaf tissue and cellulose based tissues) is affected by changes in atmospheric $\delta^{13}C$ (Arens *et al.* 2000) and thus the sections may still have the carbonate nodules at Karoo with some atmospheric variation, but this would purely be variation in the organic carbon content in the soil.

The terrestrial $\delta^{13}C_{org}$ record indicate that there are evident terrestrial excursions in Antarctica (Krull and Retallack 2001), India (deWit *et al.* 2000; Sarkar *et al.*2003), Madagascar (de Wit *et al.* 2000) and Australia (Morante 1996) but none of these coincide the anomalies seen in Russia (i.e. P3). There are also other northern hemisphere terrestrial sections such as Xinjiang

in China where there are multiple $\delta^{13}C_{org}$ anomalies in the normal polarity zone that contains the P/Tr boundary (Metcalfe *et al.* 2008) although not as pronounced as anything seen in the southern hemisphere. This may suggest that unlike the southern hemisphere, terrestrial sections in the north do no show a single marked $\delta^{13}C$ excursion just before the P/Tr Boundary. In the marine sections the $\delta^{13}C_{carb}$ bulk rock anomaly appears to occur within the normal polarity zone that contains P/Tr boundary, with the exception of Italy. However, as already stated, there may be stratigraphic issues with the magnetostratigraphic results from that the Italian Dolomites (cf. Steiner 2006).

The lack of any negative $\delta^{13}C_{carb}$ excursion in the normal polarity zone that contains the P/Tr boundary in any of the Russian sections is unexpected. As previously stated the simplest explanation for this is that the worldwide $\delta^{13}C$ excursion occurs in the period of conglomeratic and sandstone sedimentation in the South Urals and thus was not recorded. Those sections where paleosols were formed in the Earliest Permian, such as Boyevaya Gora (see Figure 8.3), do not show a prominent $\delta^{13}C$ excursion and if such an excursion did occur it must have happened before this point. However, there is a significant $\delta^{18}O_{carb}$ excursion at Sambullak recorded just prior to the tabular conglomerates boundary event and may be related to a rise in temperature linked to the P/Tr boundary. Therefore, the reason for the absence of a concurrent $\delta^{13}C_{carb}$ excursion at this point at Sambullak may be due to an large increase in atmospheric $pCO_2$ which if greater than a certain threshold will not cause a $\delta^{13}C_{carb}$ excursion (see Chapter 7). For this second hypothesis to be correct there must be a concurrent $\delta^{13}C_{org}$ excursion at the time of the excursion P4, however, due to the lack of organic carbon in the Russian paleosols at the times of the excursions, it was impossible to obtain $\delta^{13}C_{org}$ values for this paleosol using current techniques.

### *8.8.1 Palaeotemperature and palaeoenvironmental change*

The evidence from the different terrestrial palaeoenvironmental indicators from the paleosols (Table 8.1) shows a much more coherent picture. By integrating the data from the Russian sections it is now possible to say that globally there is a dramatic shift in environmental conditions across the P/Tr boundary. This shift manifests itself in a change from a stable environment to more open and less stable one. The palaeoprecipitation results appear less coherent. While Russia show a fall in MAP, Australia Antarctica and Karoo show a rise (Table 8.1). As Antarctica and Australia are at almost the same latitude (Table 8.1), latitudinal variation can be ruled out. This may suggest the simple picture of a global rise or fall in MAP is overly simplistic. Kidder and Worsley (2004) suggest one of the aspects of warming is abundant rainfall at high latitudes which could explain this increase of rainfall in the high southern hemisphere but not at lower latitudes. This suggests that, whatever the extinction, mechanism it had a profound effect on global circulation patterns. There is evidence, in the form of diffuse carbonate nodules, at both Karoo and Russia to suggest the presence of monsoonal conditions in the Permian (Retallack *et al.* 2003; Retallack 2005b; Chapter 5). In Russia it appears that this monsoonal/seasonality increases after the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ excursion (P3). This agrees with floral changes in the Upper Permian which indicate a severe climate with often changing temperatures and/or humidity/aridity (Kozur 1998). However, for the first time it is possible to observe a direct link between the isotopic anomalies and variations in seasonal activity (see Chapter 5).

What is constant across all four global terrestrial sections is the interpretation that the earliest Triassic is warmer than the Permian (see Table 8.1) which adds weight to the argument that the excursions in $\delta^{18}O_{carb}$ seen in the Russia palaeosols are linked to a rise in temperature. This interpretation is supported by the coincidence and similarity between the temperature

rise (7-8°C) observed in the Italian brachiopods and the excursion at Sambullak (P4) (Figure 8.9). However, it must always be remembered that there are many other influencing factors that can affect both brachiopods (cf. Spötl *et al.* 1992. Batt *et al.* 2007) and pedogenic carbonate (Dworkin *et al.* 2005; Quast *et al.* 2006) and can affect the estimates of exact temperature. This being said, the correlation with other indicators of temperature rise, such as those suggested from paleosols globally (Table 8.1), present a strong case for a sharp and dramatic temperature rise just before the major facies shift seen at the P/Tr boundary.

## 8.9 Summary

In summary, when comparing the data from the Russian paleosols and Italian brachiopods to the global picture it can be seen that:

1. The P/Tr $\delta^{13}C$ excursion observed in many global sections does not occur in Russia. It may have occurred at the same time as the conglomerates were being deposited. Alternatively, as described in Chapter 7, the rise in $pCO_2$ was so great that is did not cause a $\delta^{13}C_{carb}$ excursion in the pedogenic carbonate;
2. The mid-Changhsingian excursion (P3) at Boyevaya Gora and Sambullak is associated with the start of a period of extreme climate variation, including the increase of Type A dolomite and seasonal/monsoonal activity up to the facies break;
3. The temperature data suggest a rise of ~7°C preceding the P/Tr boundary, although there may be other factors that influenced both the brachiopods and paleosol estimates;
4. The paleosols show a similar change across the facies break to that observed in the Southern Hemisphere (Australia, Antarctica, and Karoo), including a shift to a less stable environment across the P/Tr boundary, and there are evident shifts in precipitation patterns and a general global environmental warming in the earliest Triassic;

5. Some of the environmental changes seen prior to the P/Tr boundary may relate to the initial eruptions of the Siberian Traps as they are time-equivalent.

# Chapter 9. Conclusions

The aim of this project was to investigate the variations in paleosol morphology, stable isotopes, temperature, precipitation and carbon dioxide variation through the Late Permian and Early Triassic in sections in the northern hemisphere. These were used to produce a comprehensive understanding of how climate and atmospheric chemistry varied through this period which can be compared to previous studies in the southern hemisphere.

The paleosols of the South Urals of Russia represent a unique window into the northern hemisphere terrestrial climate across the Permian–Triassic boundary. In the Permian the paleosols suggest the area was primarily desert scrubland. In the Triassic this dry environment continued, but the presence of possible depressed water tables and pseudo-gleys suggest an increase in the amount of waterlogging of the paleosols (Chapter 3).

Like paleosols observed in Antarctica, the Karoo and Australia (e.g. Retallack 1999; Retallack and Krull 1999; Retallack *et al.* 1999), results from Russia show a marked change in paleosols across the P/Tr boundary, from more stable, better-developed paleosols to less-developed, less stable paleosols in the earliest Triassic. This is related to a change in facies, from meandering fluvial systems to coarse conglomeratic fans (Chapter 8). These changes are seen in parallel with a drop in mean annual precipitation in the earliest Triassic at Boyevaya Gora followed by a rise in the Olenekian. The variations in mean annual precipitation are also linked to changes in the annual range of precipitation which increases after excursion P3 and up to the P/Tr boundary with an even bigger increase in the Olenekian into ranges similar to modern-day monsoonal areas (New Delhi; IAEA/WMO, 2008) suggesting an increase in seasonality in the Triassic (Chapter 5).

There is evidence that the paleosols were affected by intense evaporation, both in the presence of $\delta^{18}O_{carb}$ isotopic values greater than 0‰ as well as the presence of pedogenic dolomite. Pedogenic dolomite has been identified in the equatorial Lower Permian (Kessler *et al.* 2001) but this is the first evidence of it at palaeolatitudes as high as 30-35°N during this period. The occurrence of this pedogenic dolomite ceases at the P/Tr boundary and there is no evidence of it in the Triassic, which may suggest an increase in available water in the Triassic which would inhibit the formation of dolomite. However, the Triassic paleosols show evidence of fluctuating water tables and deep-rooting, pedogenic slickensides and pseudo-gleys which suggests the opposite. An alternative hypothesis is that pedogenic dolomite formation is linked to other factors relating to changes in soil conditions across the P/Tr boundary. If bacteria are a key component in pedogenic dolomite formation (cf. Roberts et al. 2004; Sáchez–Román 2008), then perhaps the disappearance of pedogenic dolomite reflects serious depletion of the soil microbial communities in the Early Triassic (Chapter 4, Kearsey *et al.* in review).

It has been suggested that the complex interplay between groundwater, diagenesis and surface alteration can obliterate any meteoric pedogenic signal in Palaeozoic paleosols (Quast *et al.* 2006). While there is some evidence of alteration in the sections in Russia it is possible to separate this from the pedogenic carbonate results. Also the similarity between some of the 'altered' results (especially the microcrystalline carbonates) and the pedogenic carbonates suggests that they are formed from the similar fluid and may represent meteoric values rather than a later fractionated diagenetic fluid (Chapter 4).

There is evidence at Sambullak of an $\delta^{18}O_{carb}$ negative shift (P4) across the P/Tr boundary, although this excursion is not observed at Boyevaya Gora, presumably as just below the P/Tr

boundary the carbonate component of the paleosols is exclusively dolomite at this locality. There may have been a negative $\delta^{13}C_{carb}$ excursion at the P/Tr boundary in the South Urals, as recorded in the southern hemisphere, but this has to have occurred in the period dominated by conglomerates between the P/Tr boundary and the first Triassic paleosol and thus was not recorded. Alternatively, the increase in $pCO_2$ at the P/Tr was so great that it changes the dominant control on $\delta^{13}C_{carb}$ of pedogenic carbonate from the organic carbon content of the soil to the isotopic composition of the atmosphere and thus did not produce a negative excursion in the pedogenic carbonate (Chapter 7).

There are four isotope excursions in the Changhsingian identified in the Russian paleosols which have not been record in the southern hemisphere. Of these, excursion P3 is the best constrained. P3 can be identified in pedogenic calcite at Boyevaya Gora and, to a lesser extent, at Sambullak and represents a negative shift of 6–4‰ in the $\delta^{13}C$ and $\delta^{18}O_{carb}$ values in the mid Changhsingian. The negative carbon and oxygen excursions (P3) are followed by a period of only Type B dolomite at Boyevaya Gora and an increase in type B dolomite at Sambullak. These changes are linked with a rise in MAP and the Mean Annual Range of Precipitation which both increase after this point up to the facies break at the P/Tr boundary. This suggests that these excursions were related to changes in the climate and atmosphere rather than localised changes in paleosol conditions.

If the $\delta^{18}O_{carb}$ isotopic values are completely controlled by temperature, it appears that the paleosols in Russia, as at Saratov today, showed a lack of summer rain with an increase in air temperature causing the weighting of the mean annual precipitation towards more negative $\delta^{18}O_p$ values for warmer years. Using equation (5.10) suggests an average Permian temperature of 38°C (± 14) and 40°C (± 8) in the Triassic. The excursions at Sambullak and

Boyevaya Gora (P3 and P4) represent a rise in MAT of 7°C, although the weakness of the MAT/$\delta^{18}O_p$ relationship on which equation (5.10) is based urges caution in this estimate. It is equally possible that the excursion in $\delta^{18}O_{carb}$ values represents the onset of increased seasonal rainfall rather than a rise in temperature, or even both a rise and an onset of increased seasonal rainfall. However, independent temperature estimates from unaltered brachiopods from the Italian Dolomites (Chapter 6) indicate that just before P/Tr boundary there was a rise of 7°C, although the absolute ambient temperature estimates are dependent on the predicted salinities. This suggests that there was indeed a rise in temperature just before the P/Tr boundary and that excursion P4 in Russia at least corresponds to a rise in temperature.

Calculation of the variation in $pCO_2$ shows a dramatic rise in atmospheric $CO_2$ in the earliest Triassic, which appears to be consistent with stomatal records of a similar age from Russia (Retallack and Jahren 2008). The Russian sections also show fluctuations in $pCO_2$ in the Permian. The extreme variation seen between methods may suggest the environment was not in equilibrium or that the temperature estimates produced by equation (5.10) are overestimates or the lack of control over the variation in organic carbon in the sections. The negative $\delta^{13}C_{carb}$ excursions seen at Boyevaya Gora (P2 and P3) and, to a lesser extent, at Sambullak (P3) could be explained by a rise in $pCO_2$, but only if there is a corresponding drop in organic carbon at the same time or an input of isotopically negative $\delta^{13}C$ to the atmosphere (Chapter7).

Finally, this is the first time that a negative excursion has been definitively identified in the mid-Changhsingian in a terrestrial locality. This suggests that a different pattern of environmental change occurred in the northern hemisphere compared with the southern

hemisphere, and that the environment and climate started to change before the P/Tr boundary which is time equivalent to the first eruptions of the Siberian Traps (Chapter 9).

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# Appendix 1

## Paleosol feature descriptions and field data

## (Chapter 3)

# A1.1

Pedological features of paleosols from Boyevaya Gora.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| KOR 36 | 39 | 5GY 8/1 - 10R 6/6 - 5YR 6/4 | Siltstone | Sandstone above gleyed (N8) | Only in A horizon | II | 2 | | Petronodic Haplocalcid |
| KOR 33 | 32 | 10R 6/6 and 5YR 6/4 | Siltstone | Sandstone above gleyed (N8) | Throughout | II | 3 | Nodules 'flattened' becomes platy at base | Petronodic Haplocalcid/ Ustic Calcids (Groundwater) |
| KOR 37 | 80 | 5GY 8/1 - 10R 5/4 - 5YR 6/5 | Siltstone | Sandstone above gleyed (N8) | Throughout | II | 9 | Many nodules appear flattened in top section v poor nodule development | Petronodic Haplocalcid |
| KOR 34 | 34 | 5GY 8/1 and 5YR 6/4 | Fine sandstone and Siltstone | Sandstone above gleyed (N8) | Throughout | II | eroded | | Petronodic Haplocalcid |
| KOR 32 | 51 | 5R 5/4 5YR 6/4 | Siltstone | Minor | Throughout | II | 8 | Appears to contain diagenetic calcite | Petronodic Haplocalcid |
| KOR 1 | 59 | 10R 4/6 and 7/4 (nod horizons) | Siltstone in rooted zones/VF sand in nod bands | Blue green mud cracked area extensively mottled minor mottling in rooted area | Throughout | II | 49 | Mud cracks on the top surface with strong mottles (top 10cm) | Petronodic Haplocalcid |
| KOR 1a | 105 | 10R 4/6 and 7/4 (nod horizons) | Siltstone in rooted zones/VF sand in nod bands | Minor reductions spots | In rooted and un rooted areas | III | 23 | | Ustic Petrocalcid |
| KOR 2 | 83 | 10R 5/4 | Siltstone | Minor reductions spots | Only in A horizon | II | 25 | | Petronodic Haplocalcid. |
| KOR 3 | 45 | top 10R 5/6 Bk - 10R 7/4 | Mudstone | Minor reductions spots | Throughout | IV | 8 | Slickenside | Vertic Petrocalcid |
| KOR 8 | 27 | 10R 7/4 | Siltstone | Mottled roots | Throughout | IV | Eroded | Drab root haloes | Ustic Petrocalcid |
| KOR 9 | 20 | 10R 6/6 | Mudstone | Minor reductions spots | Throughout | II | Eroded | | Petronodic Haplocalcid. |

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| KOR 4 | 137 | 10R 7/4 - 10R 5/4 | Siltstone | None | Throughout | V | 18 | Shows hummocky brecciated top | Vertic Petrocalcid |
| KOR 5 | 27 | 10R 5/4 | Siltstone | None | Throughout | II | eroded | Probably affected/part of by soil above | Vertic Haplocalcid |
| KOR 6 | 88 | 10R 5/4 | Siltstone | Minor reductions spots | Throughout | II | 34 | | Petronodic Haplocalcid |
| KOR 7 | 72 | 10R 8/2 and 10R 7/4 | Siltstone | Mottled -5B 8/2 mottled roots | Throughout | IV | 28 | | Ustic Petrocalcid |
| KOR 10 | 96 | 10R 6/6 | Siltstone | Mottled -5B 8/2 top like 1 | Throughout | III | 27 | Top boundary indistinct may have mud cracks | Ustic Calcid (Lacustrine) |
| KOR 11 | 58 | 10R 7/4 - 10R 8/2 | Siltstone | Drab root haloes | Throughout | IV | 18 | Patch calcification | Ustic Petrocalcid |
| KOR 12 | 42 | 10R 7/4 | Siltstone | Mottled roots 5G 8/1 | Only in A horizon | II | 36 | Very thin Bk horizon | Petronodic Haplocalcid |
| KOR 13 | 86 | 10R 8/2 10R 7/4 | Siltstone | None | Only in A horizon | IV | eroded | white limestone cemented top bed | Ustic Petrocalcid |
| KOR 14 | 50 | 10R 5/4 | Siltstone | None | Only in A horizon | III | 26 | Stacked horizons min 2 or 4 and possible rooted hard ground | Ustic Petrocalcid. |
| KOR 14a | 48 | 10R 5/4 | Very fine sandstone | None | Throughout | II | 8 | Stacked horizons min 2 or 4 and possible rooted hard ground | Petronodic Haplocalcid |
| KOR 14b | 27 | 10R 5/4 base 10R 8/4 | Siltstone | None | Throughout | II | 18 | Stacked horizons min 2 or 4 and possible rooted hard ground | Petronodic Haplocalcid |
| KOR 23 | 51 | 5R 5/4 | Mudstone | Erosive Gleyed sand above | Throughout | III | 28 | Possibly waterlogged horizon?? | Ustic Calcid (Groundwater) |
| KOR 22 | 76 | 10R 5/4 | Mudstone | None | Throughout | II | 64.5 | Laterally variable 23 - 70 cm thick | Petronodic Haplocalcid |
| KOR 21 | 61 | 10R 5/4 | Mudstone | None | Throughout | III | eroded | | Ustic Petrocalcid |
| KOR 15 | 55 | 10R 5/4 - N7 | Top VF sandstone and Siltstone | N7 -in mottled top - nodules mottled | Only in A horizon | II | 17 | Top possibly like 17 | Petronodic Haplocalcid |
| KOR 16 | 19 | 10R 4/1 | Siltstone | Minor reductions spots | In nodule zones | II | 13 | Stacked horizon | Petronodic Haplocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| KOR 16a | 27 | 10R 4/2 | Siltstone | Minor reductions spots | In nodule zones | II | 14 | Stacked horizon | Petronodic Haplocalcid |
| KOR 17 | 31 | top 5YR 8/4 10R 6/2 | Top VF sandstone and Siltstone | N7 in rooted area | Only 'A' Horizon | III | 24 | Contains ostracods - lacustrine. Not very laterally continuous | Ustic Calcid (Lacustrine) |
| KOR 18 | 19 | 10R 5/4 | Siltstone | Minor reductions spots | Only 'A' Horizon | III | 12 | Note 18.1-4 are different horizons than 18.5-9 | Ustic Petrocalcid |
| KOR 19 | 79 | 10R 8/2 - 10R7/4 below | Siltstone | Drab root haloes | Throughout | V | 21 | | Ustic Petrocalcid |
| KOR 20 | 59 | 10R 6/6 and 10R 5/4 | Fine sandstone | None | None | IV | Calcified channel | Calcified channel | Ustic Calcid (Lacustrine) |
| KOR 24 | 15 | 10R 6/6 and 10R 5/4 | Mudstone / VF Sandstone | None | Throughout | III | 15 | | Ustic Petrocalcid |
| KOR 25 | 29 | 10R 5/4 | | None | None | II | 21 | | Petronodic Haplocalcid |
| KOR 26 | 46 | top N8 and 10R 5/4 | Siltstone t/VF sandstone | Strongly mottled throughout (N8) | Throughout | IV | 41 | Contains ostracods - lacustrine Not very laterally continuous | Ustic Calcid (Lacustrine) |
| KOR 27 | 30 | top 10R 6/2 and | Siltstone t/VF sandstone | Minor reductions spots | Only 'A' Horizon | II | 26 | | Petronodic Haplocalcid |
| KOR 28 | 15 | 10R 5/4 and 10R 7/4 | Mudstone / Siltstone | Top 2cm mottled N8 but strongly rooted | In Bk horizon | IV | Eroded | | Ustic Petrocalcid |
| KOR 29 | 16 | 10R 8/2 and 10R 5/4 | Siltstone | None | Throughout | III | Eroded | Desiccation cracks on top | Ustic Petrocalcid |
| KOR 30 | 24 | 10R 5/4 and 10R 6/2 | Silt and VF sand | None | Throughout | IV | 18 | Poor exposure | Ustic Petrocalcid |
| KOR 31 | 28 | 5YR 8/1 and 10R 5/4 | Fine sand and clay | Sand above strongly mottled | None recorded | II | Eroded | possibly waterlogged horizon (12cm) | Petronodic Haplocalcid. |
| KOR 35 | 23 | 10R 5/4 | Mudstone | None | None recorded | II | Eroded | | Petronodic Haplocalcid. |

## A1.2

Pedological features of paleosols from Sambullak.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| SAM 1 | 66 | 10R 7/4, 10R 3/4, 10R 5/4 | Siltstone | Calcite filled slickenside at top | Only in A horizon | II | 31 | | Vertic Haplocalcid |
| SAM 4 | 80 | 10R 6/6 | Siltstone | | None observed | II | eroded | Weakly developed | Petronodic Haplocalcid |
| SAM 3 | 129 | 10R 6/6, 10R 5/4 | Siltstone | Slickenside at top of profile mottled round nodules | None observed | III | 49 | Presence of pedogenic slickensides | Vertic Haplocalcid |
| SAM 2 | 68 | 10R 6/6, | Siltstone | Lacustrine carbonate above | None observed | II | Lacust. | Top lacustrine limestone so probably palustrine | Ustic Calcid (Lacustrine) |
| SAM 12 | 20 | 10R 5/4 | Mudstone | Mottled top | Only in A horizon | II | 14 | Rootlets rare | Petronodic Haplocalcid |
| SAM 11 | 34 | 10R 5/4 and 5GY 8/1 | Mudstone | Calcite vein | Throughout | II | 28 | Poorly exposed | Petronodic Haplocalcid |
| SAM 10 | 145 | 10R 5/4, | Mudstone | Calcified top mottled | Throughout | II | 42 | Presence of pedogenic slickensides | Vertic Haplocalcid |
| SAM 10a | 103 | 5R 5/4, | Mudstone | Calcified top mottled | Throughout | II | 24 | Presence of pedogenic slickensides | Vertic Haplocalcid |
| SAM 9 | 164 | 10R 8/2, 5R 5/4, 10R 6/2 | Mudstone | Mottles in A horizon | Throughout | II | 80 | | Petronodic Haplocalcid |
| SAM 8 | 83 | 5R 8/2 | Siltstone | None | Only in A horizon | II | 18 | Top may be eroded by overlying conglomerate | Petronodic Haplocalcid |
| SAM 7 | 48 | 10R 8/2 | Mudstone | None | Throughout | IV | eroded | Top may be eroded by overlying conglomerate | Ustic Petrocalcid |
| SAM 6 | 50 | | Siltstone | Minor mottles with mottled zone at top | Throughout | none | No Bk. | | Ustic Haplocambid |
| SAM 5 | 94 | 10R 6/2, , 10R 4/6, | Mudstone | None | Throughout possible tap root/burrow | III | 37 | | Ustic Petrocalcid |
| SAM 5a | 84 | 5YR 5/6, 10R 8/2 | Siltstone | None | Throughout | III | 25 | | Ustic Petrocalcid |
| SAM 20 | 47 | 10R 8/2, 10R 7/4, 10R 6/2 | Mudstone | Slight mottles in A horizon | Throughout | II | 27 | This horizon may be a weakly calcified (A) rooted horizon and not a nodule horizon | Petronodic Haplocalcid |
| SAM 19 | 59 | 10R 7/4, 5Y 8/1, | Mudstone | Top A horizon strongly mottled | Throughout | III | 33 | | Ustic Petrocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| SAM 19a | 101 | 10R 7/4, 5R 4/2 | Mudstone | Minor mottling in A | Throughout | III | 12 | | Ustic Petrocalcid |
| SAM 18 | 46 | 5YR 8/1, 5R 7/4 | Mudstone | None | Throughout | IV | 17 | Below possible lacustrine limestone | Ustic Petrocalcid |
| SAM 17 | 52 | N7, 5R 5/4 | Mudstone | Bleached 2cm under conglomerate | Throughout | II | 39 | Top eroded by overlying conglomerate | Petronodic Haplocalcid |
| SAM 16 | 56 | 5Y 8/1, 10R 4/6 | Mudstone | Mottled top | Only in BK | II | 37 | | Petronodic Haplocalcid |
| SAM 15 | 65 | 5YR 5/2, 5YR 6/5 | Mudstone | None | Throughout | II | 27 | High degree of modern pedogenesis | Petronodic Haplocalcid. |
| SAM 14 | 40 | 5YR 5/2, 5YR 6/4 | Mudstone | Bk horizon mottled | Throughout | I/II | 15 | Poorly exposed | Petronodic Haplocalcid |
| SAM 13 | 83 | 5R 4/3, 5R 5/4 | Mudstone | None | Throughout | II | 14 | Small nodules | Petronodic Haplocalcid |
| SAM 21 | 42 | 5R 5/4 | Mudstone | Very minor mottles | Only in A horizon | II | 19 | | Petronodic Haplocalcid |
| SAM 22 | 35 | 5R 5/4, 10R 5/4, | Mudstone | Drab root haloes mottled A horizon | Only in A horizon | II | 27 | | Petronodic Haplocalcid |
| SAM 23 | 83 | 5R 5/4 | Mudstone | Minor mottles | Throughout | III | 47 | | Ustic Petrocalcid |
| SAM 24a | 61 | 5R 5/5 | Mudstone | None | None observed | II | 51 | Poorly exposed | Petronodic Haplocalcid |
| SAM 24b | 102 | 5R 5/6 | Mudstone | None | None observed | II | 31 | Poorly exposed | Petronodic Haplocalcid |
| SAM 24c | 60 | 5R 5/7 | Mudstone | None | None observed | II | 54 | Poorly exposed | Petronodic Haplocalcid |
| SAM 24d | 146 | 5R 5/8 | Mudstone | None | None observed | II | 88 | Poorly exposed | Petronodic Haplocalcid |
| SAM 24e | 133 | 5R 5/9 | Mudstone | None | None observed | II | 119 | Poorly exposed | Petronodic Haplocalcid |

## A1.3

Pedological features of paleosols from Tuyembetka.

| Horizon | Total thickness (cm) | Colour | Grain Size | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|
| *TUY 53* | 73 | 5R 4/2 | *Siltstone* | | II | Eroded | Layered groundwater nodules | Petronodic Haplocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|
| TUY 54 | 130 | 5YR 6/1 | Mudstone | | III | Eroded | Lots of spars present carbonate | Ustic Petrocalcid |
| TUY 55 | 85 | | Siltstone | | IV | 37 | | Ustic Petrocalcid |
| TUY 56 | 55 | | Mudstone | Some evidence | II | 3 | Weakly developed | Petronodic Haplocalcid |
| TUY 57 | 57 | | Mudstone | | II | 53 | | Petronodic Haplocalcid |
| TUY 58 | 98 | 5R 4/2, 10R 4/2 | Siltstone | Throughout | III | 54 | | Ustic Petrocalcid |
| TUY 59 | 23 | 5R 6/1, 5YR 4/2 | Mudstone | Some evidence | IV | Eroded | | Ustic Petrocalcid |
| TUY 60 | 32 | 5R 6/1, 5YR 4/3 | Mudstone | Some evidence | IV | Eroded | | Ustic Petrocalcid |
| TUY 61 | 34 | 10R 6/2, 5YR 6/1 | Siltstone | Only in A horizon | IV | Eroded | | Ustic Petrocalcid |
| TUY 1 | 74 | | Micrite | Some observed | V | Eroded | Laminated | Ustic Petrocalcid |
| TUY 52 | 20 | 5R 6/2 | Mudstone | Only in A horizon | IV | Eroded | Fused nodules | Ustic Petrocalcid |
| TUY 51 | 15 | 10R 6/2 | Mudstone | Some evidence | III | Eroded | Poor exposure | Ustic Petrocalcid |
| TUY 50 | 39 | 5R 8/3 | Mudstone | Only in A horizon | IV | Eroded | Mottled horizon | Ustic Petrocalcid |
| TUY 49 | 52 | 5R 8/2 | Mudstone | Only in A horizon | VI | Eroded | Brecciated top - | Ustic Petrocalcid |
| TUY 48 | 15 | 5R 5/4 5YR 6/1 | Mudstone | Some evidence | IV | Eroded | Vugs | Ustic Petrocalcid. |
| TUY 47 | 80 | | Mudstone | | IV | Eroded | Welded calrete horizons | Ustic Petrocalcid |
| TUY 2 | 82 | 5R 8/2 | Siltstone | None observed | V | 62 | Laminated | Ustic Petrocalcid |
| TUY 3 | 48 | | Mudstone | None observed | IV | 36 | | Ustic Petrocalcid |
| TUY 4 | 12 | | Siltstone | Only in A horizon | II | 26 | | Petronodic Haplocalcid |
| TUY 5 | 26 | | Mudstone | Some observed | III | 18 | | Ustic Petrocalcid |
| TUY 6 | 107 | | Mudstone | Only in A horizon (vertical) | II | 62 | Smallest nodule 1cm diffuse pattern | Petronodic Haplocalcid |
| TUY 7 | 120 | | Mudstone | Throughout | III | 26 | | Ustic Petrocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|
| TUY 8 | 60 | | Mudstone | Some observed | IV | 21 | Evidence of heave cracks on surface | Vertic Petrocalcid |
| TUY 9 | 43 | | Mudstone | Some observed | I | Poor exp. | | Petronodic Haplocalcid |
| TUY 10 | 199 | | Mudstone | Some observed | III | Poor exp | Sparry calcite in cracks | Ustic Petrocalcid |
| TUY 11 | 85 | | Mudstone | Throughout | V | Laminated | | Ustic Petrocalcid |
| TUY 11a | 95 | | Mudstone | Throughout | V | Laminated | Laminated top | Ustic Petrocalcid |
| TUY 12 | 98 | | Mudstone | Throughout | V | 45 | Sparry calcite in voids | Ustic Petrocalcid |
| TUY 13 | 87 | 10R6/2, 3/4 | Mudstone | Only in A horizon | IV | 33 | Sparry calcite in voids | Ustic Petrocalcid |
| TUY 14 | 84 | | Mudstone | Some observed | V | Eroded | Sparry calcite in voids | Ustic Petrocalcid |
| TUY 15 | 27 | 10R 5/2 | Mudstone | Sparsely | II | Eroded | Poorly exposed | Petronodic Haplocalcid |
| TUY 15a | 18 | 10R 5/2 | Mudstone | Sparsely | II | 18 | | Petronodic Haplocalcid |
| TUY 15b | 18 | 10R 5/2 | Mudstone | Sparsely | III | 16 | | Ustic Petrocalcid |
| TUY 16 | 50 | | Mudstone | Throughout | III | 120 | | Ustic Petrocalcid |
| TUY 16a | 36 | | Mudstone | Throughout | III | 25 | Poor exposure | Ustic Petrocalcid |
| TUY 16b | 36 | 10R6/2 | Mudstone | Throughout | III | 32 | Poor exposure | Ustic Petrocalcid |
| TUY 17 | 80 | 5B 9/1 | Mudstone | Roots not continuous | V | Eroded | Cracks infilled with calcite | Ustic Petrocalcid |
| TUY 18 | 17 | 10R 4/2 | Mudstone | Sparsely | II | 44 | | Petronodic Haplocalcid |
| TUY 19 | 64 | | Fine sandstone | Some observed | V | 42 | | Ustic Petrocalcid. |
| TUY 20 | 12 | | Mudstone | Some observed | V | Eroded | | Ustic Petrocalcid |
| TUY 20a | 55 | | Mudstone | Some observed | V | Eroded | Top may be brecciaed - modern weathering | Ustic Petrocalcid |
| TUY 21 | 36 | | Siltstone | Only in A horizon | III | Eroded | Poor exposure | Ustic Petrocalcid |
| TUY 22 | 55 | 10R 5/4, 5R 6/2 | Mudstone | Throughout | IV | Eroded | | Ustic Petrocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|
| TUY 23 | 61 | 5R 5/4 | Mudstone | Only in A horizon | II | 58 | Poor exposure | Petronodic Haplocalcid |
| TUY 24 | 97 | 5R 4/2 | Siltstone | Throughout | II | 48 | Sparry calcitic veins | Petronodic Haplocalcid |
| TUY 25 | 62 | | Siltstone | Throughout | V | 100 | Mottling in lower horizon Cherty | Ustic Petrocalcid |
| TUY 26 | 76 | 5YR 6/1 | Mudstone | Throughout | II | Eroded | Nodules possibly drift | Petronodic Haplocalcid |
| TUY 27 | 130 | 5R 4/2 | Siltstone | Throughout | II | Eroded | Layered nodules | Petronodic Haplocalcid |
| TUY 28 | 118 | 10R 5/4, 10R 4/2 | Mudstone | Throughout | IV | 34 | Hard calcified top | Ustic Petrocalcid |
| TUY 29 | 102 | 10R 5/4 | Siltstone | Well rooted | IV | Poor exp. | | Ustic Petrocalcid |
| TUY 30 | 98 | | Siltstone | In Bk Horizon | IV | Poor exp | Mottled rooted top | Ustic Petrocalcid |
| TUY 31 | 67 | | Mudstone | Throughout | II | 20 | | Petronodic Haplocalcid |
| TUY 32 | 30 | | Mudstone | | V | Eroded | Dark shale above | Ustic Petrocalcid |
| TUY 34 | 58 | N8 | Mudstone | Some observed | V | Eroded | Calcite filled voids | Ustic Petrocalcid |
| TUY 35 | 155 | 10R 4/2 | Siltstone | | II | Eroded | Evidence of carbonate veneer | Petronodic Haplocalcid |
| TUY 36 | 73 | 10R 6/2 | Mudstone | Only in A horizon | IV | Eroded | Calcified layer with 'rooted' horizon top | Ustic Petrocalcid |
| TUY 37 | 17 | 5R 4/2 | Mudstone | | II | Eroded | V cemented mud | Ustic Petrocalcid |
| TUY 38 | 15 | 5R 6/2 | Micrite/clay | Rooted micrite | V | Eroded | Layers of modern calcite | Ustic Petrocalcid |
| TUY 39 | 10 | | Siltstone | | II | 25 | Very thin and diffuse hard to identify institute nodules | Petronodic Haplocalcid |
| TUY 40 | 180 | 10R 3/4, 5YR 8/1 | VF sand | Only in A horizon | IV | 22 | Multiple horizons, some evidence of mottling | Ustic Petrocalcid |
| TUY 41 | 15 | 10R 4/2 | Mudstone | | II | 23 | Mottled horizons | Petronodic Haplocalcid |
| TUY 42 | 41 | 10R 4/2 | Mudstone | | III | 34 | | Ustic Petrocalcid |
| TUY 43 | 23 | | Mudstone | Some evidence | II | Eroded | Mottled horizon | Petronodic Haplocalcid |
| TUY 44 | 55 | 10R 5/6 | Mudstone | | II | Eroded | V diff from anything else I have seen some modern calcification | Petronodic Haplocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|
| TUY 45 | 22 | | Mudstone | | III | 31 | Nodules very large (8-10cm) | Ustic Petrocalcid |
| TUY 46 | 80 | 10R 5/4 | Mudstone | Deep rooting | II | 10 | Many alteration mottled top | Petronodic Haplocalcid |

## A1.4

Pedological features of paleosols from Vozdvizhenka.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| VOZ 14 | 44 | 10R 4/6 | Mudstone | Mottled above | Some evidence | II | 30 | Thin gravel above and slickensides | Vertic Haplocalcid |
| VOZ 13 | 130 | 10R 5/4 | V Fine sandstone | Mottled above | Some evidence | II | 90 | Above the powdery clay | Petronodic Haplocalcid |
| VOZ 12 | 128 | 10R 6/6 | V Fine sandstone | Mottled | Some evidence | II | Eroded. | Outcrop quite weathered | Petronodic Haplocalcid |
| VOZ 11 | 140 | 10R 5/4 | V Fine sandstone at base | | Some evidence | II | Eroded. | Diffuse | Petronodic Haplocalcid |
| VOZ 10 | 23 | 10R 6/6 | Siltstone | | Some evidence | II | Eroded. | Diffuse small nodules under blocky micaceous top | Petronodic Haplocalcid |
| VOZ 9 | 45 | 10R 6/6 | Siltstone | | Some evidence | II | Eroded. | Very large 5cm top medium sand | Petronodic Haplocalcid |
| VOZ 8 | 24 | 10R 8/2 | Siltstone | 0.5/1mm reduction spots | None observed | II | Eroded. | Very large 5cm top medium sand | Petronodic Haplocalcid |
| VOZ 17 | 260 | 10R 4/6 | V Fine sandstone Mudstone | | Some evidence | II | 30 | Large defuse horizon - fines upwards | Petronodic Haplocalcid |
| VOZ 16 | 42 | 10R 4/2 | Mudstone | | Some evidence | II | 50 | | Petronodic Haplocalcid |
| VOZ 15 | 159 | 10R 4/2 | V Fine sandstone Mudstone | Mottled | Some evidence | II | 40 | Some mottles higher up | Petronodic Haplocalcid |
| VOZ 7 | 44 | 10R 6/4 | Siltstone | | Very fine | II | 35 | Top eroded | Petronodic Haplocalcid. |
| VOZ 6 | 95 | 10R 5/4 | V Fine sandstone | Mottled | Some evidence | II | Eroded. | Overlain by micaceous horizon | Petronodic Haplocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| VOZ 5 | 167 | 5R 4/2 | | | Some evidence | III | Eroded. | | Ustic Petrocalcid |
| VOZ 3 | 80 | 5R 3/4 | Siltstone | | Some evidence | II | Eroded. | | Petronodic Haplocalcid |
| VOZ 2 | 94 | 5R 5/4 | Fine sandstone and pebble | | Some evidence | II | Eroded. | In a conglomerate lag | Petronodic Haplocalcid |
| VOZ 4 | 15 | 5R 5/4 | V Fine sandstone and silt | | None observed | II | Eroded. | top eroded | Petronodic Haplocalcid |
| VOZ 1 | 105 | 10R 4/2 | Siltstone | | Some evidence | II | Eroded. | | Petronodic Haplocalcid |

## A1.5

Pedological features of paleosols from Krasnogor.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| KRA 2 | 43 | 10R 5/4 | VF and Fine sandstone | Mottled | Some evidence | II | 22 | | Petronodic Haplocalcid |
| KRA 1 | 39 | 10R 4/6 | VF and Fine sandstone | Mottled | Some evidence | II | 27 | Base of Triassic | Petronodic Haplocalcid |
| KRA 7 | 32 | 10R 6/6 | Siltstone | | | II | 18 | Exposure very poor | Petronodic Haplocalcid |
| KRA 7a | 24 | 10R 6/6 | Siltstone | | | II | 20 | | Petronodic Haplocalcid |
| KRA 7b | 27 | 10R 6/6 | Siltstone | | | II | 10 | | Petronodic Haplocalcid |
| KRA 7c | 206 | 10R 6/6 | V fine sandstone | | | II | 18 | | Petronodic Haplocalcid |
| KRA 7d | 46 | 10R 7/4 | V fine sandstone | | | II | 31 | | Petronodic Haplocalcid |
| KRA 7e | 21 | 10R 7/4 | V fine sandstone | | | II | 13 | | Petronodic Haplocalcid |
| KRA 7f | 24 | 10R 7/4 | V fine sandstone | | | II | 14 | | Petronodic Haplocalcid |
| KRA 6 | 36 | 10R 5/4 | Siltstone | | Some evidence | IV | 102 | Poorly weak developed calcified tops | Ustic Petrocalcid |
| KRA 5 | 34 | 10R 4/2 | VF sandstone and Siltstone | Reduction spots | Some evidence | III | 35 | Stacked sequence | Ustic Petrocalcid |

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| KRA 5a | 12 | 10R 6/6 | VF sandstone and Siltstone | | Some evidence | III | 5 | Stacked sequence | Ustic Petrocalcid |
| KRA 5b | 25 | 10R 4/2 | VF sandstone and Siltstone | | | III | 16 | Stacked sequence | Ustic Petrocalcid |
| KRA 5c | 23 | 10R 7/4 | VF sandstone and Siltstone | | Some evidence | II | 7 | Stacked sequence | Petronodic Haplocalcid |
| KRA 5d | 22 | 10R 7/4 | VF sandstone and Siltstone | | | II | 15 | Stacked sequence | Petronodic Haplocalcid |

## A1.6

Pedological features of paleosols from Petropavlovka.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm)) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| PET 2a | 47 | 10R 6/6 | Fine sandstone to mudstones at base | Mottled sand top | Some evidence | II | 26 | | Ustic Calcid (Groundwater) |
| PET 2b | 43 | 10R 6/6 | Mudstone | Mottled in the nodular horizon | Some evidence | II | 20 | | Ustic Calcid (Groundwater) |
| PET 2c | 49 | 10R 6/6 | Siltstone | Mottled top with minor mottling throughout | Some evidence | II | 49 | | Ustic Calcid (Groundwater) |
| PET 1 | 167 | 5R 6/6 | Mudstone | Mottled top with minor mottling throughout | Some evidence | II | 51 | Lower part nodules form in bands | Ustic Calcid (Groundwater) |

## A1.7

Pedological features of paleosols from Mescheryakovka.

| Horizon | Total thickness (cm) | Colour | Grain Size | Contains a mottled horizon/ other alteration controls | Presence of Roots recorded | Nodule stage | Depth to Bk Horizon (cm) | Notes | Classification |
|---|---|---|---|---|---|---|---|---|---|
| MES 1 | 34 | 10YR 5/4 | Siltstone | | Some evidence | II | 24 | V. weakly Developed | Petronodic Haplocalcid |
| MES 2 | 34 | 10YR 5/4 | Siltstone | | Some evidence | IV | 28 | Lacustrine | Ustic Calcid (Lacustrine) |
| MES 3 | 169 | 10YR 5/4 | Siltstone | Yes | Minor | II | 121 | | Petronodic Haplocalcid |
| MES 4 | 56 | 10R 5/4 | Siltstone | Yes | None recorded | II | 43 | | Petronodic Haplocalcid |
| MES 5 | 127 | 10YR 5/4 | Siltstone | Yes mottled above | Some evidence | III | 45 | | Ustic Petrocalcid |
| MES 6 | 76 | 10YR 5/4 | Siltstone | | | II | Eroded | | Petronodic Haplocalcid |
| MES 7 | 108 | 10YR 5/4 | Siltstone | | Some evidence | II | Eroded | | Petronodic Haplocalcid |
| MES 8 | 89 | 5YR 4/6 | Siltstone | Pseudo - Gley | Drab root halos | II | 44 | Deep rooted (36cm) top strongly mottled | Vertic Haplocalcid |
| MES 9 | 37 | 5YR 4/6 | VF sandstone | Mottled | Some evidence | II-III | Eroded | Top eroded | Ustic Petrocalcid |
| MES 10 | 32 | 5YR 4/6 | Siltstone | | Some evidence | II | Eroded | Top eroded | Petronodic Haplocalcid |
| MES 11 | 172 | 5YR 4/6 | Mudstone | Mottled | Some evidence | II | Eroded | Pedogenic slickensides | Vertic Haplocalcid |
| MES 12 | 23 | 5YR 4/6 | Mudstone | Pseudo - Gley | Some evidence | II-III | Eroded | Large Nodules just below erosive sand | Ustic Petrocalcid |
| MES 13 | 80 | 5YR 6/4 | Siltstone | Mottled nodules | Drab root halos | II | 16 | Slickensides (calcitic) | Vertic Haplocalcid |
| MES 14 | 46 | 10R 6/6 | Siltstone | Pseudo - Gley | Drab root halos | II | 38 | Large stage 2 nodules vertically orientated | Petronodic Haplocalcid |
| MES 15 | 59 | 5R | Siltstone | Pseudo - Gley | Drab root halos | II | Eroded | Slickensides (calcitic) | Petronodic Haplocalcid |
| MES 16 | 187 | 10Y 7/2 | Siltstone | Pseudo - Gley | Drab root halos | II | 100 | Slickensides at base | Vertic Haplocalcid |
| MES 17 | 140 | 10R 4/2 | silt | Pseudo - Gley | Drab root halos | II | Eroded | Mostly nodules scattered throughout section | Petronodic Haplocalcid |

# Appendix 2

## Paleosol isotope data, XRD data and statistical data

## (Chapter 4)

# A2.1

Table of all isotope analysis from the Southern Urals of Russia. Those analyses are starting 04. (e.g. 04.8.2.f) are from the 2004 field season. No within paleosol depths were recorded in this field season so the depth recorded is the middle of the paleosol horizon. Crp = cryptocrystalline; SpC = contains sinuous veins; MCr = microcrystalline (crystals above 20μm); MCr/SpC = microcrystalline (crystals above 20μm) and contains sinuous veins. All depths to Bk horizon are uncompressed depths using a burial depth of 1.9km for the Russian sediments (Brunet *et al.* 1999) and the decompression ratio calculator proposed by Sheldon and Retallack (2001). 2004 F/S = 2004 field season, see Chapter 2.

| | | | | | | | | | | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| KOR 36 | Petronodic Haplocalcid | II | 2 | SU06 KOR 36.1 | 211.10 | 0.07 | Calcium Carbonate | SpC | 05/09/07 | -2.16 | -7.60 | -3.14 | -8.68 |
| | | | | SU06 KOR 36.2 | 211.10 | 0.07 | Calcite | SpC | 19/09/07 | -4.90 | -8.88 | -3.10 | -9.54 |
| | | | | SU06 KOR 36.3 | 210.94 | 0.24 | Calcite | SpC | 19/09/07 | -3.70 | -10.91 | – | – |
| | | | | SU06 KOR 36.4 | 210.82 | 0.37 | Quartz | SpC | 19/09/07 | -4.57 | -11.25 | – | – |
| | | | | SU06 KOR 36.5 | 210.82 | 0.37 | Calcite | SpC | 19/09/07 | -5.97 | -11.77 | – | – |
| | | | | SU06 KOR 36.6 | 210.82 | 0.37 | Quartz | SpC | 19/09/07 | -6.13 | -11.09 | – | – |
| KOR 33 | Petronodic Haplocalcid/ Ustic Calcid (Lacustrine) | II | 3 | 04.8.2.f | 199.33 | 0.16 | Calcite, magnesian | SpC | 24/03/05 | -2.18 | -7.36 | – | – |
| | | | | 04.8.2.f | 199.33 | 0.16 | Calcite, magnesian | SpC | 10/05/06 | -2.69 | -9.92 | – | – |
| | | | | 04.8.2.f | 199.33 | 0.16 | Calcite, magnesian | SpC | 10/05/06 | -2.84 | -9.84 | – | – |
| | | | | SU06 KOR 33.1 | 199.41 | 0.16 | Calcite, magnesian | SpC | 05/09/07 | -2.87 | -8.32 | -0.26 | -9.55 |
| | | | | SU06 KOR 33.2 | 199.41 | 0.16 | Calcium Carbonate | SpC | 05/09/07 | -1.00 | -7.57 | -0.75 | -8.71 |
| | | | | SU06 KOR 33.3 | 199.41 | 0.16 | Calcite | SpC | 05/09/07 | -0.91 | -8.07 | -0.88 | -8.35 |
| KOR 37 | Petronodic Haplocalcid | II | 9 | SU06 KOR 37.1 | 196.58 | 0.17 | calcite | MCr | 19/09/07 | -1.04 | -9.34 | – | – |
| | | | | SU06 KOR 37.2 | 196.58 | 0.17 | Quartz | MCr | 19/09/07 | -1.40 | -10.85 | – | – |
| | | | | SU06 KOR 37.3 | 196.58 | 0.17 | calcite | MCr | 19/09/07 | -1.53 | -9.39 | – | – |
| | | | | SU06 KOR 37.4 | 196.12 | 0.68 | calcite | SpC | 19/09/07 | -0.50 | -10.01 | – | – |
| | | | | SU06 KOR 37.5 | 196.12 | 0.68 | calcite | SpC | 19/09/07 | -0.27 | -9.54 | v | |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| KOR 34 | Petronodic | II | eroded | SU06 KOR 34.1 | 199.46 | 0.02 | Calcite | MCr/SpC | 05/09/07 | -0.45 | -7.64 | 0.39 | -8.04 |
| | Haplocalcid | | | SU06 KOR 34.2 | 199.40 | 0.09 | Calcite | MCr/SpC | 05/09/07 | -0.10 | -7.46 | -0.83 | -8.40 |
| | | | | SU06 KOR 34.3 | 199.40 | 0.22 | Calcite | MCr/SpC | 05/09/07 | -0.56 | -7.59 | -0.22 | -8.20 |
| | | | | SU06 KOR 34.4 | 199.28 | 0.22 | Calcite | MCr/SpC | 05/09/07 | -0.12 | -7.29 | – | – |
| | | | | SU06 KOR 34.5 | 199.35 | 0.14 | Calcite, magnesian | MCr/SpC | 05/09/07 | -0.08 | -7.19 | -0.48 | -10.34 |
| | | | | SU06 KOR 34.6 | 199.35 | 0.14 | Calcite | MCr/SpC | 05/09/07 | -0.38 | -7.22 | -1.21 | -8.14 |
| | | | | SU06 KOR 34.7 | 199.35 | 0.14 | Calcite | MCr/SpC | 05/09/07 | -0.42 | -7.21 | -2.35 | -8.96 |
| KOR 32 | Petronodic | II | 8 | 04.8.2.e | 198.01 | 0.17 | Calcite | MCr | 10/05/06 | -1.23 | -9.20 | – | – |
| | Haplocalcid | | | 04.8.2.e.i | 198.01 | 0.17 | Calcite | MCr | 10/05/06 | -0.92 | -9.48 | – | – |
| | | | | 04.8.2.e.ii | 198.01 | 0.17 | Calcite | MCr | 10/05/06 | -1.23 | -9.20 | – | – |
| | | | | 04.8.2.e.iii | 198.01 | 0.17 | Calcite | MCr/SpC | 10/05/06 | -0.95 | -9.21 | – | – |
| | | | | 04.8.2.e.iv | 198.01 | 0.17 | Calcite | MCr | 10/05/06 | -0.77 | -9.31 | – | – |
| | | | | SU06 KOR 32.2 | 198.08 | 0.16 | Calcite | MCr | 05/09/07 | -0.04 | -7.01 | -2.93 | -8.69 |
| | | | | SU06 KOR 32.7 | 197.95 | 0.31 | Calcite | MCr/SpC | 05/09/07 | -0.27 | -7.15 | -2.55 | -8.71 |
| | | | | SU06 KOR 32.8 | 197.95 | 0.31 | Calcite | MCr/SpC | 05/09/07 | -0.11 | -7.55 | 0.12 | -8.03 |
| KOR 1a | Ustic | III | 23 | 04.8.1.ac* | 171.16 | 0.50 | – | SpC | 24/04/5 | -0.07 | 0.50 | – | – |
| | Petrocalcid | | | 04.8.1.ac.I | 171.16 | 0.50 | – | SpC | 10/05/06 | -0.20 | 0.52 | – | – |
| | | | | 04.8.1.ac.II | 171.16 | 0.50 | – | SpC | 10/05/06 | 0.14 | -1.03 | – | – |
| | | | | SU06 KOR 1.10 | 170.46 | 0.94 | Dolomite | MCr | 24/03/05 | 0.08 | 0.08 | – | – |
| | | | | SU06 KOR 1.7 | 170.46 | 0.94 | Dolomite | SpC | 24/03/05 | 0.18 | 0.38 | -0.09 | 0.55 |
| | | | | SU06 KOR 1.8 | 170.46 | 0.94 | Dolomite | SpC | 25/08/07 | -0.09 | 0.07 | – | – |
| | | | | SU06 KOR 1.9 | 170.46 | 0.94 | Dolomite | SpC | 25/08/07 | -0.27 | -1.25 | -2.90 | -8.85 |
| KOR 2 | Petronodic | II | 25 | SU06 KOR 2.1 | 170.38 | 0.11 | Dolomite | Crp | 25/08/07 | -0.16 | 1.16 | – | – |
| | Haplocalcid | | | SU06 KOR 2.2 | 169.99 | 0.32 | Dolomite | Crp | 25/08/07 | -0.74 | 0.61 | – | – |
| | | | | SU06 KOR 2.3 | 169.99 | 0.32 | Dolomite | Crp | 25/08/07 | -1.79 | -1.33 | – | – |
| | | | | SU06 KOR 2.4 | 169.85 | 0.47 | Dolomite | MCr/SpC | 25/08/07 | -0.86 | -3.26 | -1.09 | -9.23 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | SU06 KOR 2.5 | 169.85 | 0.47 | Dolomite | Crp | 25/08/07 | -1.57 | -0.12 | – | – |
| | | | | SU06 KOR 2.6 | 169.69 | 0.64 | Dolomite | SpC | 25/08/07 | -1.37 | -0.01 | -1.16 | -3.07 |
| | | | | SU06 KOR 2.7 | 169.69 | 0.64 | Dolomite | Crp | 25/08/07 | -1.43 | 0.13 | – | – |
| | | | | SU06 KOR 2.8 | 169.55 | 0.80 | Dolomite | SpC | 25/08/07 | -1.06 | 0.06 | -1.46 | -4.41 |
| | | | | SU06 KOR 2.9 | 169.55 | 0.80 | Dolomite | Crp | 25/08/07 | -1.36 | -0.20 | – | – |
| KOR 8 | Ustic Petrocalcid | IV | 27 | 04.8.1.aa | 166.13 | 0.15 | – | SpC | 24/03/05 | -1.05 | -2.49 | – | – |
| KOR 9 | Petronodic | II | Eroded | SU06 KOR 9.1 | 164.92 | 0.11 | Dolomite | SpC | 25/08/07 | -0.44 | -0.03 | -2.03 | -6.10 |
| | Haplocalcid | | | SU06 KOR 9.2 | 164.92 | 0.11 | Dolomite | Crp | 25/08/07 | -0.64 | -0.57 | – | – |
| | | | | SU06 KOR 9.3 | 164.92 | 0.11 | Dolomite | Crp | 25/08/07 | -0.33 | 0.26 | – | – |
| KOR 4 | Vertic Petrocalcid | V | 18 | 04.8.1.w | 157.95 | 0.57 | Dolomite | SpC | 24/03/05 | -1.01 | 0.07 | – | – |
| KOR 5 | Vertic | II | Eroded | 04.8.1.z | 162.86 | 0.42 | – | SpC | 24/03/05 | -0.79 | -1.23 | – | – |
| | Haplocalcid | | | SU06 KOR 5.1 | 162.91 | 0.26 | Quartz | MCr | 25/08/07 | -0.41 | 0.33 | – | – |
| | | | | SU06 KOR 5.2 | 162.90 | 0.27 | Dolomite | SpC | 25/08/07 | -0.81 | 0.17 | -1.57 | -2.83 |
| | | | | SU06 KOR 5.3 | 162.90 | 0.27 | Dolomite | Crp | 25/08/07 | -0.94 | -0.40 | – | – |
| | | | | SU06 KOR 5.4 | 162.77 | 0.42 | Dolomite | SpC | 25/08/07 | -1.63 | -0.72 | -2.55 | -5.56 |
| | | | | SU06 KOR 5.5 | 162.77 | 0.42 | Dolomite | SpC | 25/08/07 | -1.01 | -0.80 | -2.41 | -4.19 |
| KOR 6 | Petronodic | II | | SU06 KOR 6.2 | 163.04 | 0.58 | Dolomite | SpC | 25/08/07 | -1.31 | 0.36 | -2.96 | -4.15 |
| | Haplocalcid | | | SU06 KOR 6.3 | 162.88 | 0.40 | Dolomite | SpC | 25/08/07 | -1.12 | 0.09 | -3.60 | -7.09 |
| | | | | SU06 KOR 6.4 | 162.88 | 0.40 | Dolomite | SpC | 25/08/07 | -1.55 | -1.61 | -9.20 | -10.94 |
| | | | | SU06 KOR 6.5 | 162.78 | 0.29 | Dolomite | SpC | 25/08/07 | -1.36 | -0.11 | -8.63 | -10.18 |
| | | | | SU06 KOR 6.6 | 162.78 | 0.29 | Dolomite | SpC | 25/08/07 | -1.29 | -0.24 | -2.72 | -4.84 |
| | | | | SU06 KOR 6.7 | 162.63 | 0.13 | Dolomite | SpC | 25/08/07 | -1.21 | -0.09 | -2.71 | -2.18 |
| | | | | SU06 KOR 6.8 | 162.63 | 0.13 | Dolomite | SpC | 25/08/07 | -1.07 | 0.00 | -3.46 | -5.13 |
| KOR 10 | Ustic Calcid | III | | 04.8.1.x | 159.40 | 0.67 | – | MCr/SpC | 24/03/05 | -1.23 | -0.77 | – | – |
| | (Lacustrine) | | | SU06 KOR 10.1 | 159.86 | 0.04 | – | MCr | 25/08/07 | -1.18 | 0.36 | -3.92 | -7.29 |
| | | | | SU06 KOR 10.11 | 158.97 | 1.00 | Dolomite | MCr | 25/08/07 | -1.73 | -0.24 | -2.48 | -3.65 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | SU06 KOR 10.12 | 158.97 | 1.00 | Dolomite | MCr | 25/08/07 | -1.57 | -0.56 | -1.93 | -1.78 |
| | | | | SU06 KOR 10.2 | 159.72 | 0.19 | Dolomite | MCr/SpC | 25/08/07 | -2.06 | -3.05 | -2.46 | -4.74 |
| | | | | SU06 KOR 10.3 | 159.72 | 0.19 | Dolomite | MCr | 25/08/07 | -1.45 | -0.06 | -3.98 | -8.23 |
| | | | | SU06 KOR 10.4 | 159.59 | 0.33 | Dolomite | MCr | 25/08/07 | -1.38 | -0.56 | -2.67 | -2.43 |
| | | | | SU06 KOR 10.5 | 159.59 | 0.33 | Dolomite | SpC | 25/08/07 | -1.34 | 0.46 | -3.42 | -6.86 |
| | | | | SU06 KOR 10.6 | 159.40 | 0.53 | Quartz | SpC | 25/08/07 | -2.05 | -0.55 | | |
| | | | | SU06 KOR 10.7 | 159.40 | 0.53 | Dolomite | MCr | 25/08/07 | -1.55 | -0.28 | -1.99 | -3.31 |
| | | | | SU06 KOR 10.8 | 159.10 | 0.86 | Dolomite | SpC | 25/08/07 | -1.84 | -0.83 | -2.48 | -6.78 |
| KOR 11 | Ustic Petrocalcid | IV | 18 | 04.8.1.w | 157.95 | 0.41 | – | SpC | 29/03/05 | -1.01 | 0.07 | – | – |
| KOR 12 | Petronodic | II | 36 | 04.8.1.v* | 157.13 | 0.43 | – | Crp | 24/03/05 | -0.89 | 0.24 | – | – |
| | Haplocalcid | | | 04.8.1.v.I | 157.13 | 0.43 | – | Crp | 10/05/06 | -0.85 | 1.38 | – | – |
| | | | | 04.8.1.v.II | 157.13 | 0.43 | – | SpC | 10/05/06 | -0.76 | 1.08 | – | – |
| | | | | SU06 KOR 12.1 | 157.17 | 0.43 | Dolomite | SpC | 25/08/07 | -0.77 | 0.63 | – | – |
| | | | | SU06 KOR 12.3 | 157.17 | 0.43 | Dolomite | SpC | 25/08/07 | -0.71 | 0.47 | -1.02 | 1.29 |
| KOR 13 | Ustic Petrocalcid | IV | Eroded | 04.8.1.u | 156.08 | 0.15 | – | Crp | 24/03/05 | -0.25 | 0.31 | – | – |
| KOR 14 | Ustic Petrocalcid | III | 26 | 04.8.1.t | 154.35 | 0.41 | – | SpC | 24/03/05 | -1.13 | -0.42 | – | – |
| | | | | SU06 KOR 14.10 | 154.65 | 0.41 | Dolomite | SpC | 10/09/07 | -1.67 | -2.04 | – | – |
| | | | | SU06 KOR 14.11 | 154.65 | 0.41 | Dolomite | SpC | 10/09/07 | -1.14 | -0.02 | – | – |
| | | | | SU06 KOR 14.14 | 155.03 | 0.41 | Dolomite | SpC | 10/09/07 | -1.21 | 0.24 | -2.07 | -2.50 |
| | | | | SU06 KOR 14.15 | 155.03 | 0.41 | Dolomite | SpC | 10/09/07 | -1.28 | 0.11 | -2.92 | -10.58 |
| KOR 14a | Petronodic | II | 8 | SU06 KOR 14.8 | 154.35 | 0.13 | Dolomite | SpC | 10/09/07 | -1.28 | 0.25 | -5.49 | -4.02 |
| | Haplocalcid | | | SU06 KOR 14.9 | 154.35 | 0.13 | Dolomite | SpC | 10/09/07 | -1.41 | 0.25 | – | – |
| KOR 14b | Petronodic | II | 18 | 04.8.1.s | 153.83 | 0.25 | – | SpC | 24/03/05 | -1.66 | -0.34 | – | – |
| | Haplocalcid | | | SU06 KOR 14.1 | 153.83 | 0.25 | Dolomite | SpC | 25/08/07 | -2.20 | -1.36 | -2.67 | -0.69 |
| KOR 23 | Petronodic | III | Eroded | 04.8.1.r* | 144.56 | 0.15 | Dolomite | MCr/SpC | 24/03/05 | -2.26 | -1.96 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | Haplocalcid | | | 04.8.1.r.I | 144.56 | 0.15 | Dolomite | SpC | 10/05/06 | -3.30 | -1.55 | – | – |
| | | | | 04.8.1.r.II | 144.56 | 0.15 | Dolomite | SpC | 10/05/06 | -4.36 | -1.73 | – | – |
| | | | | 04.8.1.r.III | 144.56 | 0.15 | Dolomite | SpC | 10/05/06 | -4.14 | -1.95 | – | – |
| | | | | SU06 KOR 23.1 | 144.76 | 0.05 | Calcite, magnesian | Crp | 05/09/07 | -10.81 | -11.55 | – | – |
| | | | | SU06 KOR 23.2 | 144.76 | 0.05 | Calcite, magnesian | SpC | 05/09/07 | -10.56 | -11.05 | -5.48 | -9.26 |
| | | | | SU06 KOR 23.3 | 144.57 | 0.26 | Dolomite | Crp | 05/09/07 | -4.75 | -0.68 | – | – |
| | | | | SU06 KOR 23.4 | 144.57 | 0.26 | Dolomite | Crp | 05/09/07 | -4.09 | -1.03 | – | – |
| KOR 22 | Petronodic | II | 64.5 | 04.8.1.q | 143.54 | 0.41 | – | SpC | 05/04/06 | -6.46 | -9.84 | – | – |
| | Haplocalcid | | | 04.8.1.q.I | 143.54 | 0.41 | – | SpC | 10/05/06 | -10.71 | -12.14 | – | – |
| | | | | 04.8.1.q.II | 143.54 | 0.41 | – | SpC | 10/05/06 | -10.03 | -11.30 | – | – |
| | | | | 04.8.1.q.III | 143.54 | 0.41 | – | SpC | 10/05/06 | -6.73 | -4.91 | – | – |
| | | | | SU06 KOR 22.1 | 143.26 | 0.13 | Calcite ($CaCO_3$) | SpC | 05/09/07 | -4.68 | -3.70 | -4.98 | -4.37 |
| | | | | SU06 KOR 22.10 | 143.78 | 0.70 | Calcite | Crp | 05/09/07 | -11.03 | -10.99 | – | – |
| | | | | SU06 KOR 22.11 | 143.78 | 0.70 | Calcite, magnesian | Crp | 05/09/07 | -10.53 | -10.12 | – | – |
| | | | | SU06 KOR 22.12 | 143.89 | 0.82 | Calcite | Crp | 05/09/07 | -11.06 | -11.45 | – | – |
| | | | | SU06 KOR 22.13 | 143.89 | 0.82 | Calcite | Crp | 05/09/07 | -6.44 | -6.38 | – | – |
| | | | | SU06 KOR 22.14 | 143.89 | 0.82 | Calcite, magnesian | Crp | 05/09/07 | -9.70 | -8.96 | – | – |
| | | | | SU06 KOR 22.2 | 143.26 | 0.13 | Calcite (Mg, $CaCO_3$) | Crp | 05/09/07 | -9.97 | -11.30 | -4.44 | -6.79 |
| | | | | SU06 KOR 22.4 | 143.26 | 0.13 | Calcite, magnesian | Crp | 05/09/07 | -10.76 | -11.00 | -4.24 | -4.88 |
| | | | | SU06 KOR 22.5 | 143.26 | 0.13 | Quartz | SpC | 05/09/07 | -4.90 | -5.60 | – | – |
| | | | | SU06 KOR 22.6 | 143.47 | 0.36 | Calcite | Crp | 05/09/07 | -4.96 | -4.66 | – | – |
| | | | | SU06 KOR 22.7 | 143.47 | 0.36 | Calcite | SpC | 05/09/07 | -10.34 | -10.49 | – | – |
| | | | | SU06 KOR 22.8 | 143.64 | 0.55 | Calcite | Crp | 05/09/07 | -4.90 | -5.57 | -10.87 | -12.91 |
| KOR 21 | Ustic Petrocalcid | II | Eroded | 04.8.1.p | 141.58 | 0.23 | Dolomite | SpC | 24/03/05 | -0.69 | -0.18 | – | – |
| | | | | SU06 KOR 21.10 | 141.35 | 0.59 | Dolomite | MCr/SpC | 10/09/07 | -1.33 | 0.73 | -3.20 | -6.34 |
| | | | | SU06 KOR 21.4 | 141.67 | 0.24 | Dolomite | SpC | 10/09/07 | -3.57 | -5.06 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | SU06 KOR 21.5 | 141.67 | 0.24 | Dolomite | SpC | 10/09/07 | -2.47 | -1.81 | -4.31 | -7.74 |
| | | | | SU06 KOR 21.6 | 141.55 | 0.37 | Quartz | SpC | 10/09/07 | -3.50 | -3.50 | -4.17 | -5.46 |
| | | | | SU06 KOR 21.7 | 141.55 | 0.37 | Dolomite | MCr/SpC | 10/09/07 | -1.32 | -1.09 | -4.87 | -5.90 |
| | | | | SU06 KOR 21.8 | 141.35 | 0.59 | Dolomite | SpC | 10/09/07 | -0.39 | 1.03 | -4.09 | -9.31 |
| | | | | SU06 KOR 21.9 | 141.35 | 0.59 | Dolomite | SpC | 10/09/07 | -1.51 | 0.64 | -3.06 | -3.00 |
| KOR 21a | Ustic Petrocalcid | II | Eroded | SU06 KOR 21.1 | 141.80 | 0.10 | Calcite (Mg) | SpC | 10/09/07 | -4.04 | -5.27 | -5.08 | -6.45 |
| | | | | SU06 KOR 21.2 | 141.80 | 0.10 | Calcite, magnesian | MCr/SpC | 10/09/07 | -2.32 | -4.10 | -3.99 | -7.48 |
| | | | | SU06 KOR 21.3 | 141.80 | 0.10 | Calcite ($CaCO_3$) | MCr/ | 10/09/07 | -3.72 | -5.08 | -4.17 | -7.37 |
| KOR 15 | Petronodic | II | 17 | 04.8.1.o | 139.97 | 0.39 | – | SpC | 29/03/05 | -0.91 | -1.33 | – | – |
| | Haplocalcid | | | SU06 KOR 15.2 | 140.08 | 0.23 | Dolomite | MCr/SpC | 10/09/07 | -0.46 | 0.11 | -1.09 | -0.16 |
| | | | | SU06 KOR 15.3 | 140.08 | 0.23 | Dolomite | SpC | 10/09/07 | -0.68 | 0.07 | -2.94 | -8.89 |
| | | | | SU06 KOR 15.4 | 140.08 | 0.23 | Dolomite | SpC | 10/09/07 | -0.52 | 0.17 | – | – |
| | | | | SU06 KOR 15.5 | 139.96 | 0.36 | Dolomite | SpC | 10/09/07 | -0.76 | -0.88 | -3.54 | -13.39 |
| | | | | SU06 KOR 15.6 | 139.96 | 0.36 | Dolomite | SpC | 10/09/07 | -1.85 | -4.07 | -1.78 | -2.90 |
| | | | | SU06 KOR 15.7 | 139.79 | 0.55 | Dolomite | SpC | 10/09/07 | -0.71 | -1.20 | -1.74 | -3.99 |
| | | | | SU06 KOR 15.8 | 139.79 | 0.55 | Dolomite | MCr/SpC | 10/09/07 | -1.12 | -1.03 | -1.18 | -1.22 |
| | | | | SU06 KOR 15.9 | 139.79 | 0.55 | Dolomite | SpC | 10/09/07 | -0.48 | -0.39 | -3.27 | -10.12 |
| KOR 16 | Petronodic | II | 13 | 04.8.1.n* | 136.10 | 0.22 | – | SpC | 10/09/07 | -2.20 | -6.16 | – | – |
| | Haplocalcid | | | SU06 KOR 16.10 | 136.20 | 0.33 | Calcite, magnesian | SpC | 10/09/07 | -2.97 | -8.76 | -3.44 | -8.78 |
| | | | | SU06 KOR 16.5 | 136.20 | 0.33 | Calcite, magnesian | SpC | 10/09/07 | -4.28 | -5.64 | -3.33 | -6.52 |
| | | | | SU06 KOR 16.6 | 136.20 | 0.33 | Calcite, magnesian | SpC | 10/09/07 | -3.89 | -5.15 | -2.90 | -6.32 |
| | | | | SU06 KOR 16.7 | 136.20 | 0.33 | Calcite | SpC | 10/09/07 | -3.42 | -5.50 | -3.13 | -7.15 |
| | | | | SU06 KOR 16.8 | 136.20 | 0.33 | Calcite, magnesian | SpC | 10/09/07 | -4.23 | -5.18 | -3.66 | -7.06 |
| | | | | SU06 KOR 16.9 | 136.20 | 0.33 | Calcite, magnesian | SpC | 10/09/07 | -3.45 | -6.96 | – | – |
| KOR 16 a | Petronodic | II | 14 | SU06 KOR 16.1 | 135.97 | 0.22 | Calcite, magnesian | SpC | 10/09/07 | -3.83 | -5.86 | -4.03 | -6.41 |
| | Haplocalcid | | | SU06 KOR 16.2 | 135.97 | 0.22 | Calcite, magnesian | SpC | 10/09/07 | -4.02 | -4.16 | -3.47 | -6.84 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | SU06 KOR 16.3 | 135.97 | 0.22 | Calcite | MCr | 10/09/07 | -4.54 | -5.51 | -3.05 | -7.57 |
| | | | | SU06 KOR 16.4 | 135.97 | 0.22 | Calcite, magnesian | SpC | 10/09/07 | -4.68 | -5.08 | -3.10 | -7.16 |
| KOR 17 | Ustic Calcid | III | 24 | 04.8.1.m* | 136.10 | 0.30 | – | MCr | 29/03/05 | -0.01 | -3.96 | – | – |
| | (Lacustrine) | | | SU06 KOR 17.2 | 135.68 | 0.24 | Calcite | MCr | 10/09/07 | -0.02 | -1.70 | – | – |
| | | | | SU06 KOR 17.3 | 135.68 | 0.24 | Dolomite | MCr | 10/09/07 | 0.75 | -0.54 | -0.75 | -2.36 |
| KOR 18 | Ustic Petrocalcid | III | 12 | 04.8.1.l | 128.42 | 0.19 | Dolomite | Crp | 29/03/05 | 0.86 | 0.82 | – | – |
| | | | | 04.8.1.l.I | 128.42 | 0.19 | Dolomite | Crp | 10/05/06 | 2.60 | 2.07 | – | – |
| | | | | 04.8.1.l.II | 128.42 | 0.19 | Dolomite | Crp | 10/05/06 | 2.52 | 2.52 | – | – |
| | | | | 04.8.1.l.III | 128.42 | 0.19 | Dolomite | Crp | 10/05/06 | 2.53 | 2.20 | – | – |
| KOR 19 | Ustic Petrocalcid | V | 21 | 04.8.1.k | 123.57 | 0.00 | – | MCr/SpC | 29/03/05 | -0.04 | -0.56 | – | – |
| KOR 20 | Ustic Calcid(Lacustrine) | IV | 59 | 04.8.1.j | 116.70 | 0.00 | – | SpC | 29/03/05 | -1.01 | 0.30 | – | – |
| KOR 24 | | III | 15 | 04.8.1.i | 114.34 | 0.25 | Dolomite | MCr | 10/05/06 | -2.16 | -5.97 | – | – |
| | | | | 04.8.1.i.I | 114.34 | 0.25 | – | MCr | 10/05/06 | -2.69 | -6.61 | – | – |
| | | | | 04.8.1.i.II | 114.34 | 0.25 | – | MCr | 10/05/06 | -3.23 | -7.56 | – | – |
| | | | | 04.8.1.i.III | 114.34 | 0.25 | – | MCr | 10/05/06 | -3.67 | -8.50 | – | – |
| | | | | SU06 KOR 24.5 | 114.23 | 0.36 | Calcite | MCr | 05/09/07 | 0.31 | -5.49 | – | – |
| | | | | SU06 KOR 24.6 | 114.23 | 0.36 | Calcite, magnesian | MCr | 05/09/07 | 0.68 | -4.70 | – | – |
| KOR 25 | Ustic Petrocalcid | II | 21 | SU06 KOR 25.1 | 104.66 | 0.27 | Calcite | SpC | 05/09/07 | -10.18 | -11.31 | -9.05 | -12.24 |
| | | | | SU06 KOR 25.3 | 104.66 | 0.27 | – | Crp | 05/09/07 | -10.18 | -11.24 | – | – |
| | | | | SU06 KOR 25.4 | 104.66 | 0.27 | – | Crp | 05/09/07 | -9.90 | -11.29 | – | – |
| | | | | SU06 KOR 25.5 | 104.66 | 0.27 | Calcite, magnesian | Crp | 05/09/07 | -9.88 | -11.01 | – | – |
| KOR 26 | Ustic Calcid(Lacustrine) | IV | 41 | 04.8.1.g* | 98.73 | 0.00 | Calcite | SpC | 29/03/05 | -0.65 | -6.04 | – | – |
| KOR 27 | Petronodic | II | 26 | 04.8.1.f* | 98.59 | 0.31 | Calcite | SpC | 29/03/05 | -1.05 | -4.10 | – | – |
| | *Haplocalcid* | | | SU06 KOR 27.2 | 98.59 | 0.31 | Calcite | SpC | 28/11/07 | 0.46 | -8.84 | – | – |
| | | | | SU06 KOR 27.4 | 98.59 | 0.31 | Quartz | SpC | 28/11/07 | 0.36 | -9.26 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| KOR 28 | Ustic Petrocalcid | IV | Eroded | 04.8.1.e | 95.56 | 0.08 | Dolomite | SpC | 29/03/05 | -1.50 | -2.38 | – | – |
| KOR 29 | Ustic Petrocalcid | III | Eroded | 04.8.1.c | 88.20 | 0.11 | Dolomite | Crp | 10/05/06 | -1.52 | -0.75 | – | – |
| | | | | 04.8.1.c.I | 88.20 | 0.11 | Dolomite | Crp | 10/05/06 | -1.90 | 1.45 | – | – |
| | | | | 04.8.1.c.II | 88.20 | 0.11 | Dolomite | Crp | 10/05/06 | -1.90 | 0.38 | – | – |
| | | | | 04.8.1.c.III | 88.20 | 0.11 | Dolomite | Crp | 10/05/06 | -2.64 | -0.37 | – | – |
| KOR 31 | () | II | Eroded | 04.8.1.b* | 79.51 | 0.23 | Calcite | SpC | 10/05/06 | -2.64 | -2.64 | – | – |
| | Haplocalcid | | | 04.8.1.b.I | 79.51 | 0.23 | Calcite | SpC | 10/05/06 | -4.11 | -5.85 | – | – |
| | | | | 04.8.1.b.II | 79.51 | 0.23 | Calcite | SpC | 10/05/06 | -4.42 | -5.54 | – | – |
| | | | | 04.8.1.b.III | 79.51 | 0.23 | Calcite | SpC | 10/05/06 | -4.48 | -5.64 | – | – |
| | | | | SU06 KOR 31.1 | 79.51 | 0.23 | Calcite, magnesian | SpC | 05/09/07 | -4.61 | -5.17 | – | – |
| | | | | SU06 KOR 31.2 | 79.51 | 0.23 | Calcite | SpC | 05/09/07 | -4.49 | -4.17 | – | – |
| | | | | SU06 KOR 31.5 | 79.51 | 0.23 | Calcite | SpC | 05/09/07 | -5.15 | -6.95 | -5.13 | -8.09 |
| KOR 35 | Petronodic | II | Eroded | 04.8.1.a | 79.22 | 0.25 | – | SpC | 29/03/05 | -3.07 | -6.00 | – | – |
| | Haplocalcid | | | SU06 KOR 35.1 | 79.22 | 0.25 | Calcite, magnesian | SpC | 05/09/07 | -4.62 | -6.79 | -8.42 | -8.94 |
| | | | | SU06 KOR 35.3 | 79.22 | 0.25 | Quartz | Crp | 05/09/07 | -12.44 | -9.76 | – | – |
| | | | | SU06 KOR 35.5 | 79.22 | 0.25 | Calcite, syn | SpC | 05/09/07 | -7.07 | -8.79 | -8.50 | -9.88 |

## Sambullak

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| SAM 1 | Vertic | II | 31 | 04.7.24.u | 131.13 | 0.52 | – | SpC | 29/03/06 | -3.00 | -10.03 | – | – |
| | Haplocalcid | | | 04.7.24.u.I | 131.13 | 0.52 | – | SpC | 10/05/06 | -5.88 | -14.15 | – | – |
| | | | | 04.7.24.u.II | 131.13 | 0.52 | – | SpC | 10/05/06 | -5.00 | -12.82 | – | – |
| | | | | SU06 SAM 1.1 | 131.13 | 0.52 | Calcite, magnesian | SpC | 11/11/07 | -4.12 | -8.81 | -2.80 | -8.21 |
| | | | | SU06 SAM 1.2 | 131.13 | 0.52 | Calcite | SpC | 11/11/07 | -2.26 | -7.50 | -2.08 | -7.09 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | SU06 SAM 1.3 | 131.13 | 0.52 | Calcite | SpC | 11/11/07 | -6.23 | -13.07 | -5.23 | -11.26 |
| | | | | SU06 SAM 1.4 | 131.13 | 0.52 | Calcite | SpC | 11/11/07 | -5.89 | -8.91 | -5.23 | -11.33 |
| | | | | SU06 SAM 1.5 | 131.13 | 0.52 | Calcite, magnesian | SpC | 11/11/07 | -6.68 | -11.38 | -4.30 | -8.45 |
| SAM 4 | Petronodic | II | eroded | 04.7.24.t | 131.1 | 0.35 | – | MCr | 29/03/06 | -3.31 | -9.50 | – | – |
| | Haplocalcid | | | 04.7.24.t.I | 131.1 | 0.35 | – | MCr | 10/05/06 | -4.74 | -7.95 | – | – |
| | | | | 04.7.24.t.II | 131.1 | 0.35 | – | MCr | 10/05/06 | -2.71 | -7.99 | – | – |
| | | | | 04.7.24.t.III | 131.1 | 0.35 | – | MCr | 10/05/06 | -0.04 | -7.57 | – | – |
| | | | | SU06 SAM 4.3 | 130.22 | 0.53 | Calcite, magnesian | MCr | 12/11/07 | -6.00 | -12.98 | – | – |
| | | | | SU06 SAM 4.4 | 130.14 | 0.61 | Calcite | MCr | 12/11/07 | -5.55 | -12.77 | – | – |
| 2004F/S | | III? | | 04.7.24.r | 123.68 | | – | SpC | 21/03/05 | -4.01 | -9.54 | – | – |
| SAM 3 | Vertic | III | 49 | 04.7.24.s | 122.62 | 0.325 | Calcite | MCr | 21/03/05 | -3.77 | -9.29 | – | – |
| | Haplocalcid | | | SU06 SAM 3.1 | 122.62 | 0.83 | Calcite, magnesian | MCr | 11/11/07 | -7.21 | -12.93 | – | – |
| | | | | SU06 SAM 3.2 | 122.62 | 0.83 | Calcite | SpC | 11/11/07 | -7.76 | -13.64 | -8.18 | -12.94 |
| | | | | SU06 SAM 3.3 | 122.33 | 1.12 | Dolomite | SpC | 11/11/07 | -5.00 | -5.94 | – | – |
| | | | | SU06 SAM 3.4 | 122.33 | 1.12 | Dolomite | SpC | 11/11/07 | -5.62 | -8.15 | – | – |
| | | | | SU06 SAM 3.5 | 122.33 | 1.12 | Dolomite | SpC | 11/11/07 | -4.19 | -4.50 | – | – |
| 2004F/S | | IV | | 04.7.24.q | 121.96 | | Calcite, magnesian | SpC | 21/03/05 | -3.62 | -6.80 | – | – |
| SAM 2 | Ustic Calcid | II | Lacust. | SU06 SAM 2.1 | 114.84 | 0.11 | Calcite, magnesian | SpC | 12/11/07 | -5.71 | -7.69 | – | – |
| | (Lacustrine) | | | SU06 SAM 2.2 | 114.72 | 0.23 | Dolomite | SpC | 12/11/07 | -2.48 | -5.52 | -4.24 | -10.66 |
| | | | | SU06 SAM 2.3 | 114.51 | 0.44 | Calcite, magnesian | SpC | 12/11/07 | -3.10 | -5.69 | – | – |
| | | | | 04.7.24.p | 114.48 | 0.35 | Calcite | SpC | 21/03/05 | -3.13 | -9.61 | -4.68 | -11.92 |
| | | | | SU06 SAM 2.4 | 114.48 | 0.47 | Calcite, magnesian | SpC | 12/11/07 | -5.92 | -13.53 | -4.76 | -11.88 |
| SAM 12 | Petronodic | II | 14 | SU06 SAM 12.1 | 114.38 | 0.17 | Calcite | Crp | 11/11/07 | -5.83 | -9.78 | – | – |
| | Haplocalcid | | | SU06 SAM 12.2 | 114.38 | 0.17 | Dolomite | MCr | 11/11/07 | -5.49 | -9.90 | – | – |
| SAM 10 | | II | 42 | SU06 SAM 10.8 | 123.28 | 0.555 | Dolomite | SpC | 12/11/07 | -4.31 | -5.93 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | Vertic Haplocalcid | | | SU06 SAM 10.9 | 123.28 | 0.555 | Calcite, magnesian | SpC | 12/11/07 | -4.53 | -7.72 | -4.65 | -6.03 |
| | | | | SU06 SAM 10.7 | 123.07 | 0.805 | Dolomite | SpC | 12/11/07 | -4.70 | -6.09 | – | – |
| | | | | SU06 SAM 10.6 | 122.94 | 0.99 | Dolomite | SpC | 12/11/07 | -3.93 | -4.68 | -5.32 | -9.02 |
| SAM 10a | Vertic | II | 24 | SU06 SAM 10.5 | 122.6 | 0.27 | Dolomite | SpC | 11/11/07 | -3.76 | -3.75 | -5.48 | -11.39 |
| | Haplocalcid | | | SU06 SAM 10.3 | 122.44 | 0.39 | Dolomite | SpC | 11/11/07 | -3.61 | -3.62 | -4.49 | -6.00 |
| | | | | SU06 SAM 10.4 | 122.44 | 0.41 | Dolomite | Crp | 11/11/07 | -3.39 | -2.52 | – | – |
| | | | | SU06 SAM 10.2 | 122.3 | 0.54 | Dolomite | SpC | 11/11/07 | -3.93 | -3.85 | -7.45 | -6.57 |
| | | | | SU06 SAM 10.1 | 121.89 | 1 | Dolomite | SpC | 11/11/07 | -4.01 | -3.41 | -6.67 | -6.36 |
| SAM 9 | Petronodic | II | 80 | 04.7.24.m | 102.48 | 0.65 | Dolomite | MCr | 21/03/05 | -1.75 | -2.39 | – | – |
| | Haplocalcid | | | SU06 SAM 9.3 | 102.48 | 0.81 | Dolomite | Crp | 12/11/07 | -4.55 | -5.49 | -6.00 | -11.34 |
| | | | | SU06 SAM 9.4 | 102.48 | 0.81 | Dolomite | SpC | 12/11/07 | -5.18 | -5.33 | – | – |
| | | | | SU06 SAM 9.2 | 102.14 | 0.47 | Dolomite | SpC | 12/11/07 | -4.92 | -5.14 | -5.20 | -5.36 |
| SAM 8 | Petronodic | II | 18 | SU06 SAM 8.5 | 98.61 | 0.49 | Calcite | SpC | 11/11/07 | -6.31 | -8.55 | -5.51 | -11.00 |
| | Haplocalcid | | | 04.7.24.l | 98.43 | 0.5 | Dolomite | SpC | 21/03/05 | -2.22 | -3.52 | – | – |
| | | | | SU06 SAM 8.2 | 98.43 | 0.31 | Calcite | SpC | 11/11/07 | -5.24 | -7.61 | -5.47 | -9.65 |
| | | | | SU06 SAM 8.3 | 98.43 | 0.31 | Calcite | SpC | 11/11/07 | -6.00 | -8.32 | -7.65 | -10.20 |
| | | | | SU06 SAM 8.4 | 98.43 | 0.31 | Calcite, magnesian | Crp | 11/11/07 | -5.74 | -8.33 | – | – |
| | | | | SU06 SAM 8.1 | 98.27 | 0.15 | Calcite, magnesian | SpC | 11/11/07 | -5.57 | -7.45 | -7.84 | -9.83 |
| SAM 5a | Ustic | III | 25 | 04.7.24.k | 98.13 | 0.72 | Dolomite | MCr | 21/03/05 | -2.51 | -3.67 | – | – |
| | Petrocalcid | | | 04.7.24.k.I | 98.13 | 0.72 | Dolomite | MCr | 10/05/06 | -3.86 | -4.73 | – | – |
| | | | | 04.7.24.k.II | 98.13 | 0.72 | Dolomite | MCr | 10/05/06 | -4.46 | -5.03 | – | – |
| | | | | 04.7.24.k.III | 98.13 | 0.72 | Dolomite | MCr | 10/05/06 | -4.17 | -5.00 | – | – |
| SAM 20 | Petronodic | II | 27 | 04.7.24.j | 87.76 | 0.36 | Dolomite | Crp | 21/03/05 | -2.47 | -3.69 | – | – |
| | Haplocalcid | | | SU06 SAM 20.2 | 87.76 | 0.36 | Dolomite | Crp | 12/11/07 | -3.77 | -4.85 | – | – |
| | | | | SU06 SAM 20.3 | 87.76 | 0.36 | Dolomite | SpC | 12/11/07 | -5.00 | -6.90 | – | – |
| | | | | SU06 SAM 20.4 | 87.76 | 0.36 | Dolomite | SpC | 12/11/07 | -3.93 | -5.26 | -4.27 | -5.93 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C$‰ VPDB | $\delta^{18}O$‰ VPDB | $\delta^{13}C$‰ VPDB | $\delta^{18}O$‰ VPDB |
| | | | | SU06 SAM 20.5 | 87.76 | 0.36 | Dolomite | SpC | 12/11/07 | -3.71 | -4.69 | -5.45 | -6.72 |
| SAM 19a | Ustic Petrocalcid | III | 12 | 04.7.24.i | 91.88 | 0.46 | Dolomite | SpC | 21/03/05 | -2.44 | -3.06 | – | – |
| SAM 18 | Ustic Petrocalcid | IV | 17 | 04.7.24.h | 90.53 | 0.315 | Dolomite | SpC | 21/03/05 | -2.62 | -3.83 | – | – |
| 2004F/S | | IV | | 04.7.24.g | | 0.125 | Dolomite | SpC | 21/03/05 | -2.04 | -2.58 | – | – |
| 2004F/S | | IV | | 04.7.24.f | | 0.325 | Dolomite | MCr/SpC | 21/03/05 | -1.94 | -2.62 | – | – |
| SAM 17 | Petronodic Haplocalcid | II | 39 | SU06 SAM 17.1 | 80.435 | 0.065 | Calcite | SpC | 11/11/07 | -5.98 | -8.61 | – | – |
| | | | | SU06 SAM 17.2 | 80.435 | 0.065 | Calcite | SpC | 11/11/07 | -5.27 | -7.46 | -6.32 | -9.97 |
| | | | | SU06 SAM 17.3 | 80.435 | 0.065 | Calcite | SpC | 11/11/07 | -5.57 | -8.40 | – | – |
| | | | | SU06 SAM 17.4 | 80.435 | 0.065 | Calcium Carbonate | SpC | 11/11/07 | -6.13 | -8.75 | – | – |
| SAM 14 | Petronodic Haplocalcid | I/II | 15 | SU06 SAM 14.1 | 68.205 | 0.125 | Calcite, magnesian | SpC | 12/11/07 | -7.82 | -6.27 | -7.72 | -6.35 |
| | | | | SU06 SAM 14.2 | 68.205 | 0.125 | Calcite, magnesian | SpC | 12/11/07 | -6.46 | -7.97 | -6.29 | -8.12 |
| | | | | SU06 SAM 14.3 | 68.205 | 0.125 | Calcite, magnesian | Crp | 12/11/07 | -5.54 | -7.45 | – | – |
| SAM 13 | Petronodic Haplocalcid | II | 14 | SU06 SAM 13.3 | 66.8 | 0.33 | Calcite, magnesian | SpC (MCr areas) | 12/11/07 | -5.63 | -8.23 | -6.28 | -10.41 |
| | | | | SU06 SAM 13.4 | 66.8 | 0.33 | Calcite, magnesian | SpC | 12/11/07 | -5.50 | -8.54 | -5.77 | -9.14 |
| | | | | SU06 SAM 13.5 | 66.8 | 0.33 | Calcite, magnesian | SpC | 12/11/07 | -5.88 | -8.63 | -6.64 | -10.41 |
| | | | | SU06 SAM 13.2 | 66.67 | 0.2 | Calcite, magnesian | SpC | 12/11/07 | -5.55 | -8.08 | -6.80 | -11.43 |
| | | | | SU06 SAM 13.1 | 66.49 | 0.02 | Calcite | SpC | 12/11/07 | -5.43 | -8.18 | -6.38 | -9.87 |
| SAM 21 | Petronodic Haplocalcid | II | 19 | SU06 SAM 21.1 | 62.44 | 0.3 | Calcite | Crp | 11/11/07 | -6.22 | -7.68 | – | – |
| | | | | SU06 SAM 21.2 | 62.44 | 0.3 | Calcite, magnesian | Crp | 11/11/07 | -5.75 | -7.45 | – | – |
| | | | | SU06 SAM 21.3 | 62.44 | 0.3 | Calcite, magnesian | Crp | 11/11/07 | -6.67 | -7.15 | – | – |
| | | | | SU06 SAM 21.4 | 62.44 | 0.3 | Calcite | SpC | 11/11/07 | -6.19 | -7.53 | -5.81 | -8.25 |
| | | | | SU06 SAM 21.5 | 62.44 | 0.3 | Calcium Carbonate | Crp | 11/11/07 | -7.39 | -7.00 | – | – |
| SAM 22 | Petronodic Haplocalcid | II | 27 | SU06 SAM 22.1 | 60.97 | 0.33 | Calcite, magnesian | Crp | 11/11/07 | -5.51 | -7.79 | – | – |
| SAM 23 | Petronodic Haplocalcid | III | 47 | SU06 SAM 23.2 | 60.15 | 0.7 | Dolomite | SpC | 11/11/07 | -5.35 | -8.28 | -6.13 | -10.69 |
| | | | | SU06 SAM 23.3 | 60.15 | 0.7 | Calcite | SpC | 11/11/07 | -5.78 | -8.96 | -6.11 | -10.87 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| SAM 24a | Petronodic Haplocalcid | II | 51 | SU06 SAM 24.1 | 57.44 | 1.36 | Calcite | SpC | 12/11/07 | -5.61 | -8.21 | -5.59 | -8.74 |
| SAM 24b | Petronodic Haplocalcid | II | | SU06 SAM 24.3 | 57.02 | 1.78 | Calcite | Crp | 12/11/07 | -5.57 | -9.49 | – | – |
| | | | | SU06 SAM 24.4 | 56.945 | 1.855 | Calcite | SpC | 12/11/07 | -5.26 | -8.62 | – | – |
| SAM 24c | Petronodic Haplocalcid | II | | SU06 SAM 24.5 | 57.61 | 1.19 | Calcite, magnesian | SpC | 12/11/07 | -5.60 | -8.12 | -5.28 | -8.63 |
| | | | | SU06 SAM 24.6 | 56.29 | 2.51 | Calcite | SpC | 12/11/07 | -6.52 | -7.93 | -5.82 | -10.03 |
| SAM 24d | Petronodic Haplocalcid | II | | SU06 SAM 24.8 | 56.28 | 3.47 | Calcite, magnesian | SpC | 12/11/07 | -5.19 | -8.16 | -5.30 | -8.60 |
| | | | | SU06 SAM 24.9 | 55.27 | 3.53 | Calcite | SpC | 12/11/07 | -5.13 | -8.36 | -5.55 | -10.05 |
| | | | | SU06 SAM 24.10 | 55.58 | 3.59 | Calcite | SpC | 12/11/07 | | | -5.04 | -8.21 |
| | | | | SU06 SAM 24.11 | 55.21 | 3.59 | Calcite, magnesian | SpC | 12/11/07 | -5.32 | -8.90 | -5.52 | -9.18 |
| SAM 24e | Petronodic Haplocalcid | II | | SU06 SAM 24.12 | 54.06 | 4.74 | Calcite | SpC | 12/11/07 | -4.67 | -8.14 | – | – |
| | | | | SU06 SAM 24.13 | 54 | 4.8 | Calcite | SpC | 12/11/07 | -5.05 | -8.67 | -5.26 | -8.62 |
| | | | | SU06 SAM 24.14 | 53.95 | 4.85 | Calcite | SpC | 12/11/07 | -5.13 | -8.22 | – | – |
| 2004F/S | II | | | 04.7.24.d | 50.91 | 0.285 | Calcite, magnesian | SpC | 10/05/06 | -3.38 | -4.98 | -6.37 | -8.86 |
| 2004F/S | II | | | 04.7.24.d | 50.91 | 0.285 | Calcite, magnesian | SpC | 10/05/06 | -5.24 | -6.27 | – | – |
| 2004F/S | III | | | 04.7.24.c | 46.93 | 0.15 | Dolomite | SpC | 21/03/05 | -2.21 | -3.89 | – | – |
| 2004F/S | III | | | 04.7.24.b | 43.53 | 0.05 | Dolomite | Crp | 21/03/05 | -3.62 | -4.84 | -6.09 | -5.77 |
| 2004F/S | III | | | 04.7.24.a | 38.61 | 0.08 | Dolomite | SpC | 29/03/06 | -2.53 | -3.81 | – | – |
| 2004F/S | III | | | 04.7.24.a.I | 38.61 | 0.08 | Dolomite | SpC | 10/05/06 | -4.02 | -5.08 | – | – |
| 2004F/S | III | | | 04.7.24.a.II | 38.61 | 0.08 | Dolomite | SpC | 10/05/06 | -4.48 | -5.54 | – | – |
| 2004F/S | II | | | 04.7.23.o | 33.13 | 0.10 | Dolomite | Crp | 21/03/05 | -1.85 | -2.97 | -4.27 | -7.88 |
| 2004F/S | IV | | | 04.7.23.n | 15.11 | 0.13 | Dolomite | Crp | 21/03/05 | -1.94 | -2.93 | – | – |
| 2004F/S | IV | | | 04.7.23.l | 12.74 | 0.04 | Dolomite | MCr | 21/03/05 | -2.71 | -3.64 | – | – |
| 2004F/S | V/lacustrine | | | 04.7.23.k | 11.63 | 0.08 | Dolomite | SpC | 21/03/05 | -1.80 | -2.95 | – | – |
| 2004F/S | II | | | 04.7.23.j | 10.58 | 0.08 | Dolomite | Crp | 21/03/05 | -1.55 | -2.87 | -3.07 | -4.42 |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| 2004F/S | | II | | 04.7.23.h | 9.53 | 0.15 | Dolomite | SpC | 21/03/05 | -2.67 | -4.07 | -3.95 | -1.34 |
| 2004F/S | | II | | 04.7.23.i | 9.53 | 0.15 | – | SpC | 21/03/05 | -1.75 | -2.75 | -2.79 | -4.14 |
| 2004F/S | | II | | 04.7.23.i.I | 9.53 | 0.15 | Dolomite | SpC | 10/05/06 | -2.44 | -3.75 | – | – |
| 2004F/S | | II | | 04.7.23.i.II | 9.53 | 0.15 | Dolomite | SpC | 10/05/06 | -2.38 | -3.14 | – | – |
| 2004F/S | | IV | | 04.7.23.g | 8.45 | 0.1 | Dolomite | SpC | 21/03/05 | -2.64 | -4.28 | – | – |
| 2004F/S | | IV | | 04.7.23.f | 7.58 | 0.18 | Dolomite | SpC | 21/03/05 | -2.54 | -3.50 | – | – |
| 2004F/S | | IV | | 04.7.23.e | 3.75 | 0.15 | Dolomite | SpC | 21/03/05 | -2.22 | -3.17 | – | – |

## Tuyembetka

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| TUY 53 | Petronodic Haplocalcid | II | Eroded | 04.7.26.b | 110.49 | 0.20 | Dolomite | SpC | 21/03/06 | -2.85 | -3.61 | – | – |
| TUY 54 | Ustic Petrocalcid | III | Eroded | 04.7.26.d | 108.64 | 0.30 | Dolomite | MCr | 21/03/05 | -2.98 | -3.72 | – | – |
| | | | | 04.7.26.c | 109.51 | 0.30 | Dolomite | MCr | 21/03/05 | -2.86 | -3.29 | – | – |
| | | | | 04.7.26.c.I | 109.51 | 0.72 | Dolomite | MCr | 10/05/06 | -4.87 | -4.40 | – | – |
| | | | | 04.7.26.c.II | 109.51 | 0.72 | Dolomite | MCr | 10/05/06 | -4.73 | -3.76 | – | – |
| TUY 55 | Ustic Petrocalcid | IV | 37 | 04.7.26.f | 107.49 | 0.47 | Dolomite | MCr | 21/03/05 | -2.81 | -3.65 | – | – |
| | | | | 04.7.26.e | 107.89 | 0.13 | Dolomite | SpC | 21/03/05 | -2.96 | -3.57 | – | – |
| TUY 56 | Petronodic Haplocalcid | II | 3 | 04.7.26.g | 106.29 | 0.16 | Dolomite | SpC | 21/03/05 | -2.94 | -3.96 | – | – |
| TUY 57 | Petronodic Haplocalcid | II | 53 | 04.7.26.h | 104.86 | 0.29 | Dolomite | MCr | 21/03/05 | -2.79 | -4.62 | – | – |
| TUY 58 | Ustic Petrocalcid | III | 54 | 0.4.7.26.i | 103.74 | 0.25 | Dolomite | MCr | 21/03/05 | -3.23 | -4.16 | – | – |
| | | | | 0.4.7.26.j | 103.09 | 0.72 | Dolomite | MCr | 29/03/06 | -3.05 | -4.01 | – | – |
| TUY 59 | Ustic Petrocalcid | IV | Eroded | 0.4.7.26.k | 102.56 | 0.20 | Dolomite | MCr | 29/03/06 | -2.98 | -3.96 | – | – |
| TUY 61 | Ustic Petrocalcid | IV | Eroded | 0.4.7.26.l | 102.21 | 0.18 | Dolomite | SpC | 29/03/06 | -2.97 | -3.98 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| TUY 1 | Ustic Petrocalcid | V | Eroded | 0.4.7.26.o | 100.74 | 0.50 | Dolomite | MCr | 29/03/06 | -2.58 | -4.22 | – | – |
| | | | | 0.4.7.26.n | 101.04 | 0.50 | Dolomite | SpC | 29/03/06 | -2.89 | -4.79 | – | – |
| | | | | 0.4.7.26.m | 101.34 | 0.50 | Dolomite | SpC | 29/03/06 | -2.97 | -4.52 | – | – |
| TUY 52 | Ustic Petrocalcid | IV | Eroded | 0.4.7.26.p | 100.24 | 0.20 | Dolomite | SpC | 29/03/06 | -2.91 | -5.32 | – | – |
| TUY 56 | Petronodic Haplocalcid | II | Eroded | 0.4.7.26.q | 98.91 | 0.29 | Dolomite | MCr | 29/03/06 | -2.24 | -3.96 | – | – |
| | | | | 04.7.26.q.I | 98.91 | 0.29 | Dolomite | MCr | 10/05/06 | -3.80 | -4.60 | – | – |
| | | | | 04.7.26.q.II | 98.91 | 0.29 | Dolomite | MCr | 10/05/06 | -3.66 | -4.88 | – | – |
| | | | | 04.7.26.q.III | 98.91 | 0.29 | Dolomite | MCr | 10/05/06 | -3.67 | -4.65 | – | – |
| TUY 49 | Ustic Petrocalcid | VI | Eroded | 0.4.7.26.r* | 96.81 | 0.28 | Dolomite | MCr | 29/03/06 | -2.39 | -4.63 | – | – |
| TUY 2 | Ustic Petrocalcid | VI | 62 | 0.4.7.26.s | 94.79 | 0.70 | Dolomite | MCr | 29/03/06 | -2.81 | -4.14 | – | – |
| TUY 3 | Ustic Petrocalcid | IV | 36 | 0.4.7.26.t | 89.98 | 0.24 | Dolomite | MCr | 29/03/06 | -2.76 | -3.88 | – | – |
| TUY 54 | Ustic Petrocalcid | III | 17 | 04.7.26.u* | 79.78 | 0.75 | Halite? | MCr | 29/03/06 | -2.72 | -4.00 | – | – |
| TUY 23 | Petronodic Haplocalcid | II | | TUY 23.4 | 39.59 | 0.05 | Dolomite | MCr | 21/05/08 | -4.15 | -5.06 | | |
| | | | | TUY 23.2 | 39.565 | 0.03 | Dolomite | MCr | 21/05/08 | -4.28 | -5.73 | -4.80 | -5.53 |
| | | | | TUY 23.3 | 39.565 | 0.03 | Dolomite | MCr | 21/05/08 | -5.50 | -5.74 | -12.22 | -11.56 |
| TUY 27 | Petronodic Haplocalcid | II | | TUY 27.3 | 47.46 | 0.77 | Dolomite | SpC | 21/05/08 | -4.28 | -5.25 | -4.83 | -5.78 |
| | | | | TUY 27.7 | 47.07 | 1.16 | Dolomite | SpC | 21/05/08 | -3.46 | -5.78 | – | – |
| TUY 31 | Petronodic Haplocalcid | II | 20 | TUY 31.3 | 61.0875 | 0.50 | Dolomite | SpC | 21/05/08 | -4.12 | -5.43 | -5.39 | -11.08 |
| | | | | TUY 31.4 | 60.92 | 0.67 | Dolomite | SpC | 21/05/08 | -4.48 | -5.46 | -5.35 | -11.27 |
| TUY 38 | Ustic Petrocalcid | V | | TUY 38.1 | 73.84 | 0.15 | Dolomite | SpC | 21/05/08 | -4.98 | -7.22 | -10.26 | -11.82 |

## Krasnogor

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| KRA 2 | Petronodic Haplocalcid | II | 22 | KRA 2.2 | 7.08 | 0.36 | calcite | MCr | 21/05/08 | -1.01 | -8.37 | -1.36 | -8.57 |
| KRA 1 | Petronodic Haplocalcid | II | 27 | KRA 1.3 | 6.07 | 0.22 | calcite | MCr | 21/05/08 | -0.84 | -7.76 | -0.80 | -8.51 |
| KRA 7a | Petronodic Haplocalcid | II | 20 | KRA 7.12 | 5.49 | 0.23 | – | MCr | 21/05/08 | -1.67 | -2.83 | -1.19 | -3.88 |
| KRA 7d | Petronodic Haplocalcid | II | 31 | KRA 7.4 | 4.35 | 0.34 | – | MCr | 21/05/08 | -2.76 | -4.05 | -2.91 | -7.36 |
| KRA 7e | Petronodic Haplocalcid | II | 13 | KRA 7.3 | 4.12 | 0.16 | – | MCr | 21/05/08 | -2.40 | -3.36 | – | – |
| KRA 5a | Ustic Petrocalcid | III | 5 | KRA 5.4 | 0.82 | 1.15 | – | MCr | 21/05/08 | -2.94 | -3.15 | -1.83 | -2.47 |
| KRA 5c | Petronodic Haplocalcid | II | 7 | KRA 5.11 | 0.27 | 0.14 | – | MCr | 21/05/08 | -2.32 | -3.01 | -2.60 | -3.72 |
| KRA 5d | Petronodic Haplocalcid | II | 15 | KRA 5.14 | 0 | 0.15 | Dolomite | MCr | 21/05/08 | -2.53 | -3.60 | -1.18 | -4.06 |

## Mescheryakovka

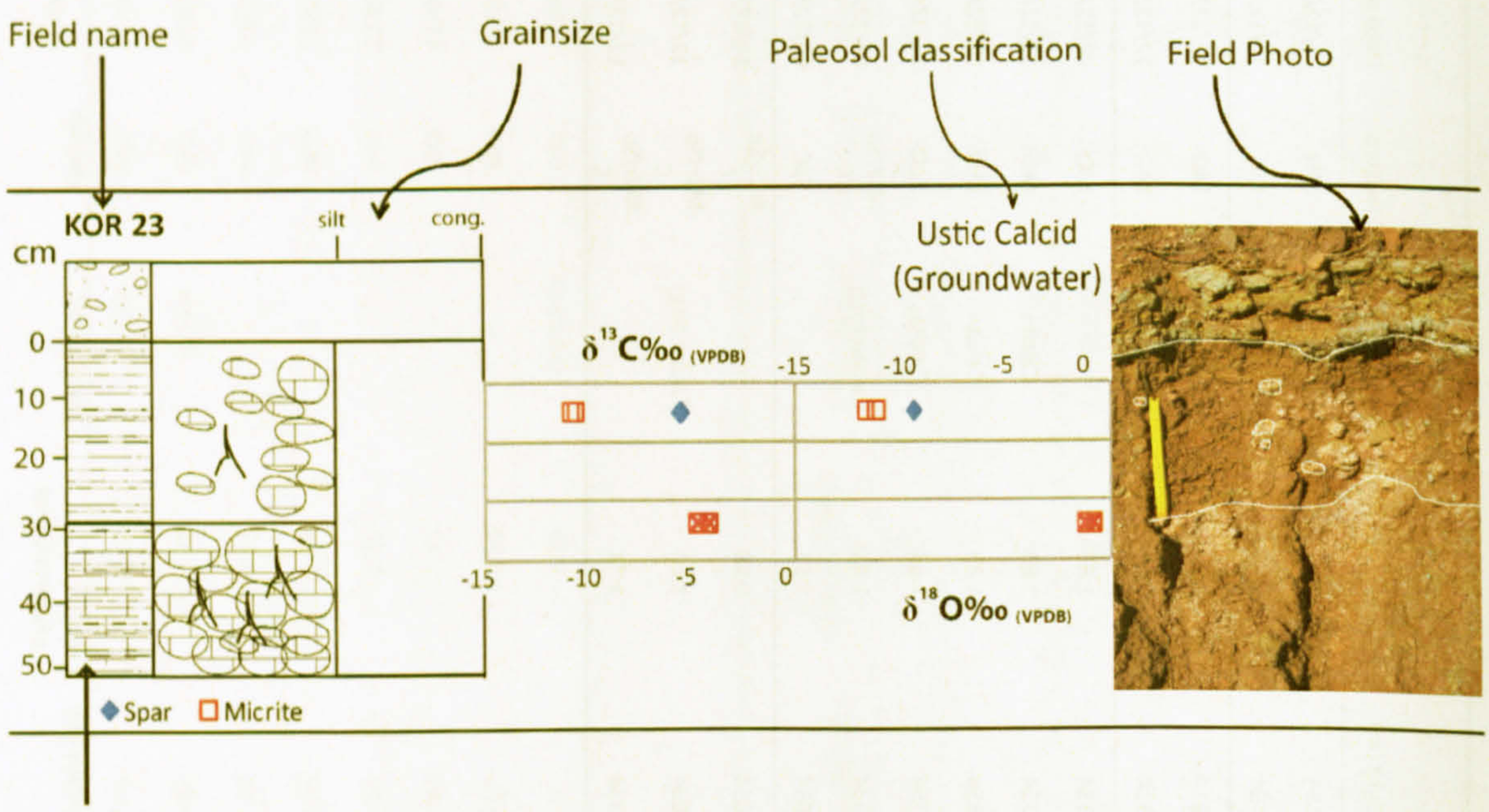
| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| MES 7 | Petronodic Haplocalcid | II | Eroded | MES 7.2 | 4.87 | 0.97 | Calcite | MCr | 12/12/07 | -9.70 | -11.09 | – | – |
| MES 3 | Ustic Calcid | II | 121 | MES 3.2 | 7.44 | 1.42 | – | SpC | 12/12/07 | -9.60 | -3.68 | – | – |
| | (Lacustrine) | | | MES 3.3 | 7.44 | 1.42 | Calcite | SpC | 12/12/07 | -9.82 | -1.53 | -9.77 | -7.75 |
| MES 1 | Petronodic Haplocalcid | II | 24 | MES 1.2 | 9.35 | 0.31 | Calcite (mg) | SpC | 12/12/07 | -10.48 | -9.52 | -10.66 | -9.14 |
| | | | | MES 1.3 | 9.35 | 0.31 | Calcite | SpC | 12/12/07 | -10.62 | -9.43 | – | – |
| | | | | MES 1.4 | 9.35 | 0.31 | Calcite | SpC | 12/12/07 | -10.49 | -10.08 | – | – |
| MES 8 | Vertic) | II | 44 | MES 8.4 | 79.82 | 0.58 | Calcite | MCr | 09/12/07 | -9.45 | -16.93 | -8.28 | -16.13 |
| | Haplocalcid | | | MES 8.5 | 79.82 | 0.58 | Calcite (mg) | MCr | 09/12/07 | -9.09 | -16.96 | -9.26 | -17.15 |
| | | | | MES 8.2 | 79.87 | 0.52 | Calcite | SpC | 09/12/07 | -7.78 | -9.85 | -10.99 | -14.38 |
| | | | | MES 8.1 | 79.89 | 0.50 | Calcium Carbonate | MCr | 09/12/07 | -9.34 | -17.66 | -8.54 | -16.54 |
| *MES 10* | *Petronodic Haplocalcid* | II | *Eroded* | MES 10.3 | 137.454 | 0.55 | Calcite | MCr | 12/12/07 | -8.38 | -16.39 | – | – |

| Horizon | Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | XRD Result | Texture | Date run | Micrite | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| | | | | MES 10.4 | 137.454 | 0.55 | Calcite | MCr | 12/12/07 | -8.62 | -16.71 | -11.90 | -12.87 |
| | | | | MES 10.5 | 137.454 | 0.55 | Calcite | MCr | 12/12/07 | -8.71 | -14.85 | – | – |
| MES 15 | Petronodic | II | Eroded | MES 15.3 | 183.114 | 0.16 | Calcite (mg) | MCr | 12/12/07 | -6.42 | -8.25 | -6.93 | -7.83 |
| | Haplocalcid | | | MES 15.5 | 182.814 | 0.49 | – | MCr | 12/12/07 | -6.48 | -9.44 | -6.82 | -9.74 |
| MES 16 | Vertic | II | 100 | MES 16.3 | 183.354 | 1.83 | – | MCr | 09/12/07 | -7.58 | -8.35 | -5.92 | -8.59 |
| | Haplocalcid | | | MES 16.4 | 183.354 | 1.83 | Calcite | MCr | 12/12/07 | -6.98 | -8.92 | -7.84 | -9.58 |
| | | | | MES 16.5 | 183.354 | 1.83 | Calcite | MCr | 12/12/07 | -7.00 | -6.86 | -7.14 | -6.00 |
| | | | | MES 16.6 | 183.354 | 1.83 | Calcite | SpC | 12/12/07 | -7.29 | -8.12 | -7.70 | -7.30 |
| | | | | MES 16.1 | 183.634 | 1.53 | Calcite (mg) | MCr/SpC | 09/12/07 | -7.83 | -7.64 | -7.52 | -9.50 |
| | | | | MES 16.2 | 183.634 | 1.53 | – | SpC | 09/12/07 | -7.12 | -8.66 | – | – |
| MES 17 | Petronodic | II | Eroded | MES 17.10 | 185.054 | 0.98 | – | MCr/SpC | 12/12/07 | -8.03 | -8.62 | -8.45 | -8.23 |
| | Haplocalcid | | | MES 17.9 | 186.034 | 1.09 | Calcite (mg) | MCr/SpC | 12/12/07 | -7.92 | -7.00 | -9.01 | -10.00 |
| | | | | MES 17.8 | 186.234 | 1.31 | – | MCr/SpC | 12/12/07 | -7.88 | -9.54 | -8.46 | -9.72 |

# A2.2

Variation in stable isotope results for individual paleosols. Paleosols from Boyevaya Gora, Sambullak, Tuyembetka and Mescheryakovka which contained three or more isotope analysis are displayed here

## Key to Diagrams




*Paleosol features*

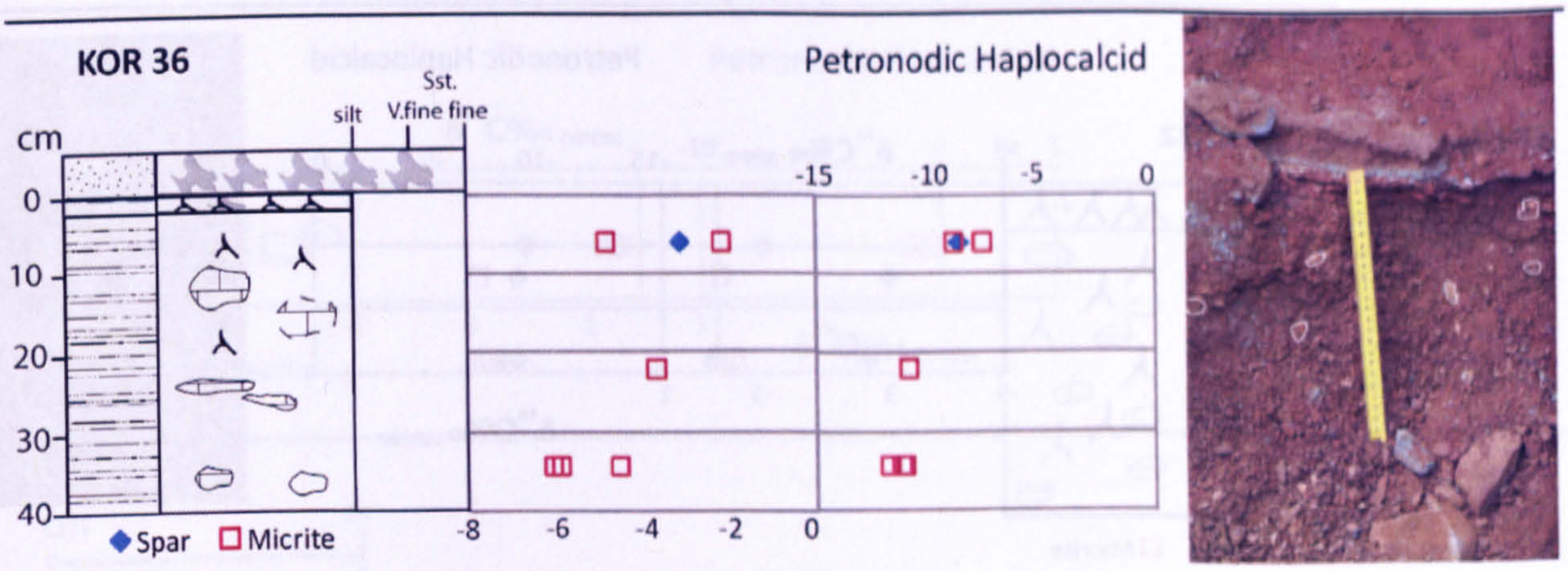
- Pseudo-Gley
- Minor mottelling
- Drab root halos
- Root traces
- Desiccation cracks
- Parallel lamination
- Pedogenic slickensides
- Carbonate nodule
- Ephemeral nodule
- Coalesced nodules

*Isotope results*

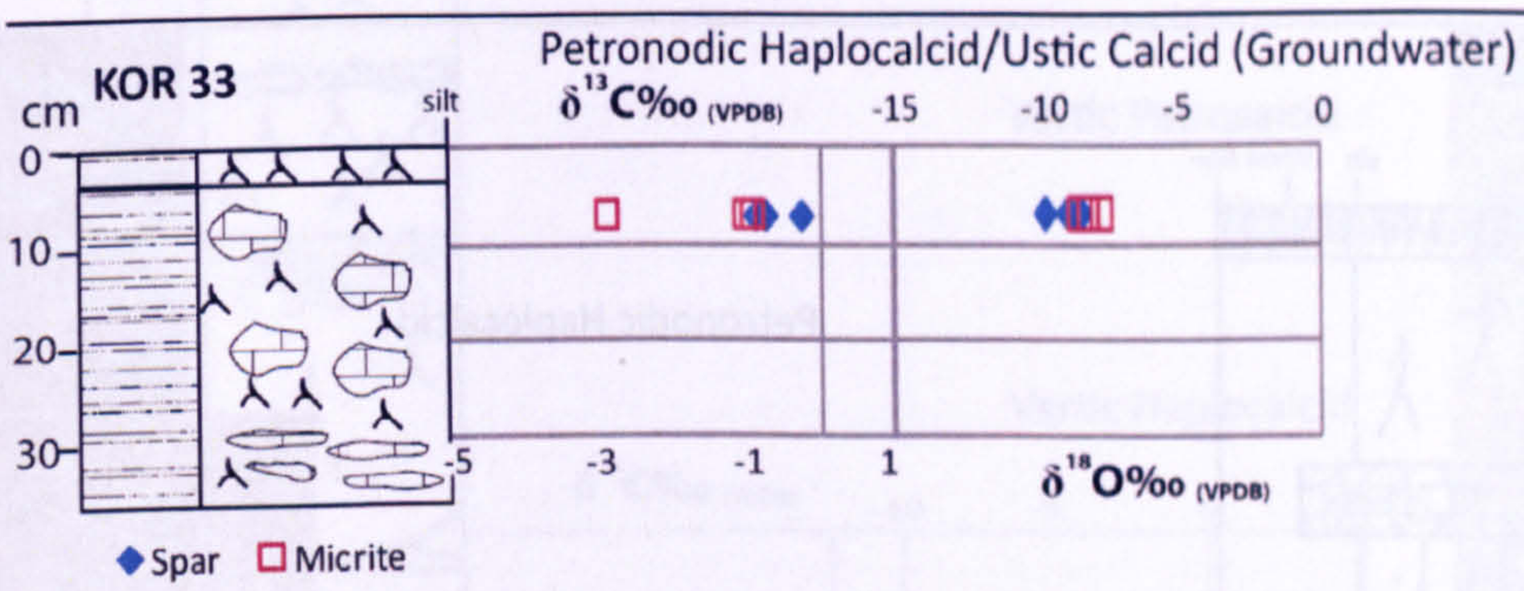
- Dolomite micrite isotopic values
- Calcite micrite isotopic values
- Spar isotopic values from sinous veins

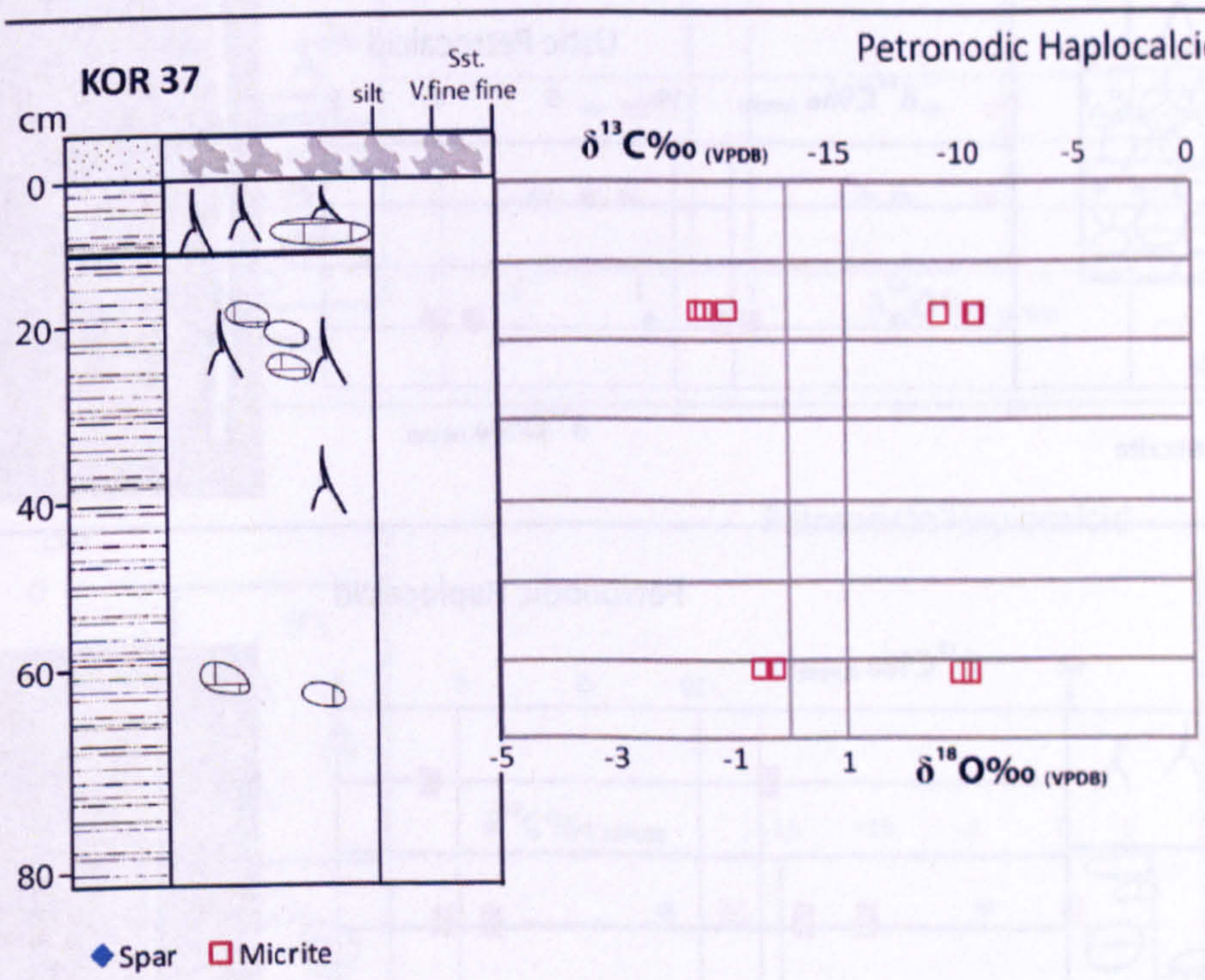
*Lithological Key*

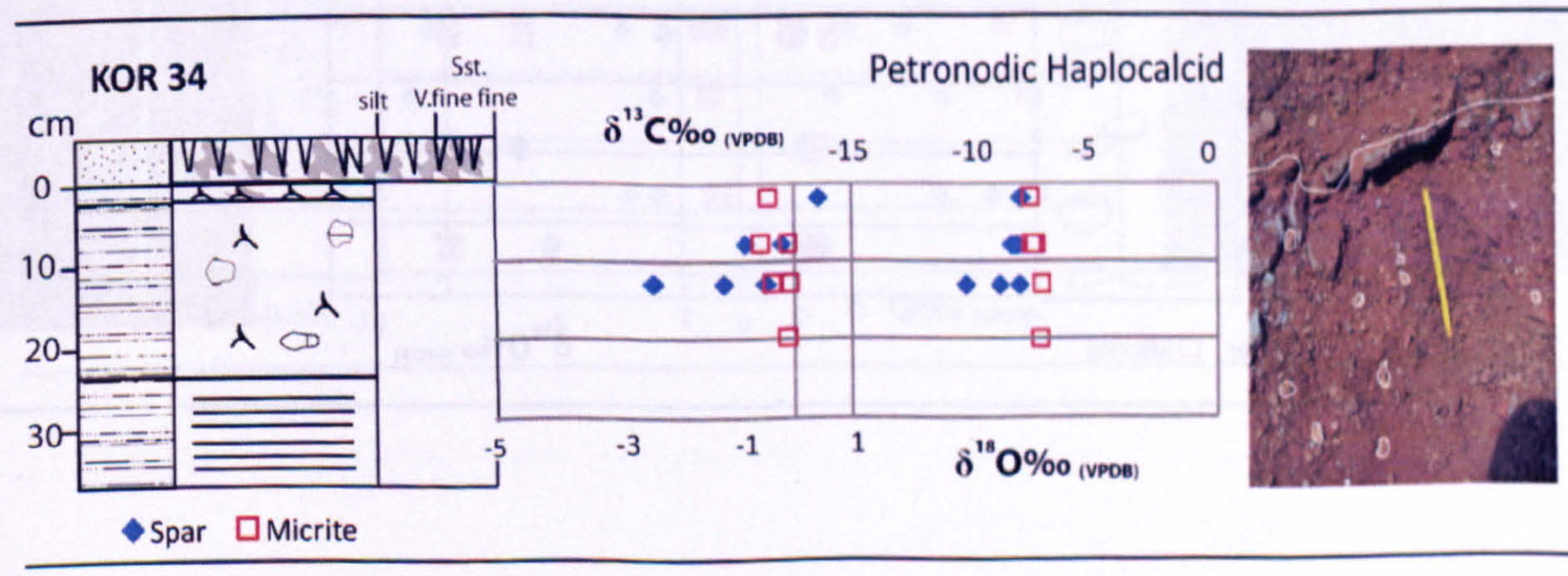
- Mudstone/Siltstone
- Sandstone
- Conglomerate
- Calcified horizons (above 50% carbonate)
- Limestone

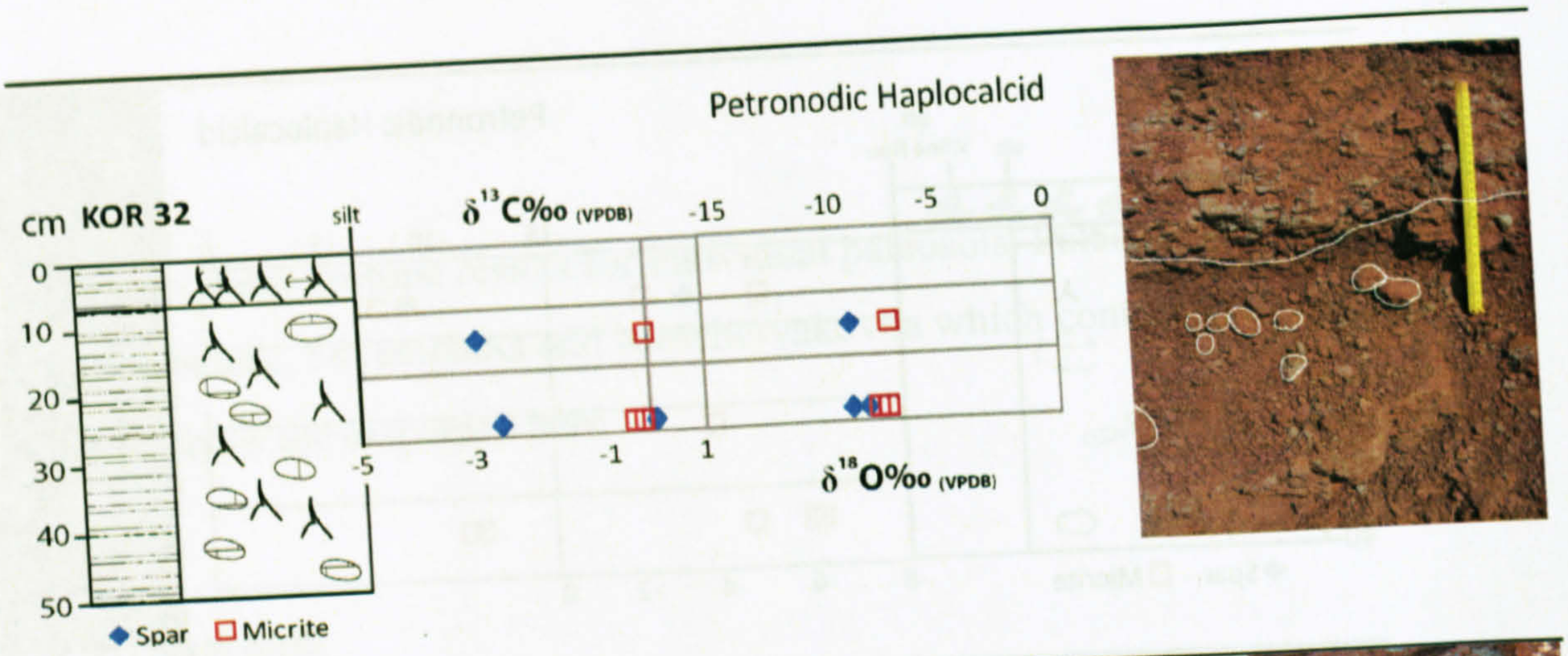

KOR 36
Petronodic Haplocalcid
Sst.
silt
V.fine fine
cm
0
10
20
30
40
-15
-10
-5
0
-8
-6
-4
-2
0
Spar
Micrite

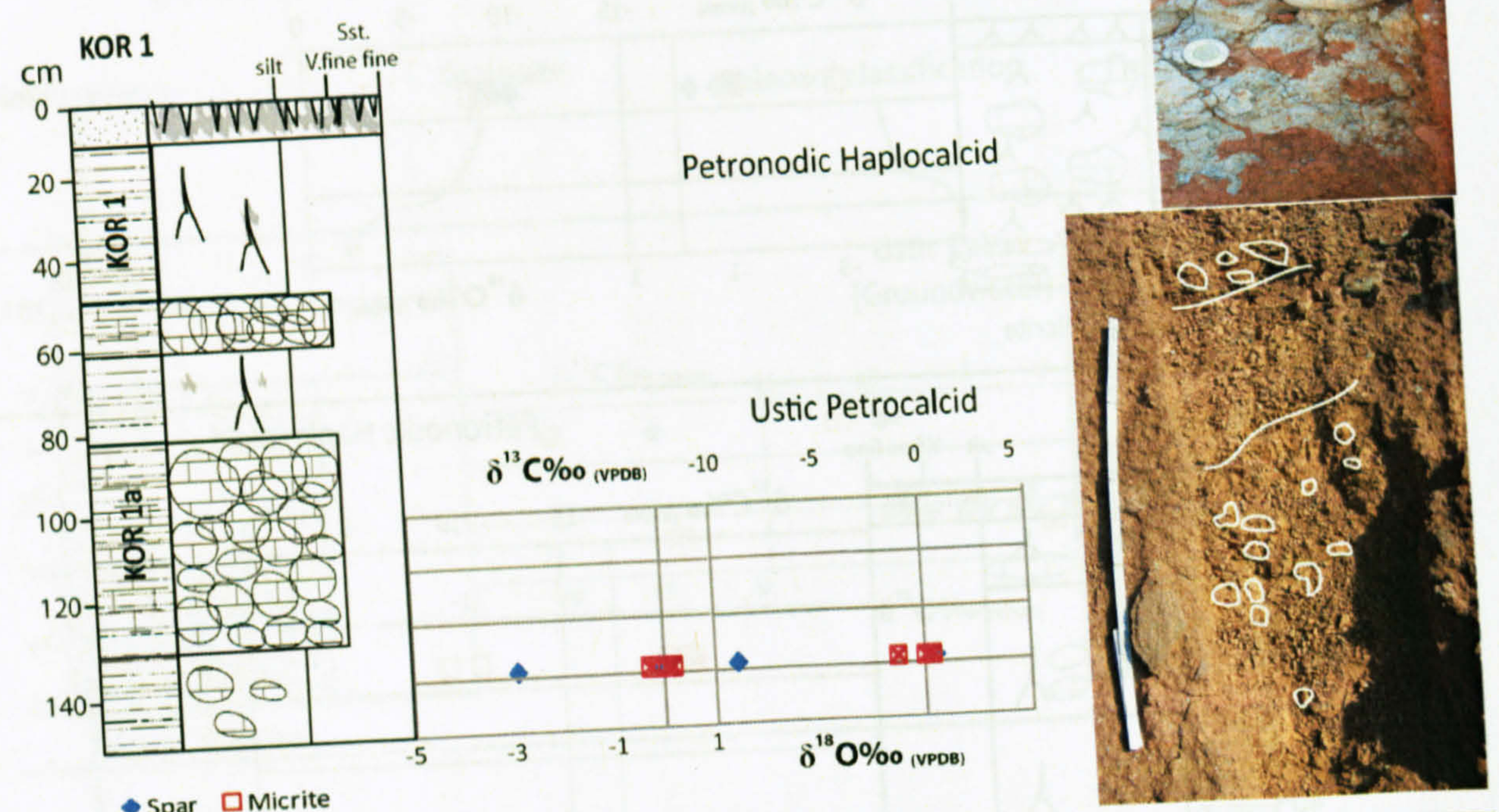


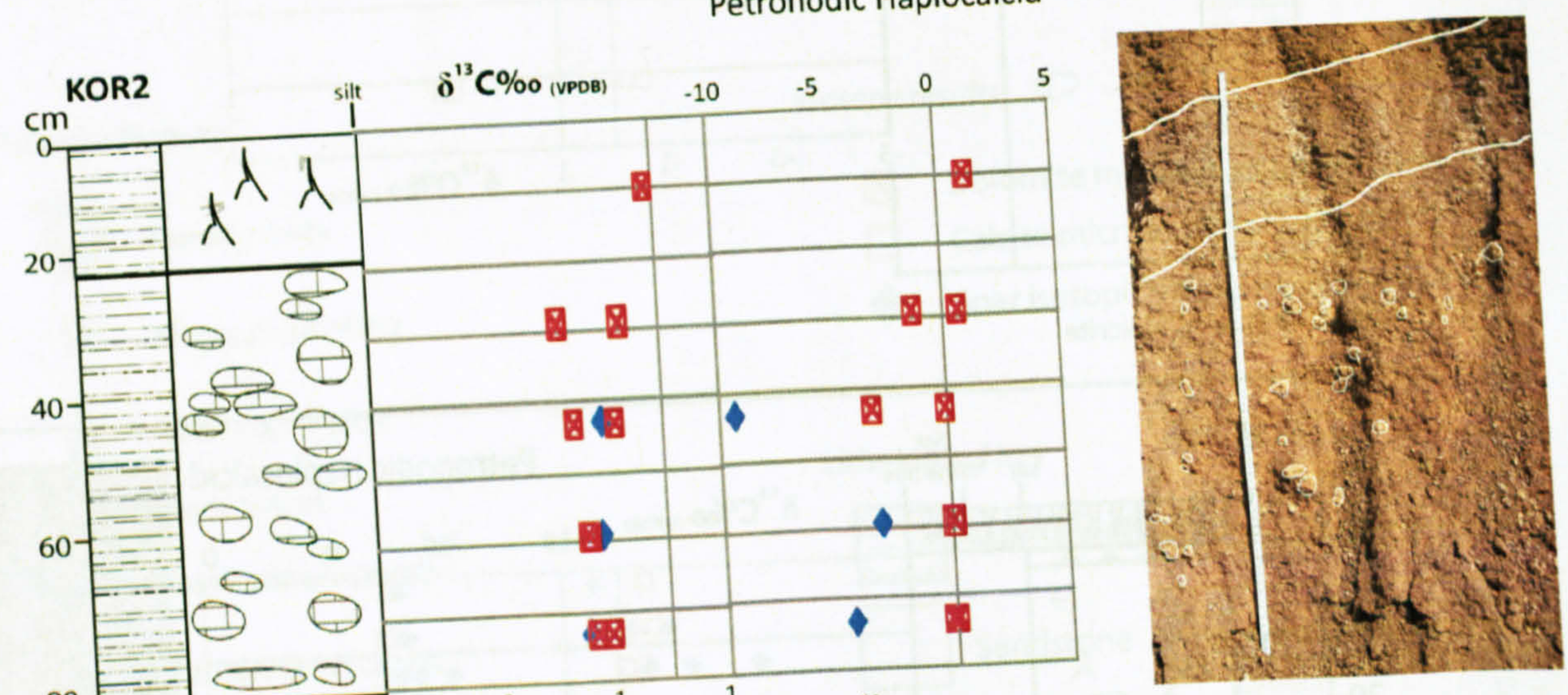

Petronodic Haplocalcid/Ustic Calcid (Groundwater)
KOR 33
cm
silt
δ13C‰ (VPDB)
-15
-10
-5
0
0
10
20
30
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

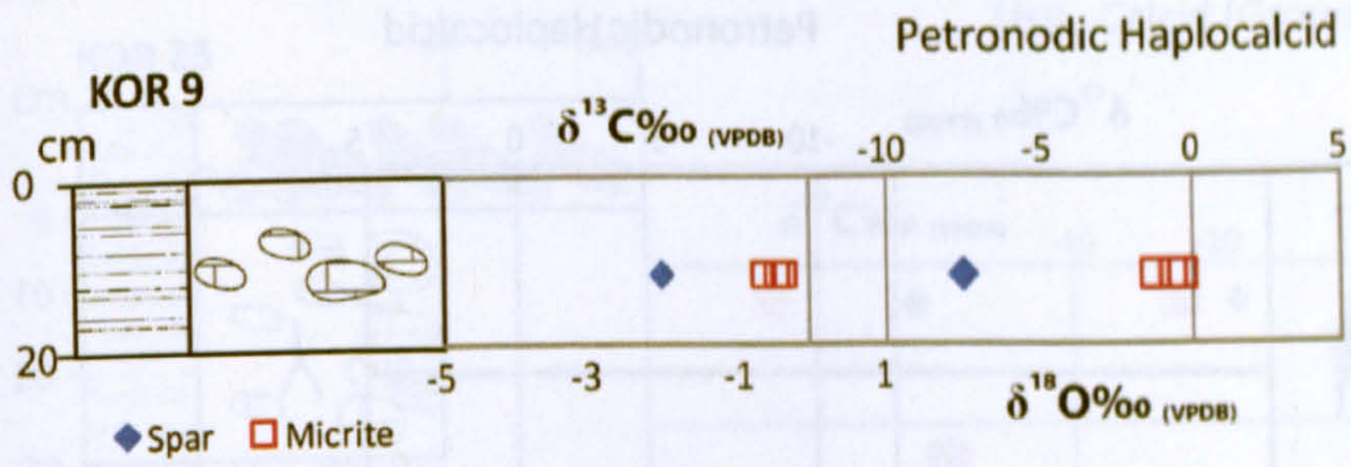

KOR 37
Petronodic Haplocalcid
Sst.
silt
V.fine fine
cm
δ13C‰ (VPDB)
-15
-10
-5
0
0
20
40
60
80
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

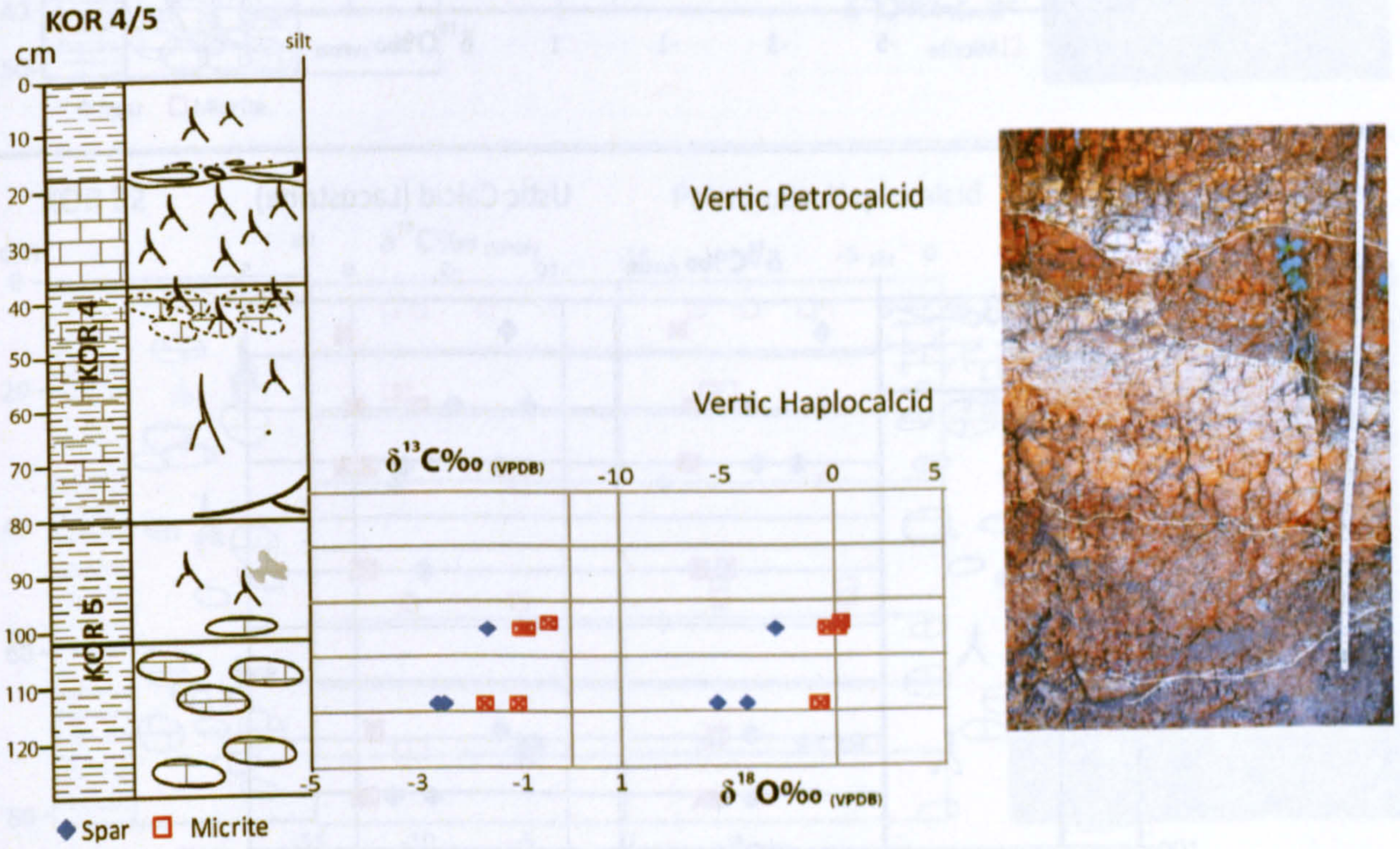

KOR 34
Petronodic Haplocalcid
Sst.
silt
V.fine fine
cm
δ13C‰ (VPDB)
-15
-10
-5
0
0
10
20
30
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite


Petronodic Haplocalcid
cm KOR 32
silt
δ13C‰ (VPDB)
-15
-10
-5
0
0
10
20
30
40
50
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

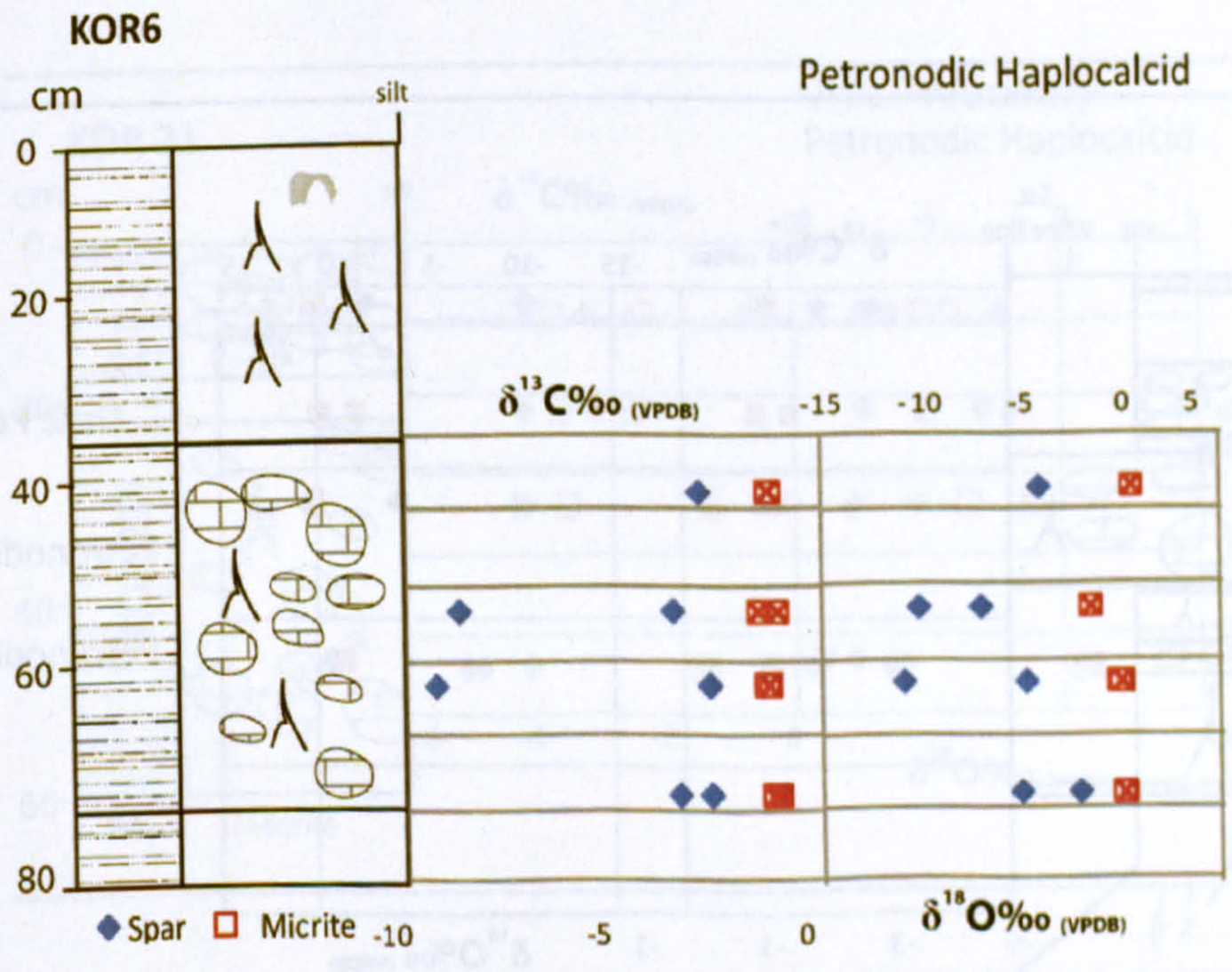

KOR 1
cm
silt
Sst.
V.fine fine
0
20
40
60
80
100
120
140
KOR 1
KOR 1a
Petronodic Haplocalcid
Ustic Petrocalcid
δ13C‰ (VPDB)
-10
-5
0
5
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

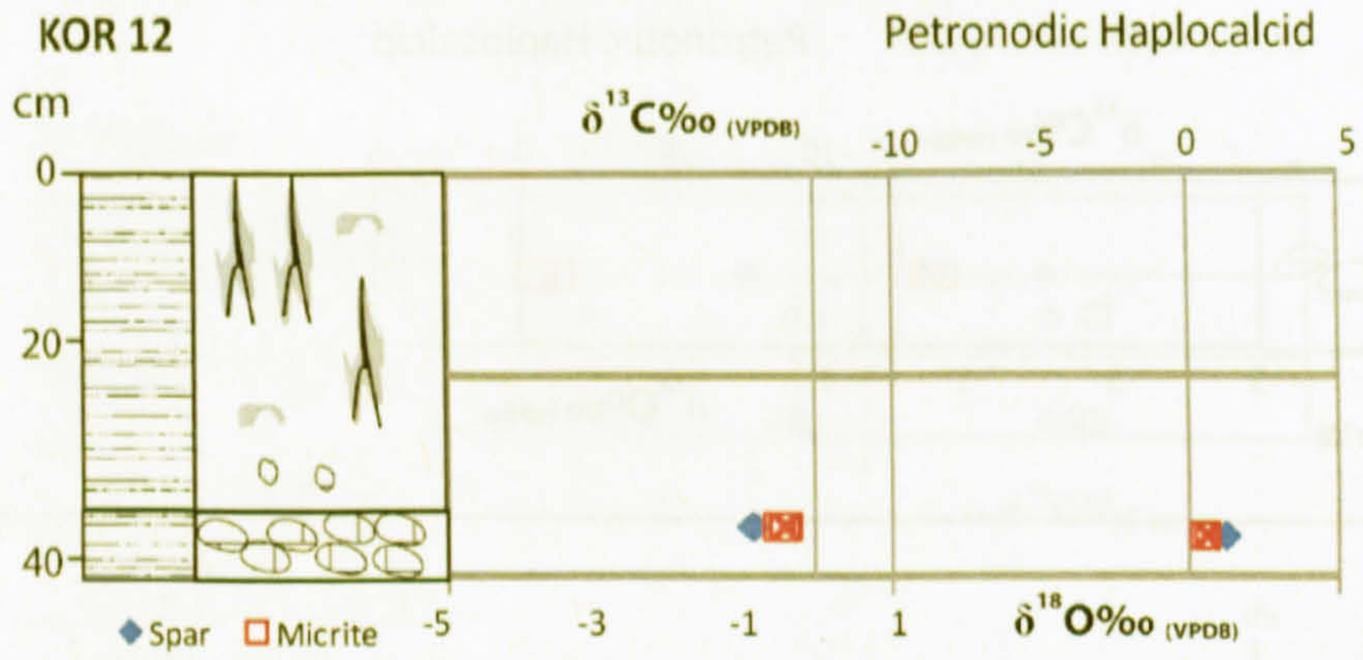

Petronodic Haplocalcid
KOR2
cm
silt
δ13C‰ (VPDB)
-10
-5
0
5
0
20
40
60
80
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

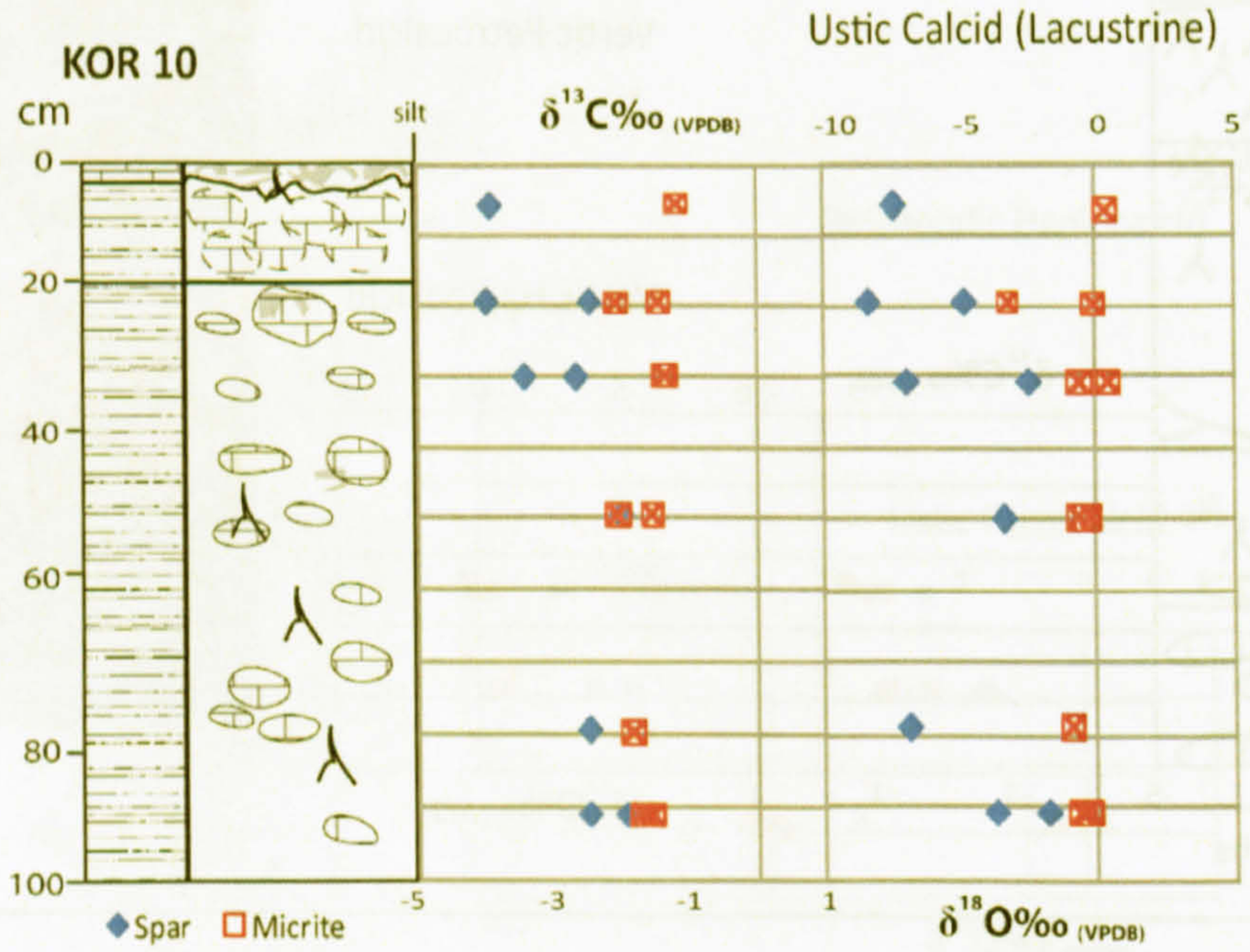

KOR 9
Petronodic Haplocalcid
cm
0
20
δ13C‰ (VPDB)
-10
-5
0
5
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

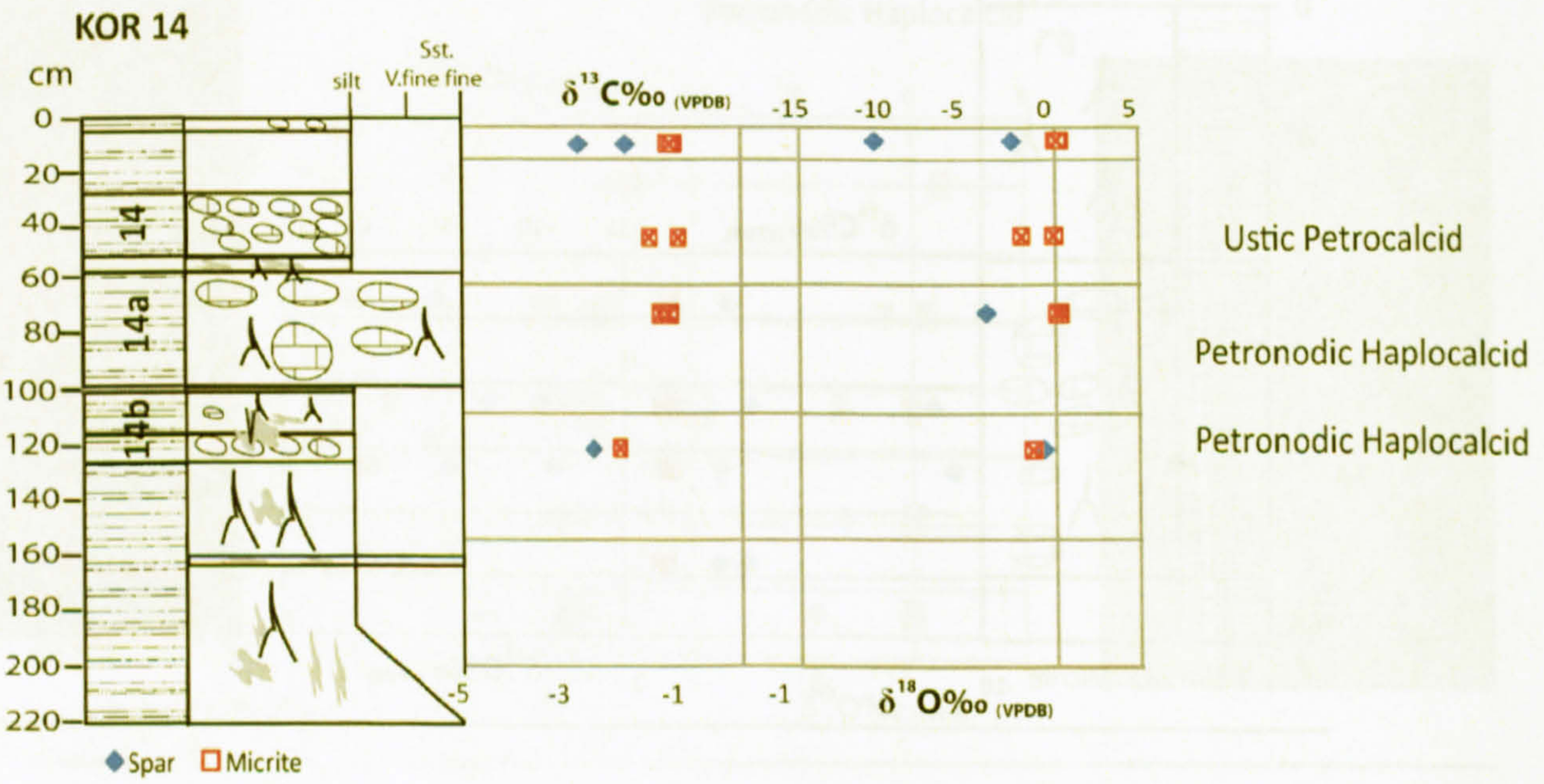

KOR 4/5
cm
silt
0
10
20
30
40
50
60
70
80
90
100
110
120
KOR 4
KOR 5
Vertic Petrocalcid
Vertic Haplocalcid
δ13C‰ (VPDB)
-10
-5
0
5
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

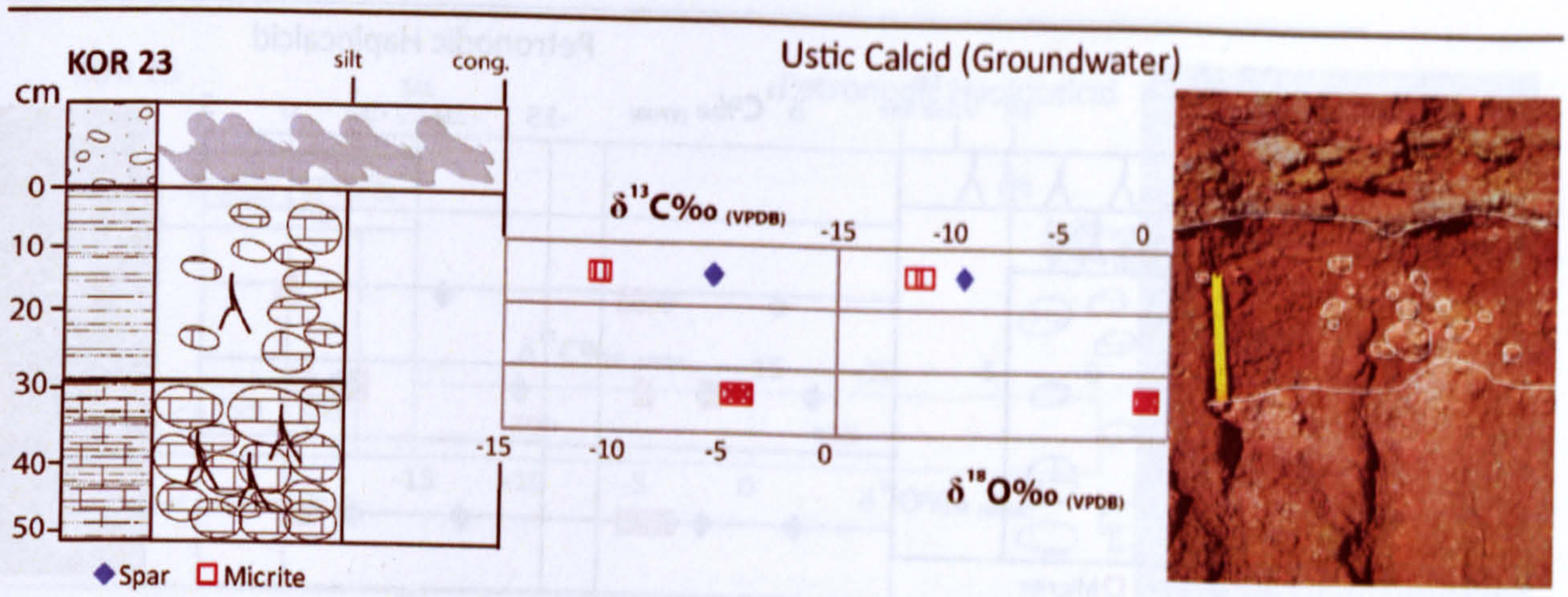


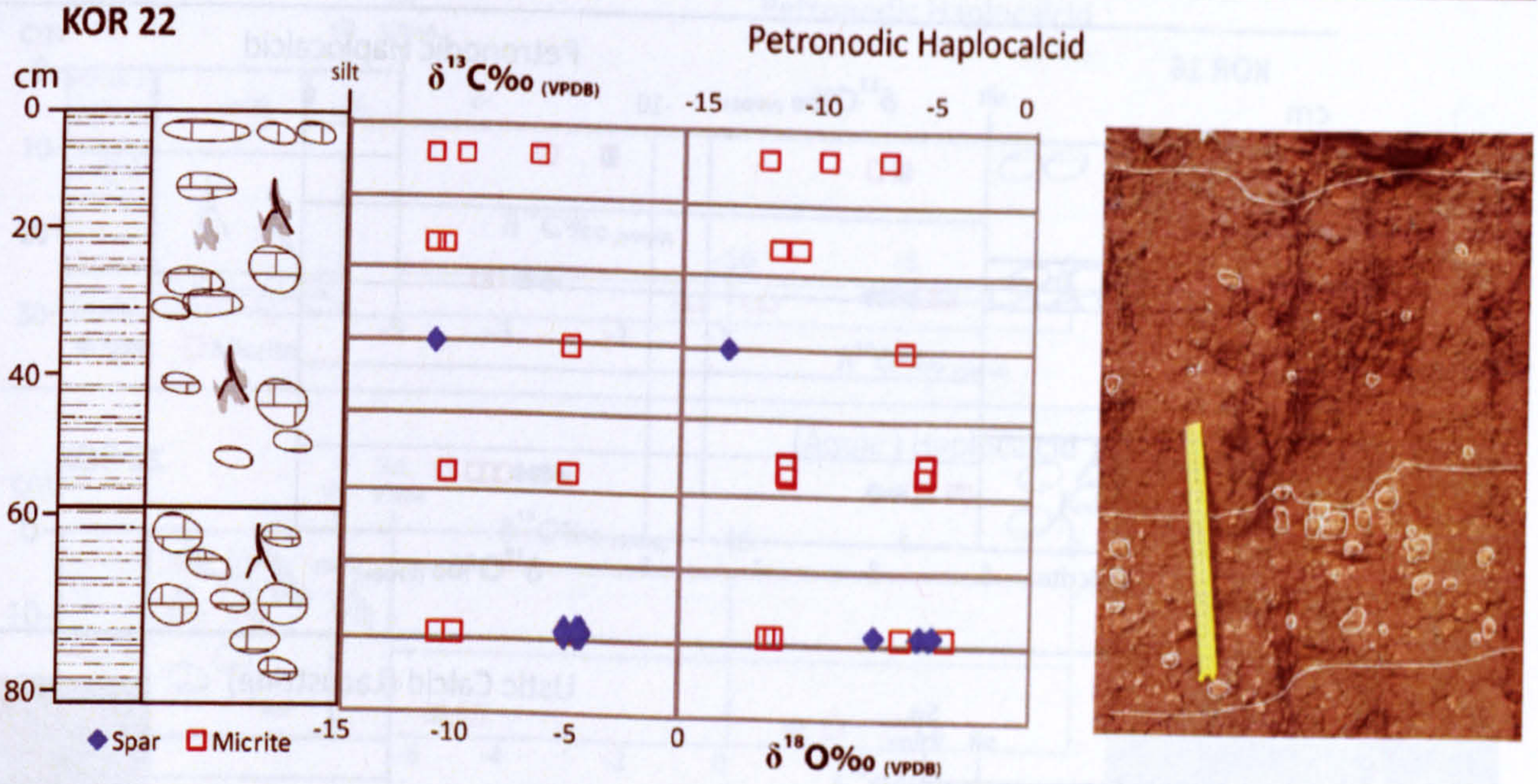

KOR6
cm
silt
0
20
40
60
80
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
5
-10
-5
0
δ18O‰ (VPDB)
Spar
Micrite

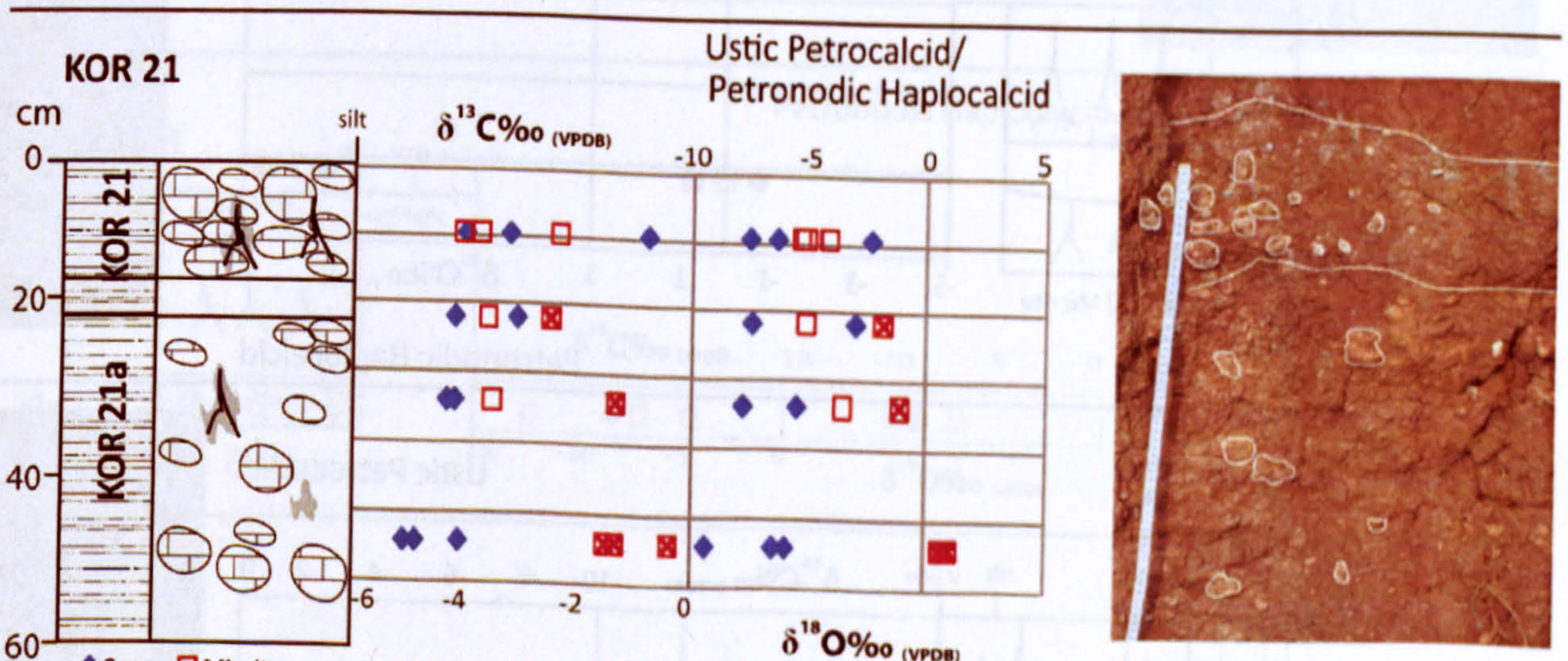

KOR 12
Petronodic Haplocalcid
cm
δ13C‰ (VPDB)
-10
-5
0
5
0
20
40
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

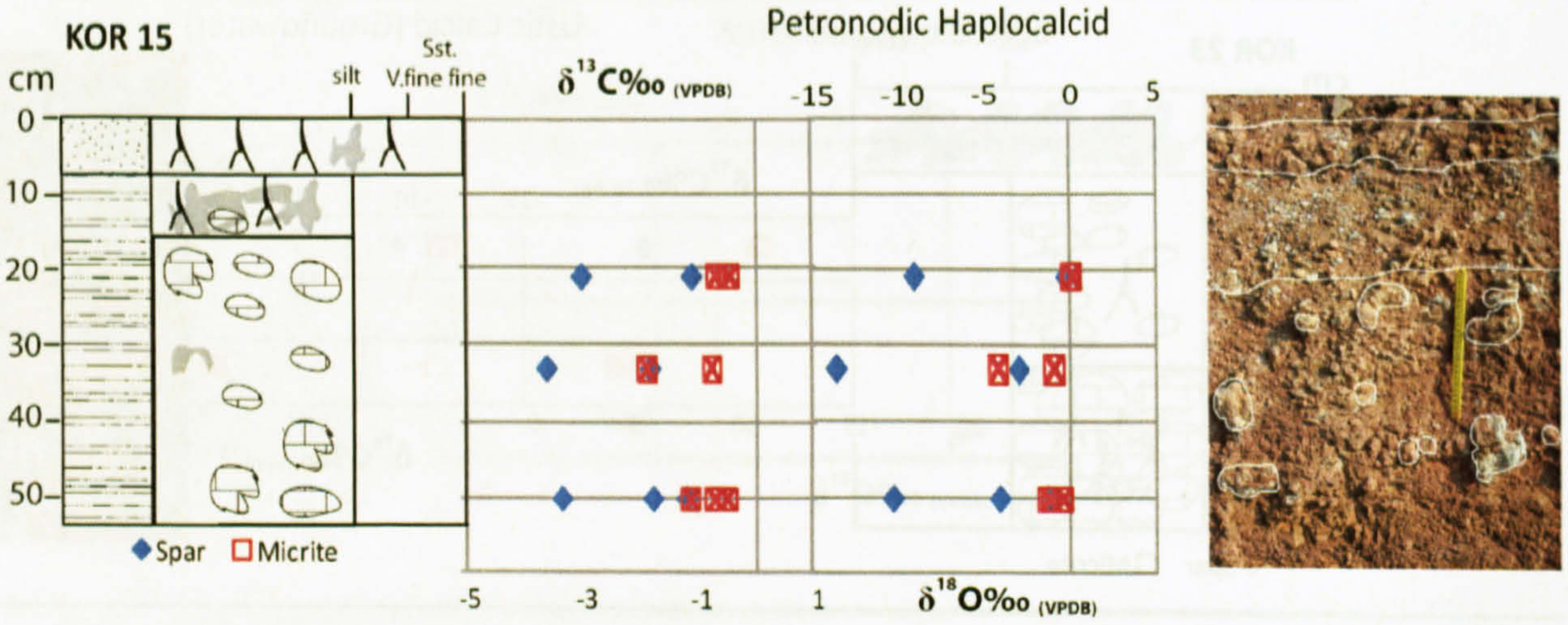

KOR 10
Ustic Calcid (Lacustrine)
cm
silt
δ13C‰ (VPDB)
-10
-5
0
5
0
20
40
60
80
100
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite

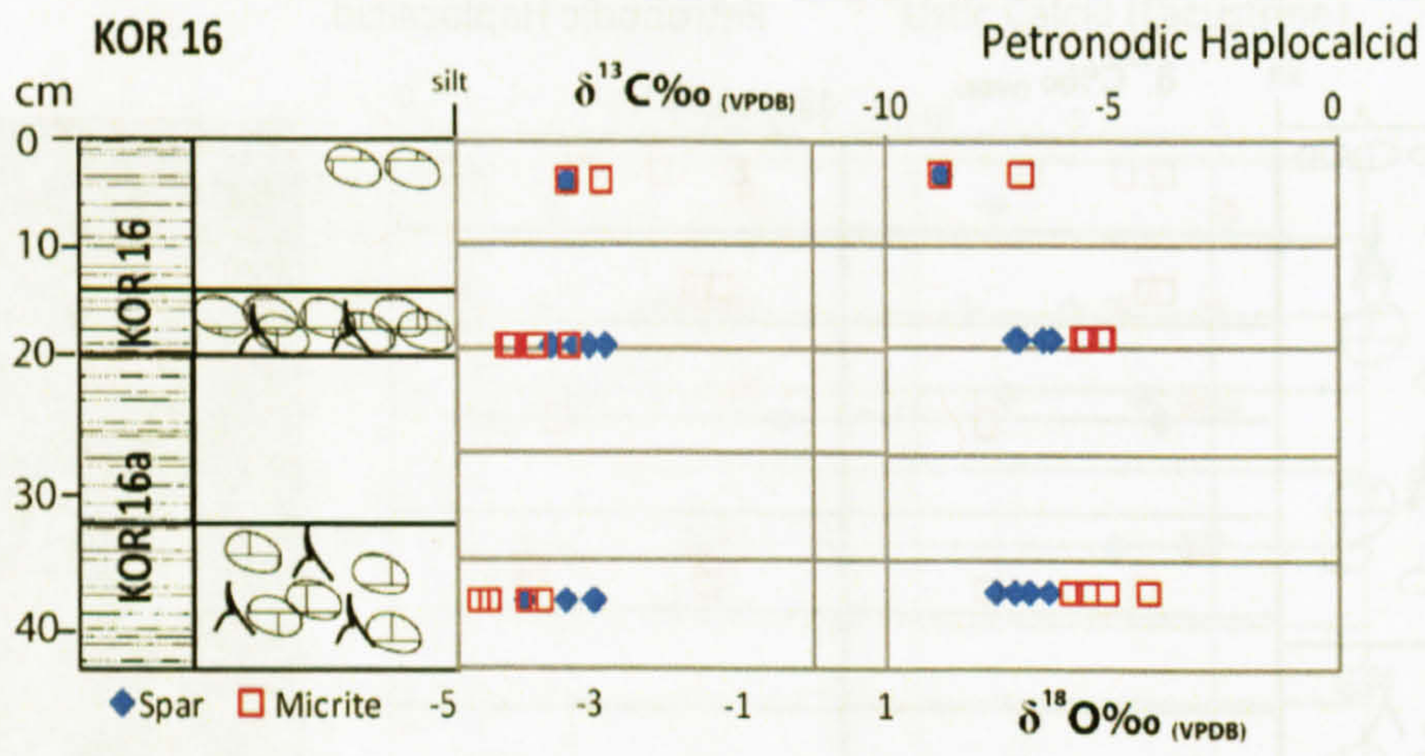

KOR 14
cm
silt
Sst.
V.fine fine
δ13C‰ (VPDB)
-15
-10
-5
0
5
0
20
40
60
80
100
120
140
160
180
200
220
14
14a
14b
-5
-3
-1
-1
δ18O‰ (VPDB)
Spar
Micrite
Ustic Petrocalcid
Petronodic Haplocalcid
Petronodic Haplocalcid

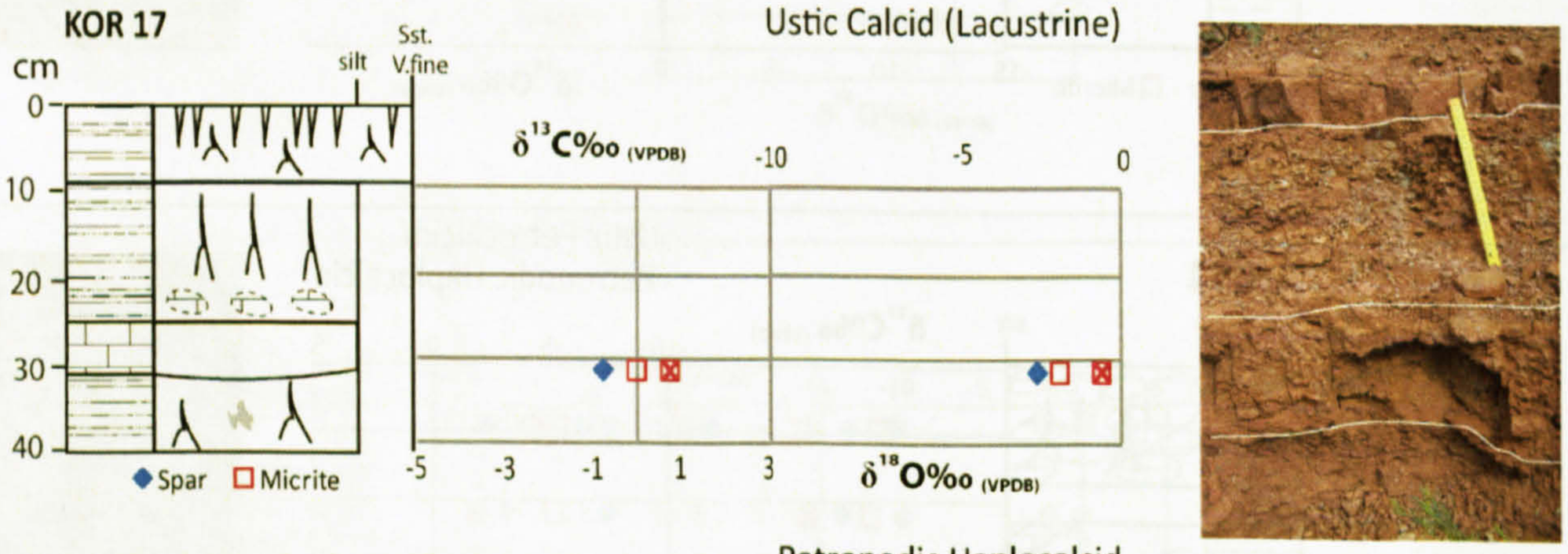

KOR 23
silt
cong.
cm
0
10
20
30
40
50
Spar
Micrite
Ustic Calcid (Groundwater)
δ13C‰ (VPDB)
-15
-10
-5
0
δ18O‰ (VPDB)


KOR 22
cm
silt
0
20
40
60
80
Spar
Micrite
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
δ18O‰ (VPDB)


KOR 21
cm
silt
0
20
40
60
KOR 21
KOR 21a
Spar
Micrite
Ustic Petrocalcid/
Petronodic Haplocalcid
δ13C‰ (VPDB)
-10
-5
0
5
-6
-4
-2
0
δ18O‰ (VPDB)

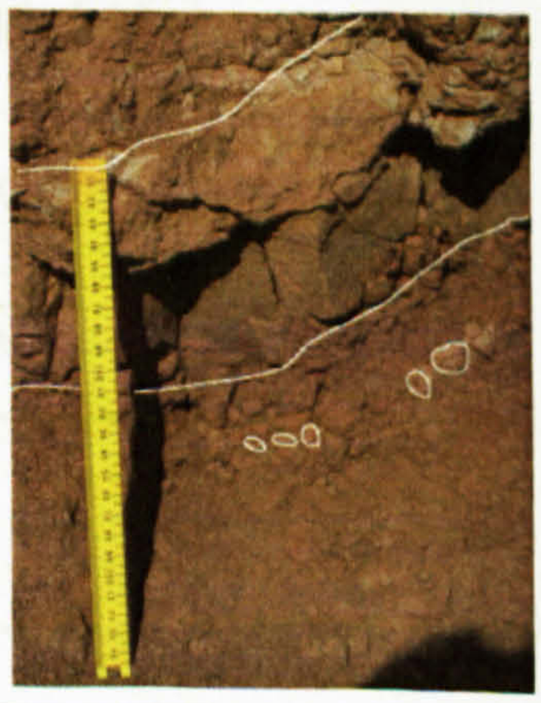


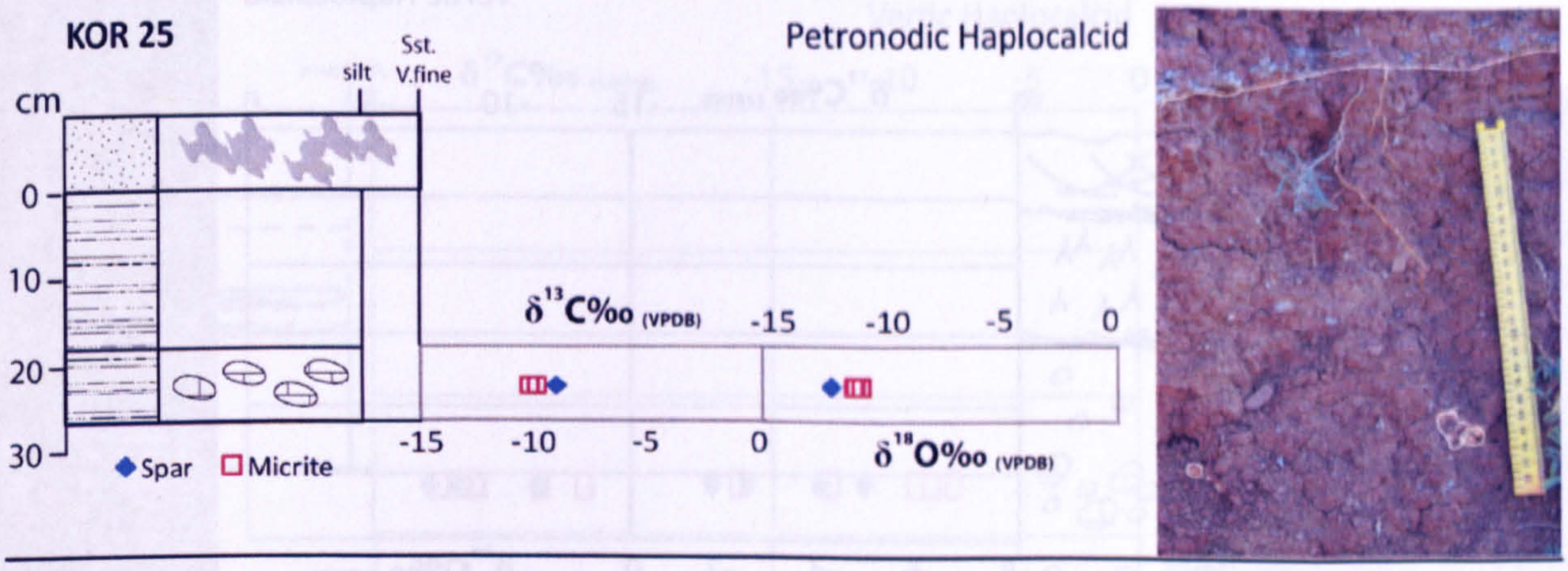



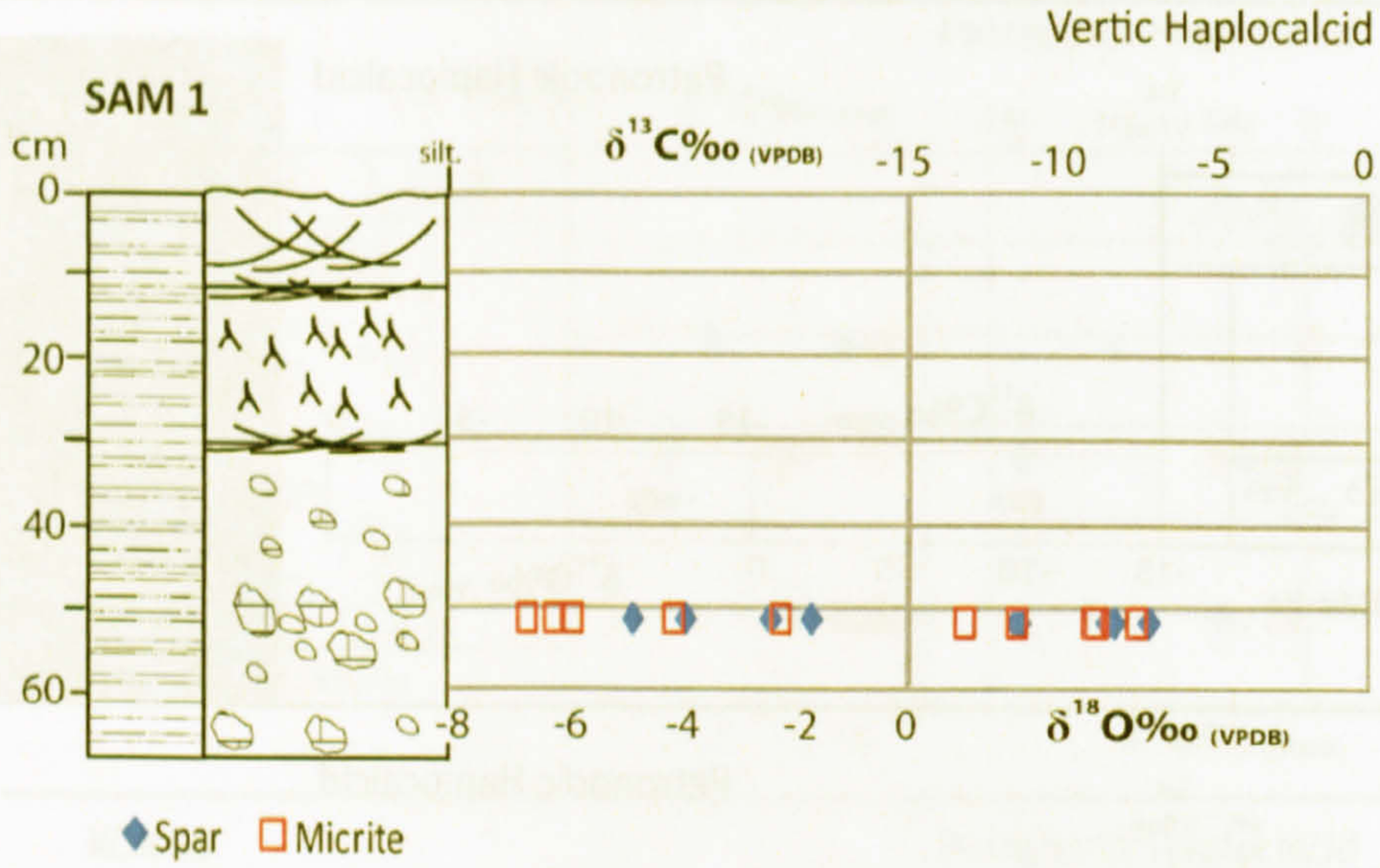

Petronodic Haplocalcid

Ustic Petrocalcid

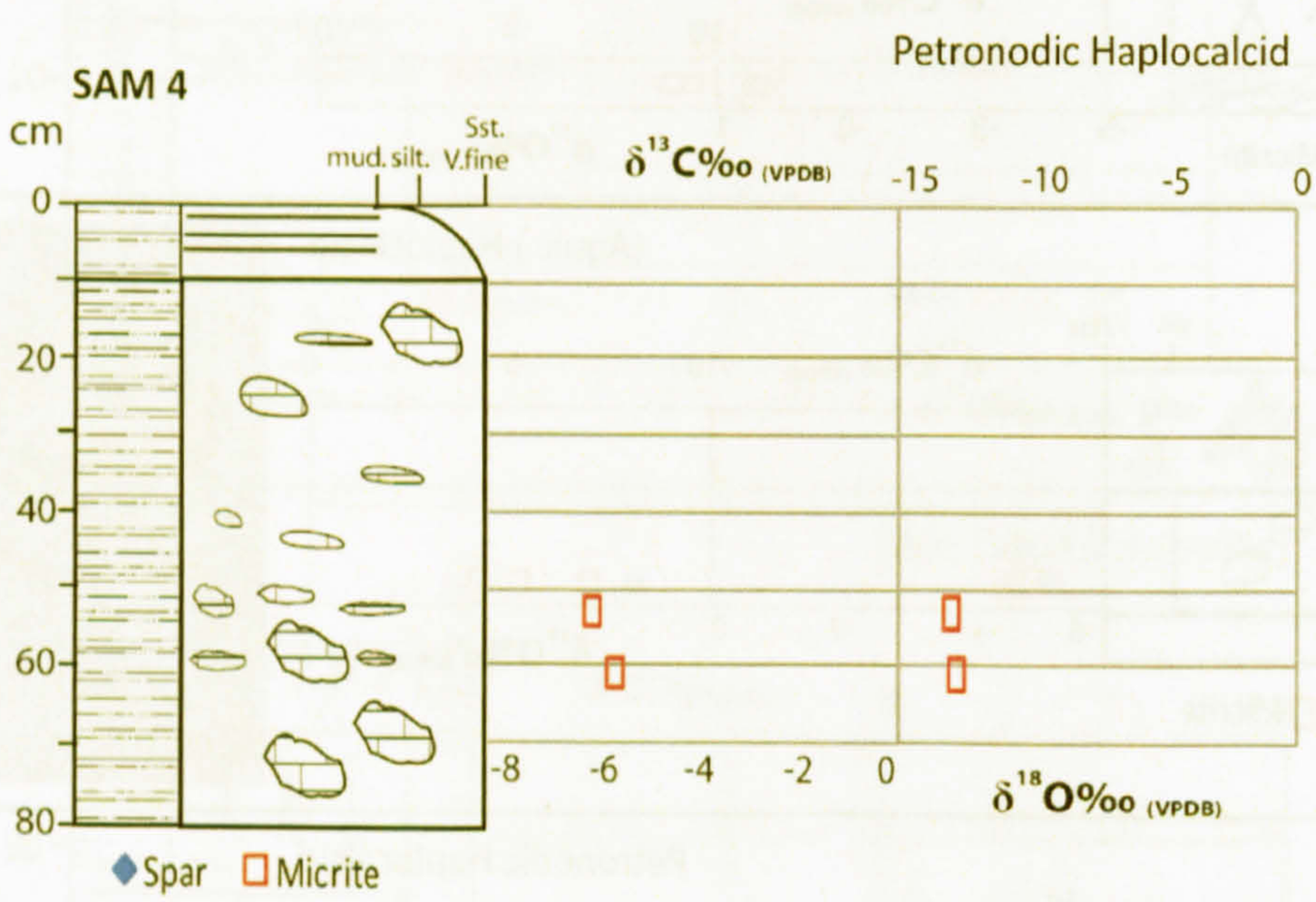



KOR 25
Petronodic Haplocalcid
silt
Sst.
V.fine
cm
0
10
20
30
δ13C‰ (VPDB)
-15
-10
-5
0
-15
-10
-5
0
δ18O‰ (VPDB)
Spar
Micrite
KOR 27
Petronodic Haplocalcid
silt
Sst.
V.fine
cm
0
10
20
30
δ13C‰ (VPDB)
-10
-5
0
-5
-3
-1
1
δ18O‰ (VPDB)
Spar
Micrite
KOR 31
(Aquic ) Haplocalcid
silt
Sst.
V.fine
cm
0
10
20
30
δ13C‰ (VPDB)
-10
-5
0
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite
KOR 35
Petronodic Haplocalcid
silt
V.fine
fine
Sst.
cm
0
10
20
δ13C‰ (VPDB)
-15
-10
-5
0
-15
-10
-5
0
δ18O‰ (VPDB)
Spar
Micrite

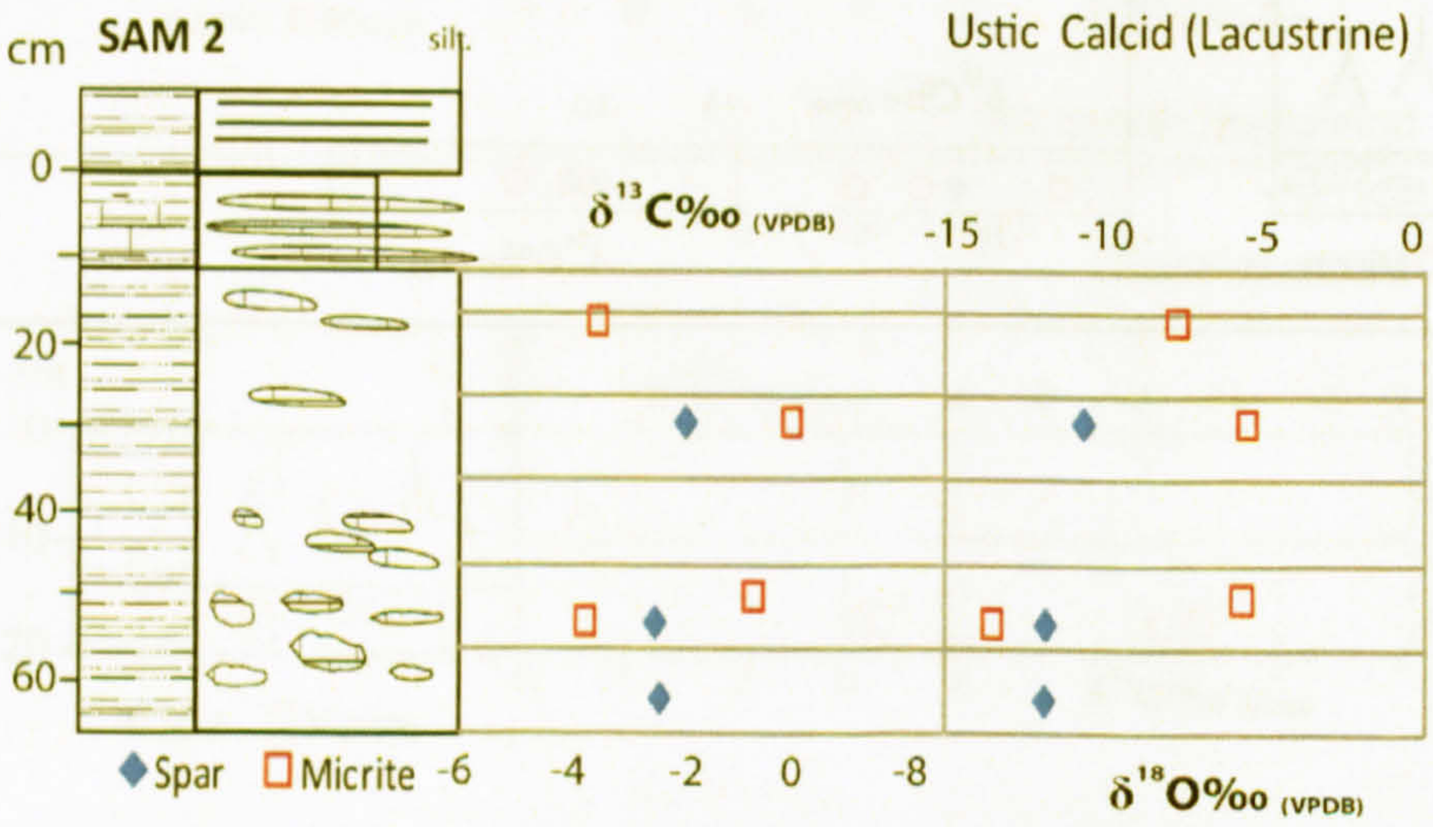
Vertic Haplocalcid



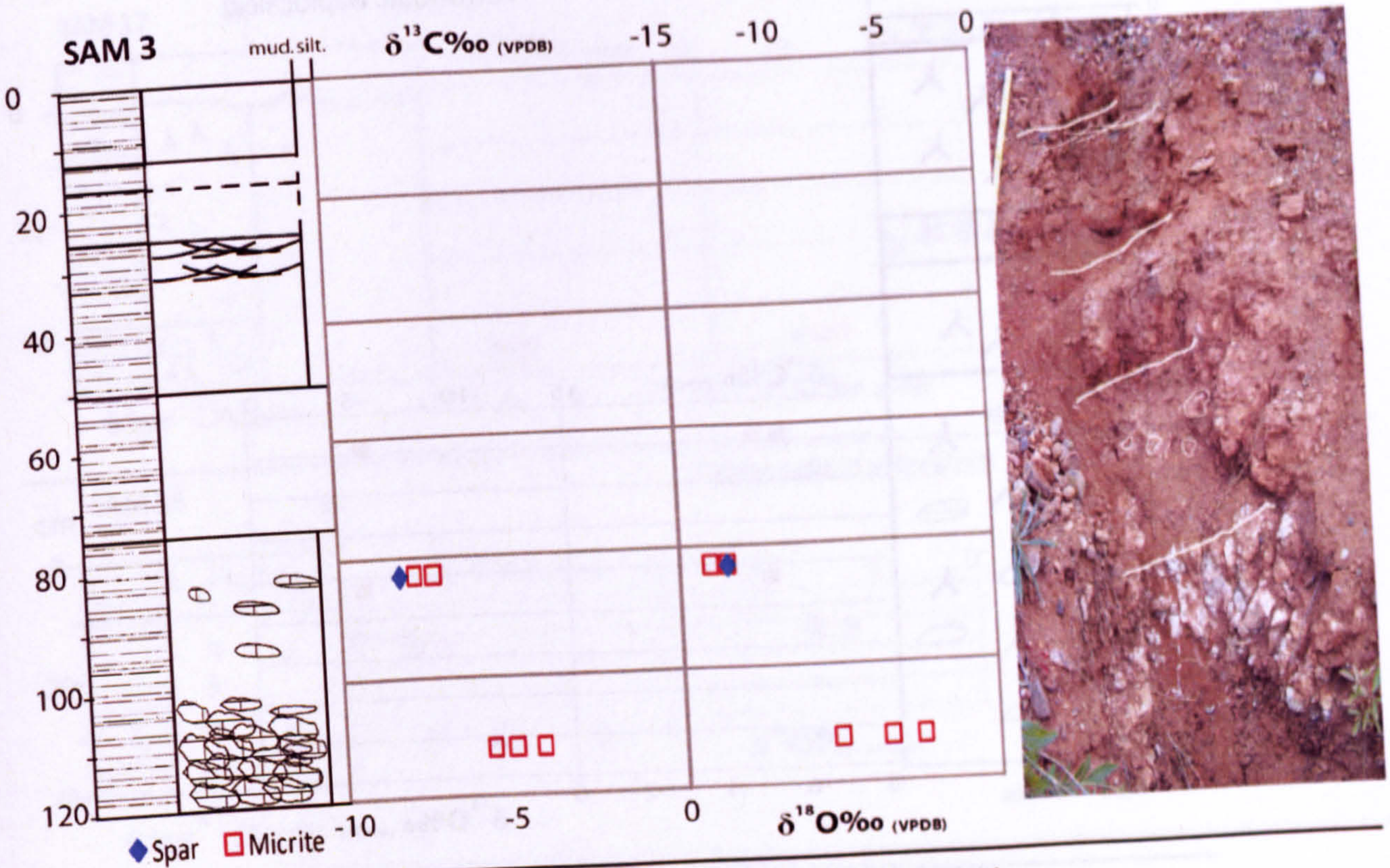

Petronodic Haplocalcid



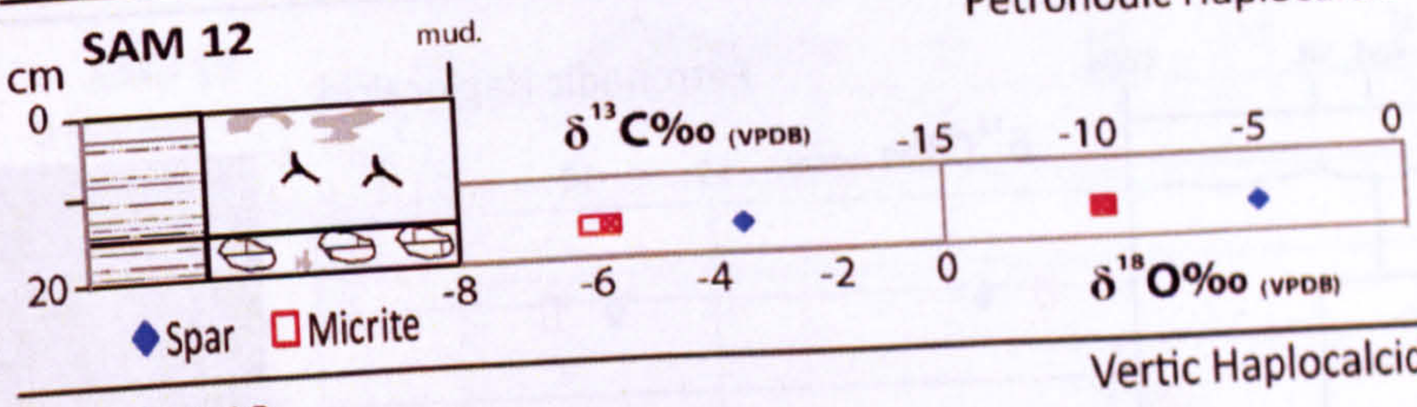

Ustic Calcid (Lacustrine)



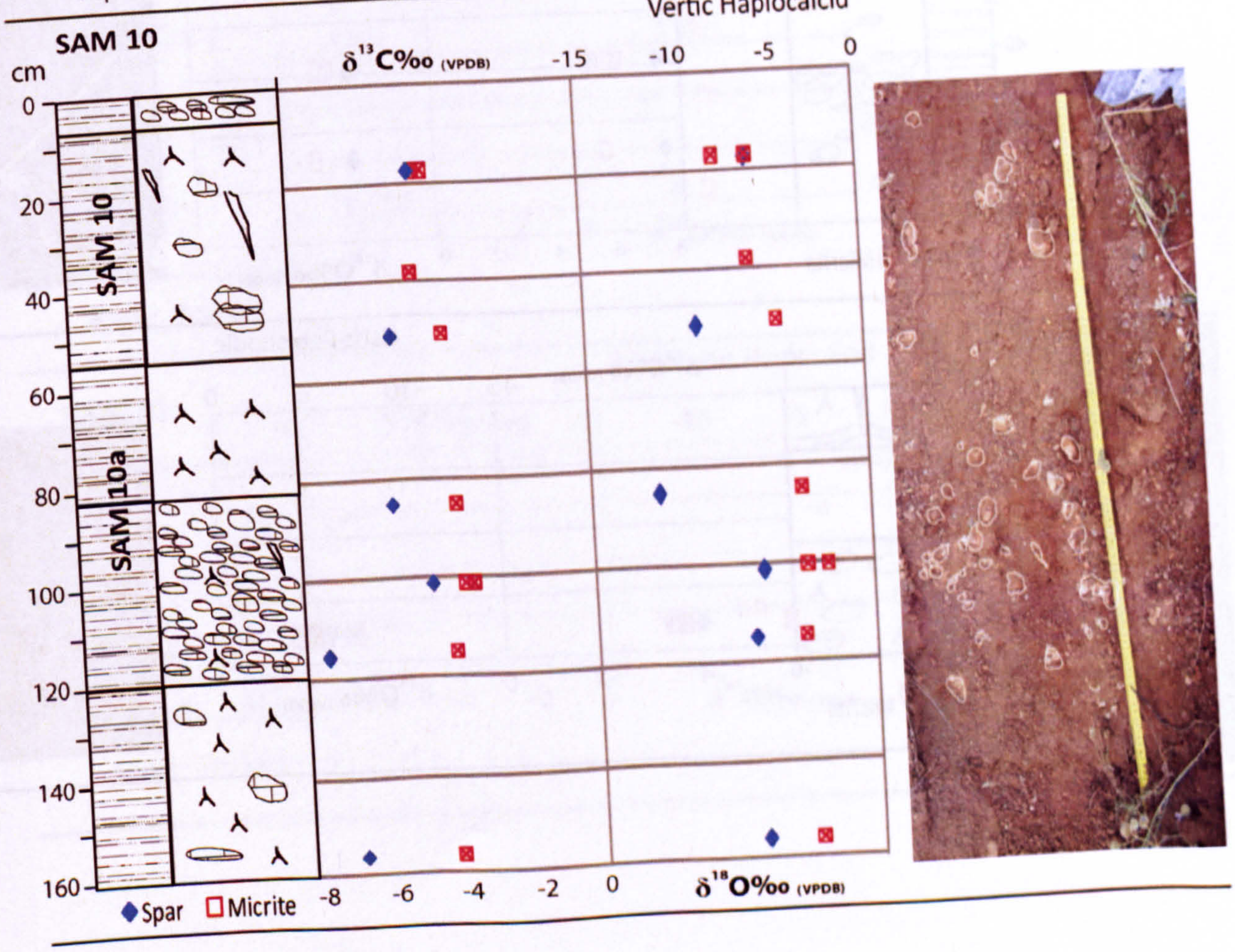
Vertic Haplocalcid

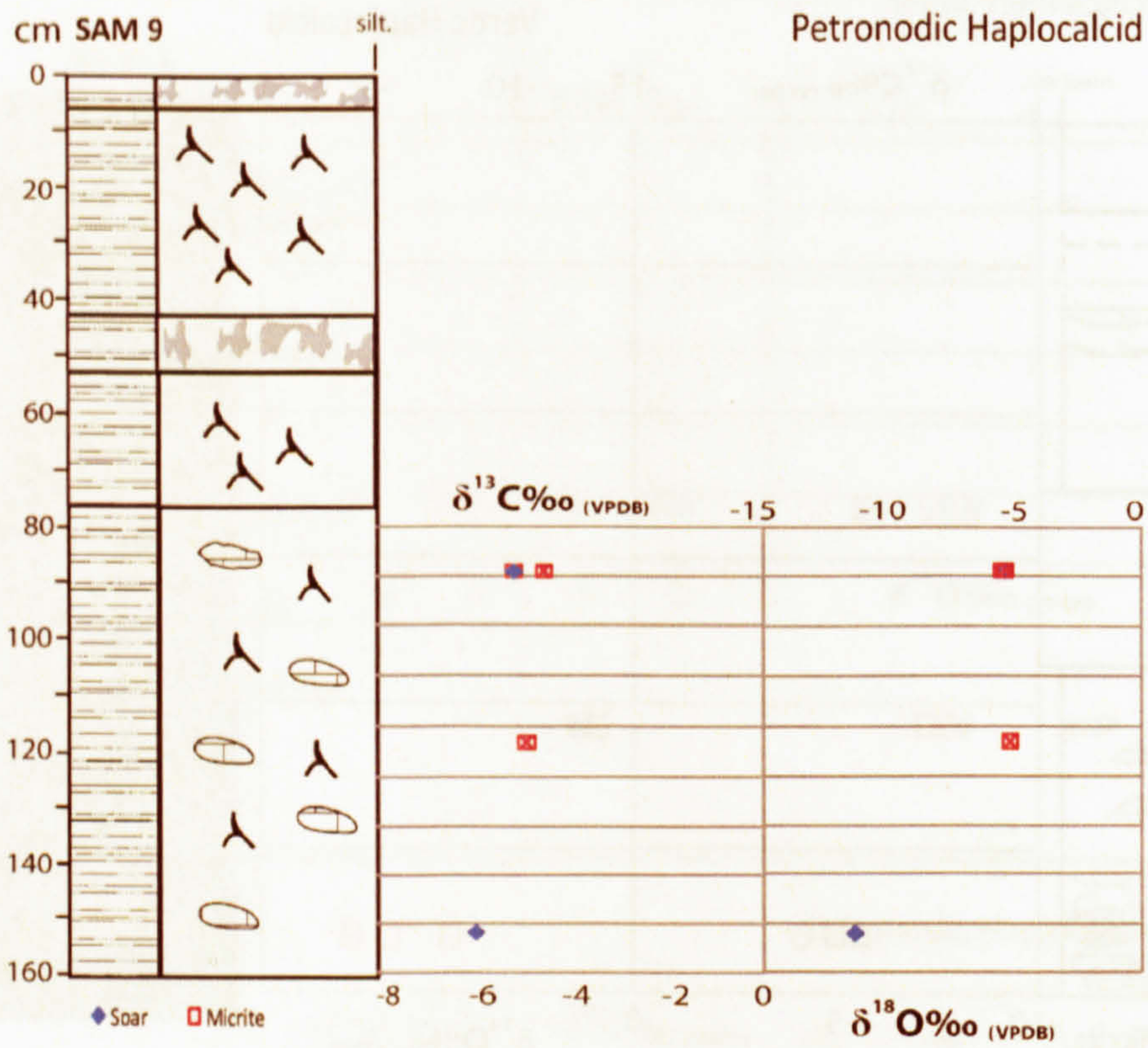


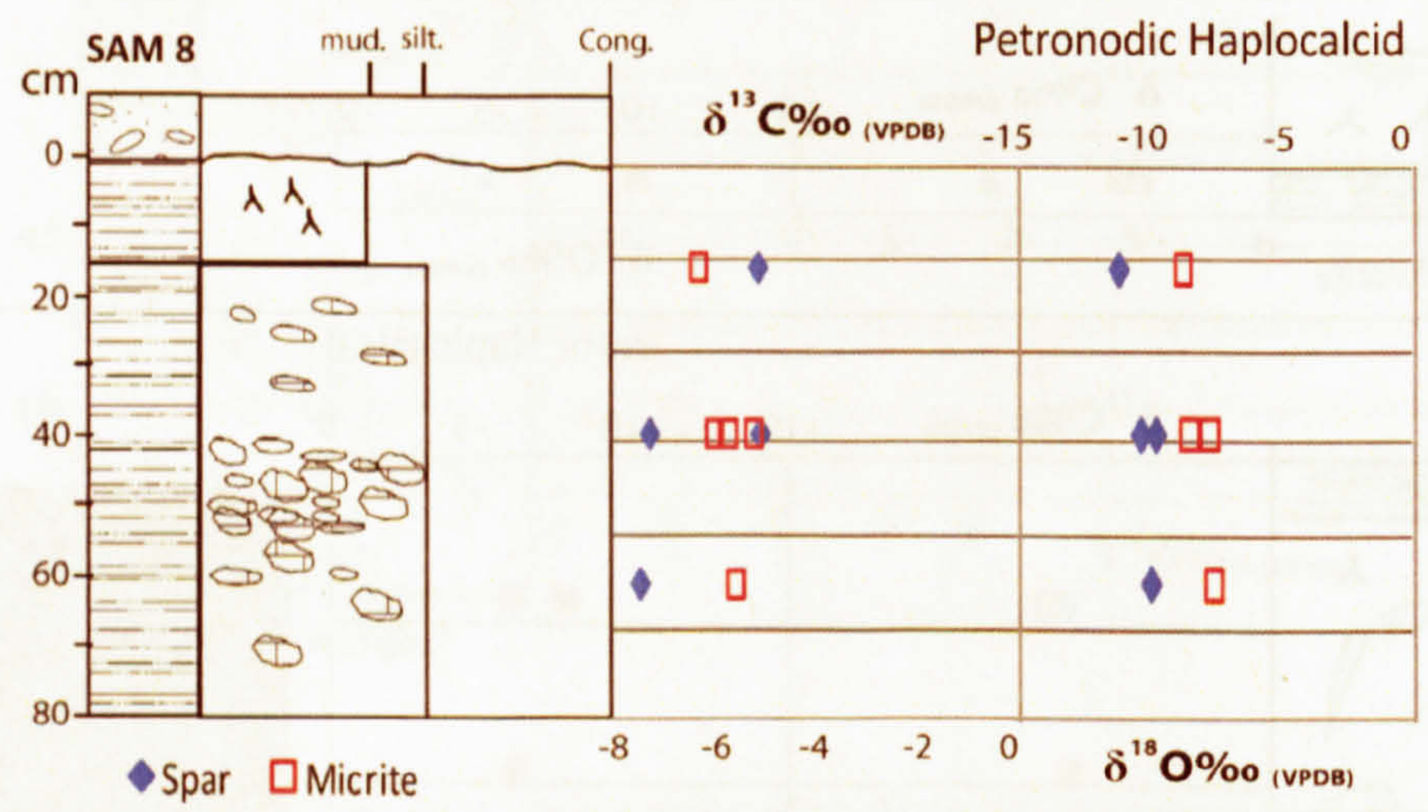

Petronodic Haplocalcid

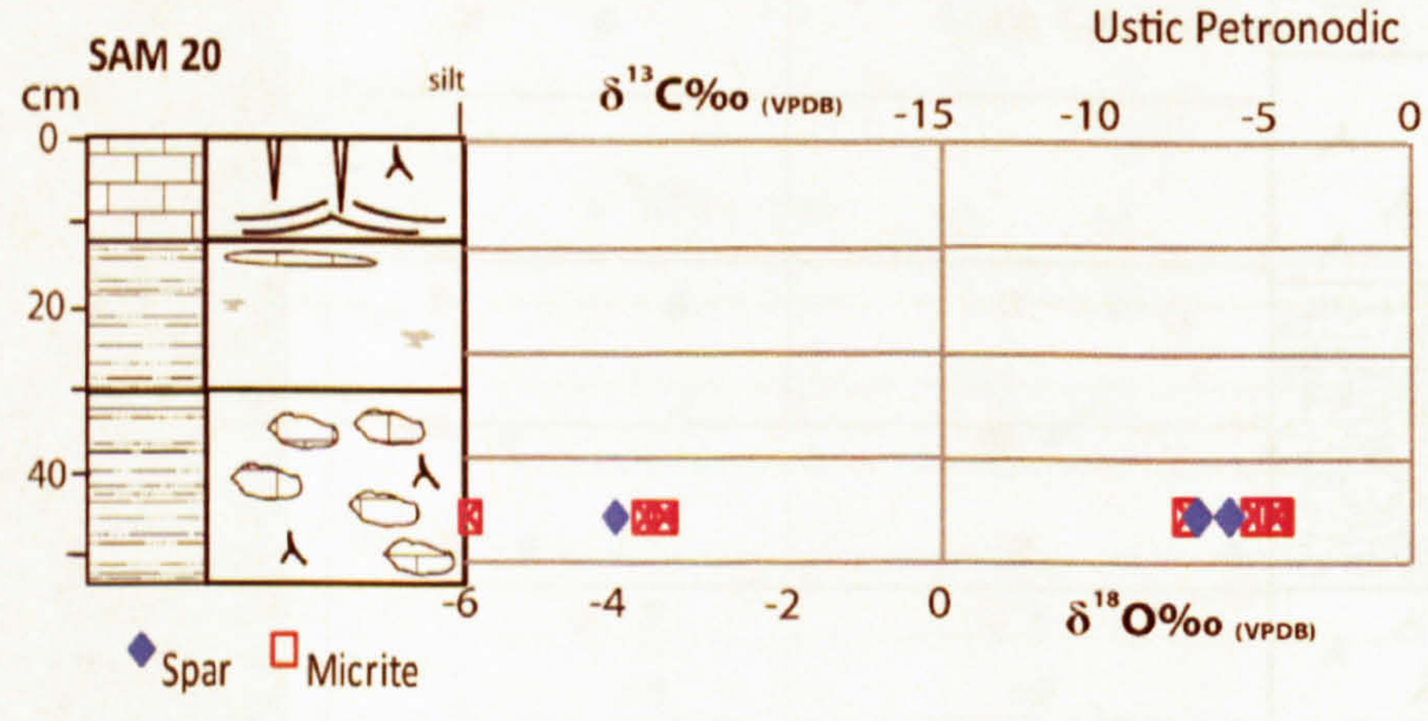


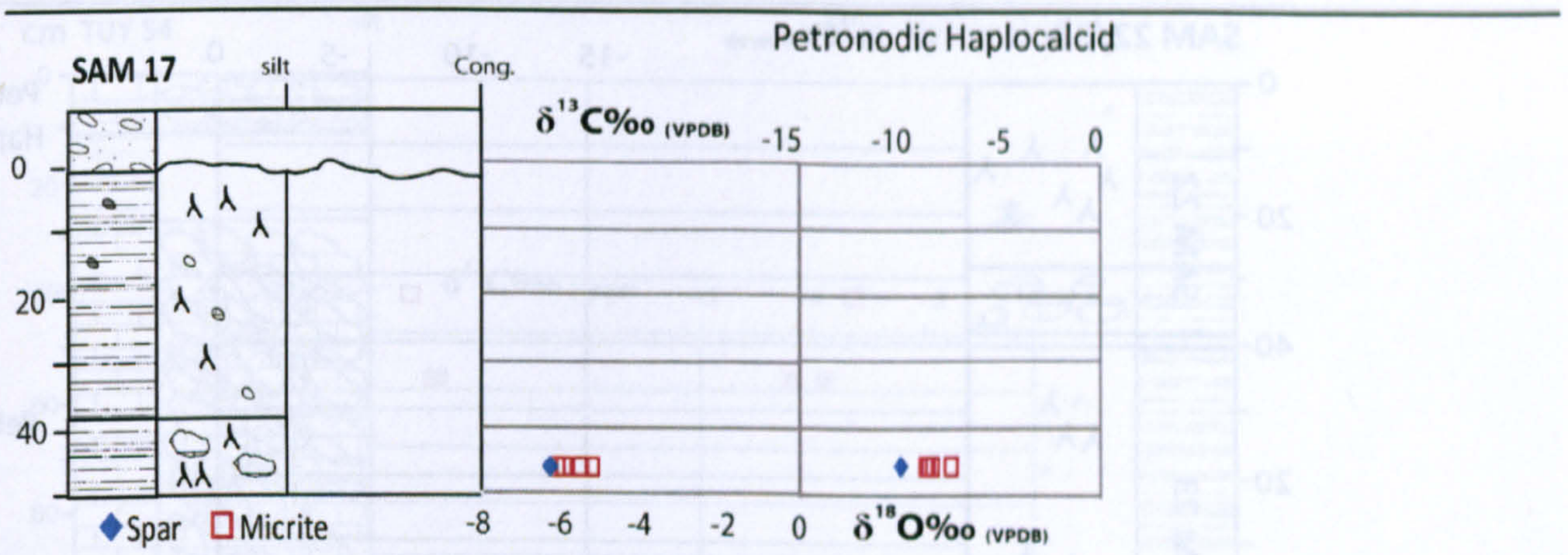

Vertic Haplocalcid

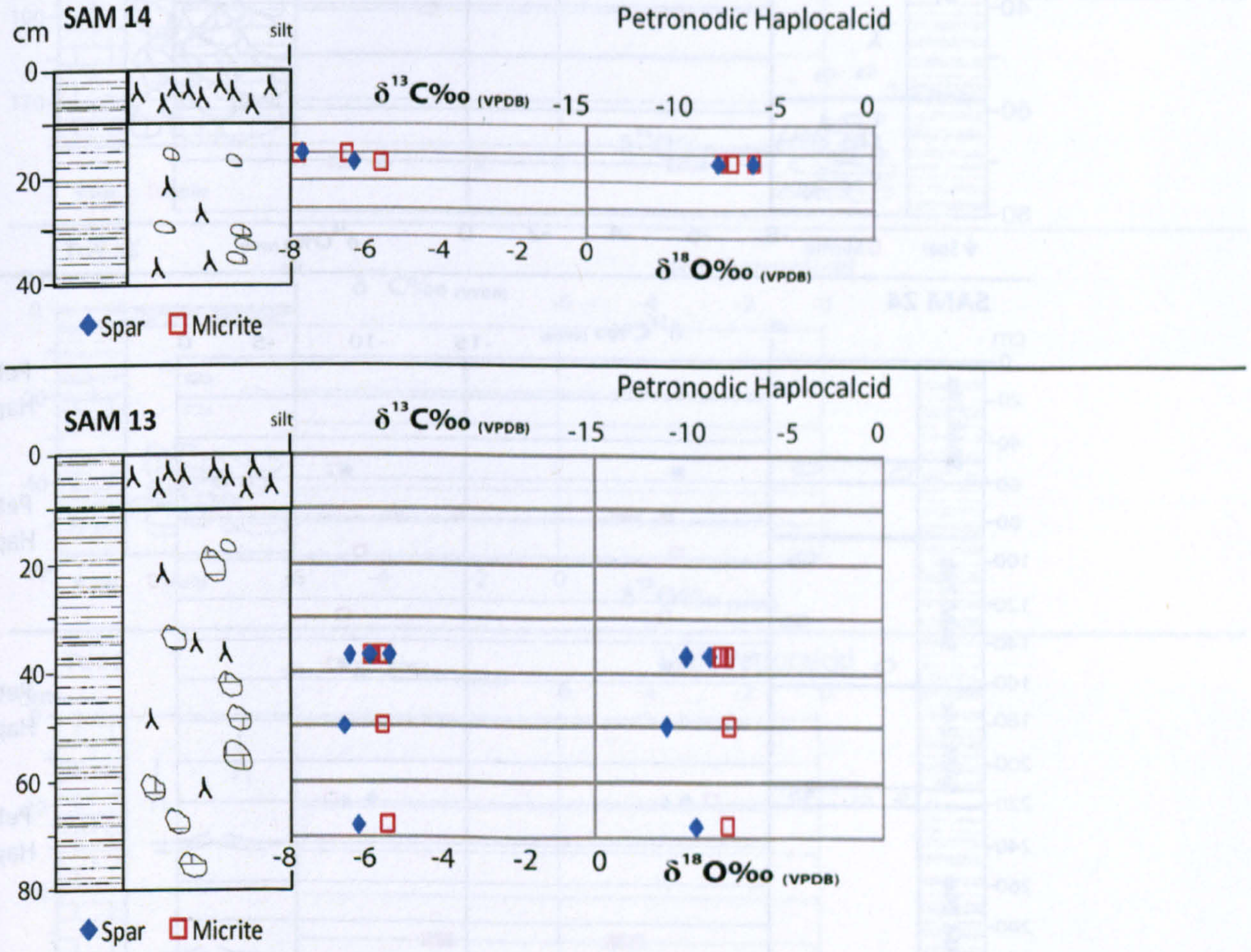



cm SAM 9
silt.
Petronodic Haplocalcid
0
20
40
60
80
100
120
140
160
δ13C‰ (VPDB)
-15
-10
-5
0
-8
-6
-4
-2
0
δ18O‰ (VPDB)
Soar
Micrite

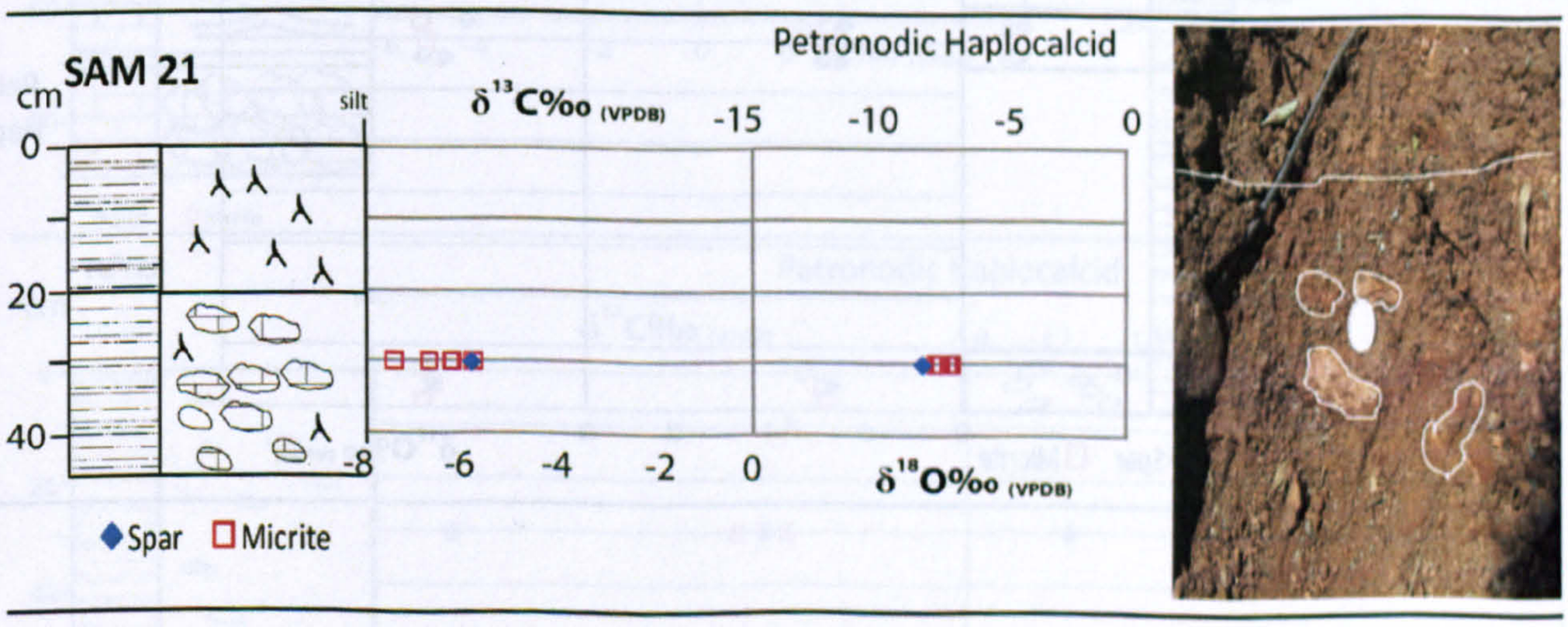

SAM 8
mud. silt.
Cong.
Petronodic Haplocalcid
cm
0
20
40
60
80
δ13C‰ (VPDB)
-15
-10
-5
0
-8
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite

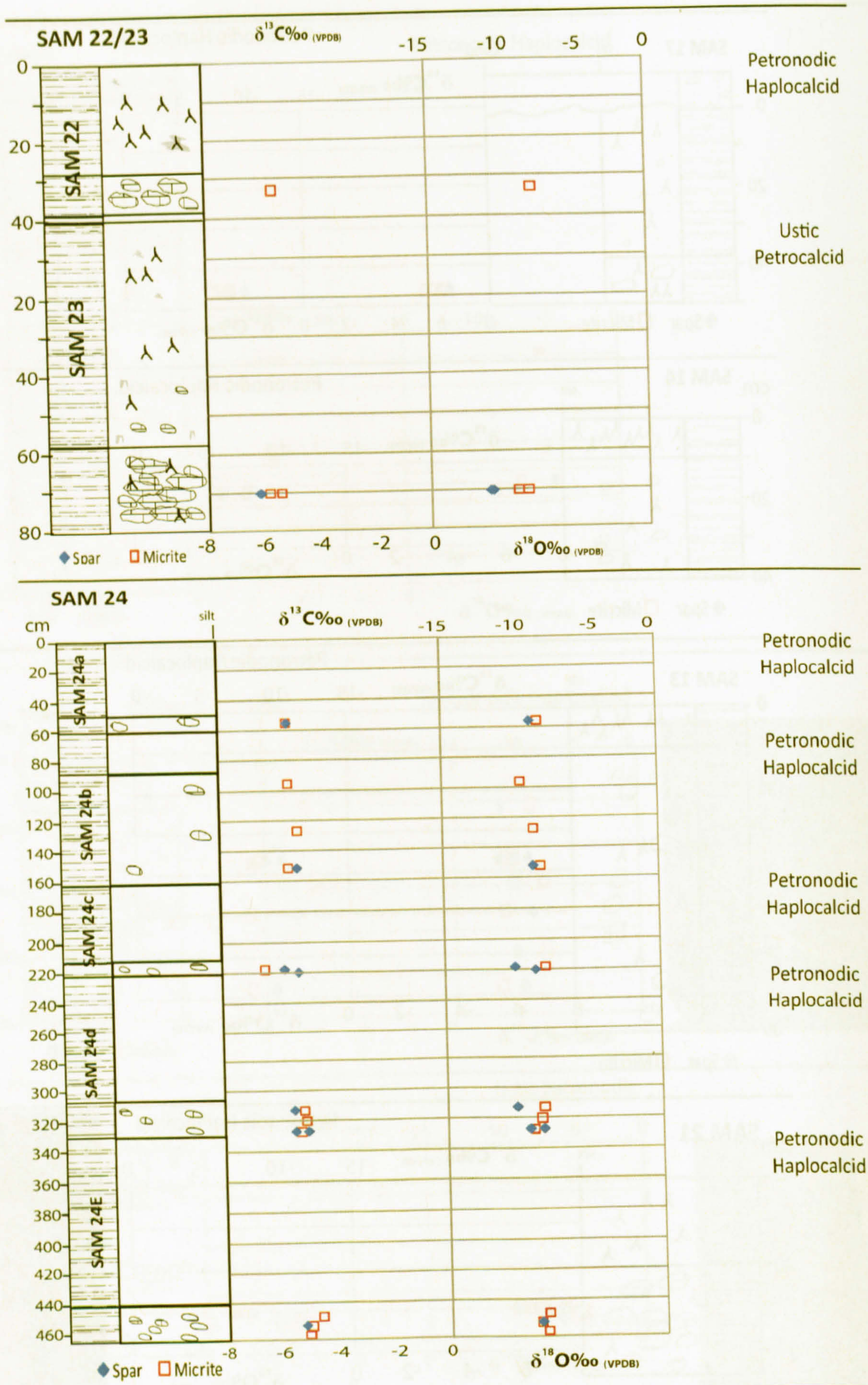

SAM 20
cm
silt
Ustic Petronodic
0
20
40
δ13C‰ (VPDB)
-15
-10
-5
0
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite

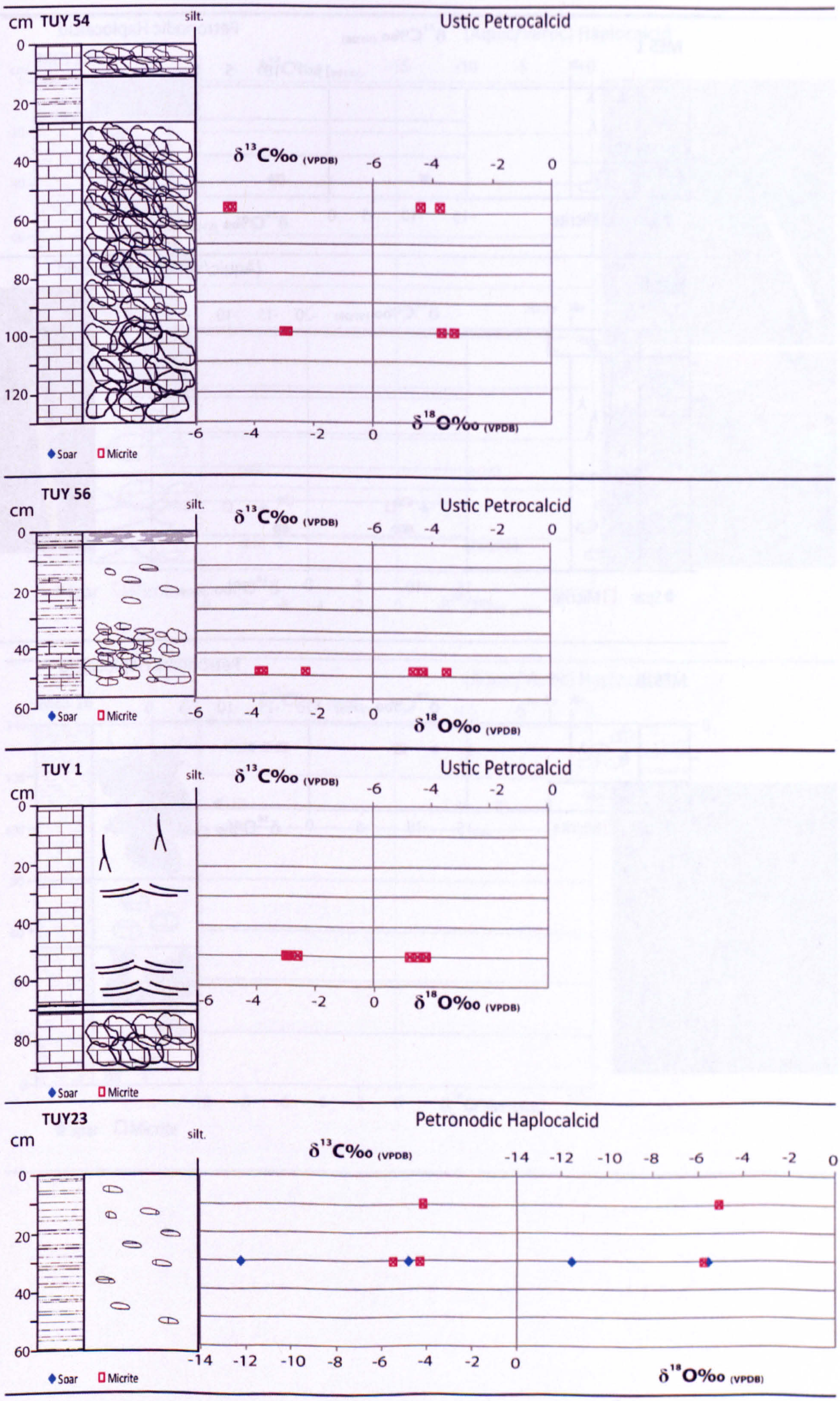

SAM 17
silt
Cong.
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
0
20
40
Spar
Micrite
-8
-6
-4
-2
0
δ18O‰ (VPDB)


cm
SAM 14
silt
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
0
20
40
-8
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite


SAM 13
silt
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
0
20
40
60
80
-8
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite

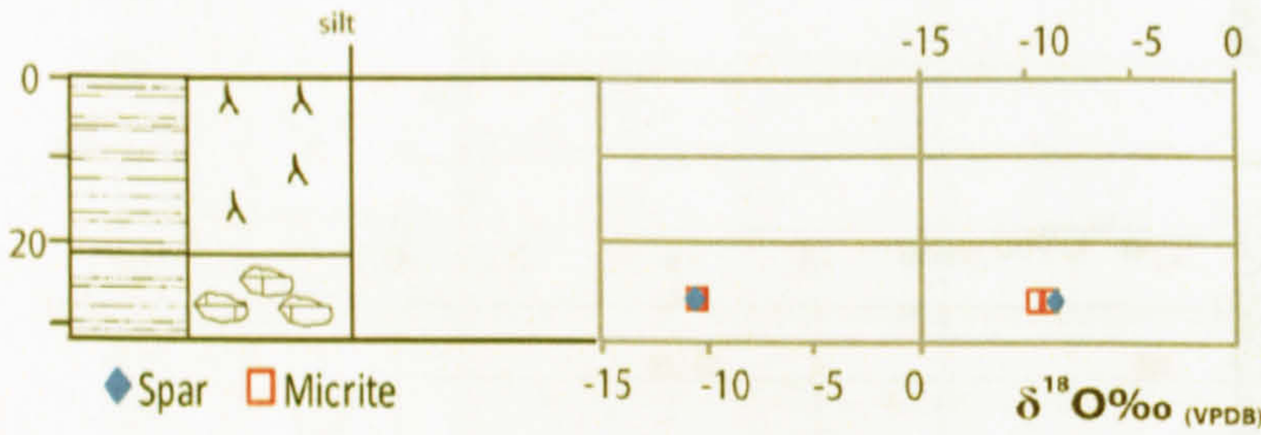

SAM 21
cm
silt
Petronodic Haplocalcid
δ13C‰ (VPDB)
-15
-10
-5
0
0
20
40
-8
-6
-4
-2
0
δ18O‰ (VPDB)
Spar
Micrite


SAM 22/23
δ13C‰ (VPDB)
-15
-10
-5
0
SAM 22
SAM 23
0
20
40
60
80
Petronodic Haplocalcid
Ustic Petrocalcid
Spar
Micrite
-8
-6
-4
-2
0
δ18O‰ (VPDB)
SAM 24
cm
silt
δ13C‰ (VPDB)
-15
-10
-5
0
SAM 24a
SAM 24b
SAM 24c
SAM 24d
SAM 24E
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
Petronodic Haplocalcid
Petronodic Haplocalcid
Petronodic Haplocalcid
Petronodic Haplocalcid
Spar
Micrite
-8
-6
-4
-2
0
δ18O‰ (VPDB)


cm TUY 54
silt.
Ustic Petrocalcid
δ13C‰ (VPDB)
-6
-4
-2
0
0
20
40
60
80
100
120
δ18O‰ (VPDB)
Spar
Micrite
TUY 56
cm
silt.
Ustic Petrocalcid
δ13C‰ (VPDB)
δ18O‰ (VPDB)
Spar
Micrite
TUY 1
cm
silt.
Ustic Petrocalcid
δ13C‰ (VPDB)
δ18O‰ (VPDB)
Spar
Micrite
TUY23
cm
silt.
Petronodic Haplocalcid
δ13C‰ (VPDB)
-14
-12
-10
-8
δ18O‰ (VPDB)
Spar
Micrite

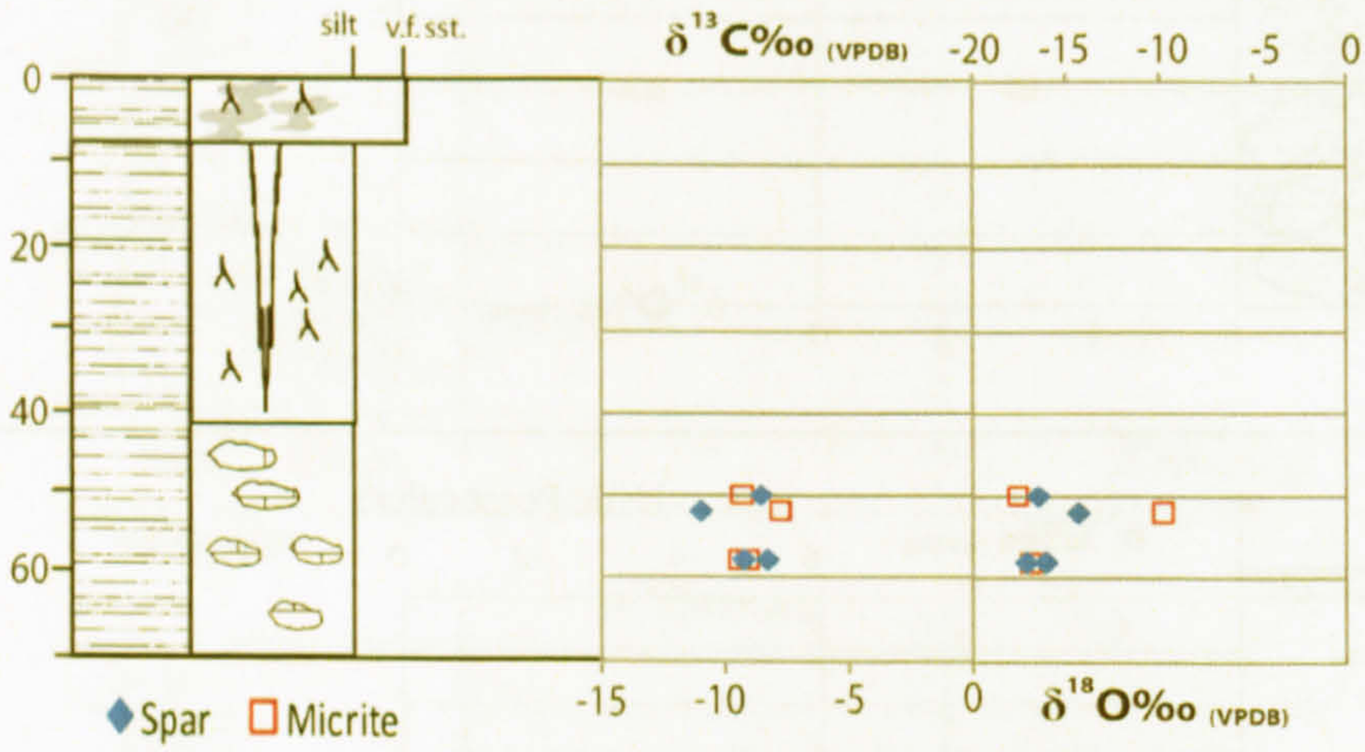
MES 1

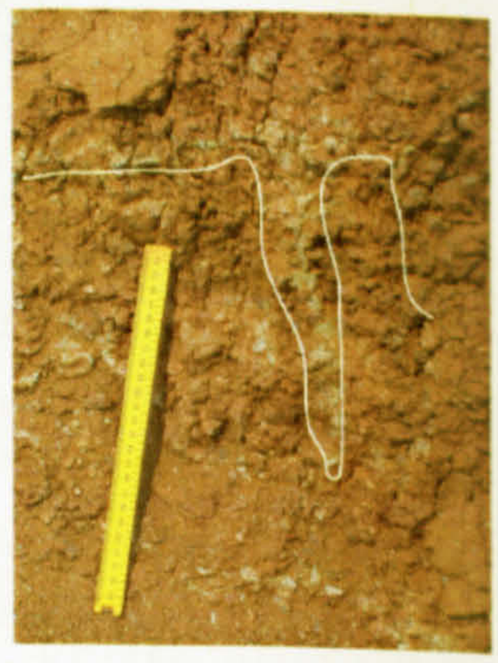
Petronodic Haplocalcid




MES8

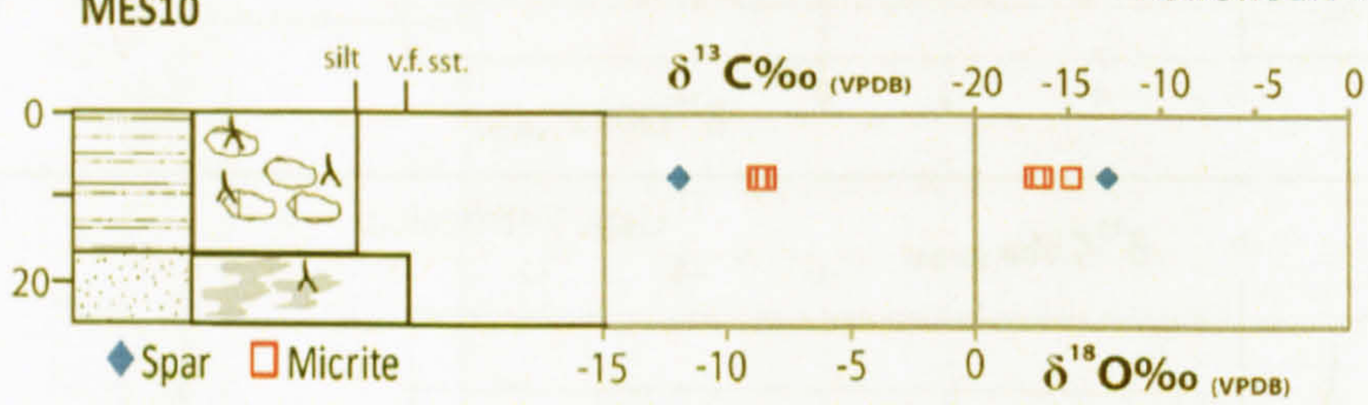
(Aquic/Vertic) Haplocalcid

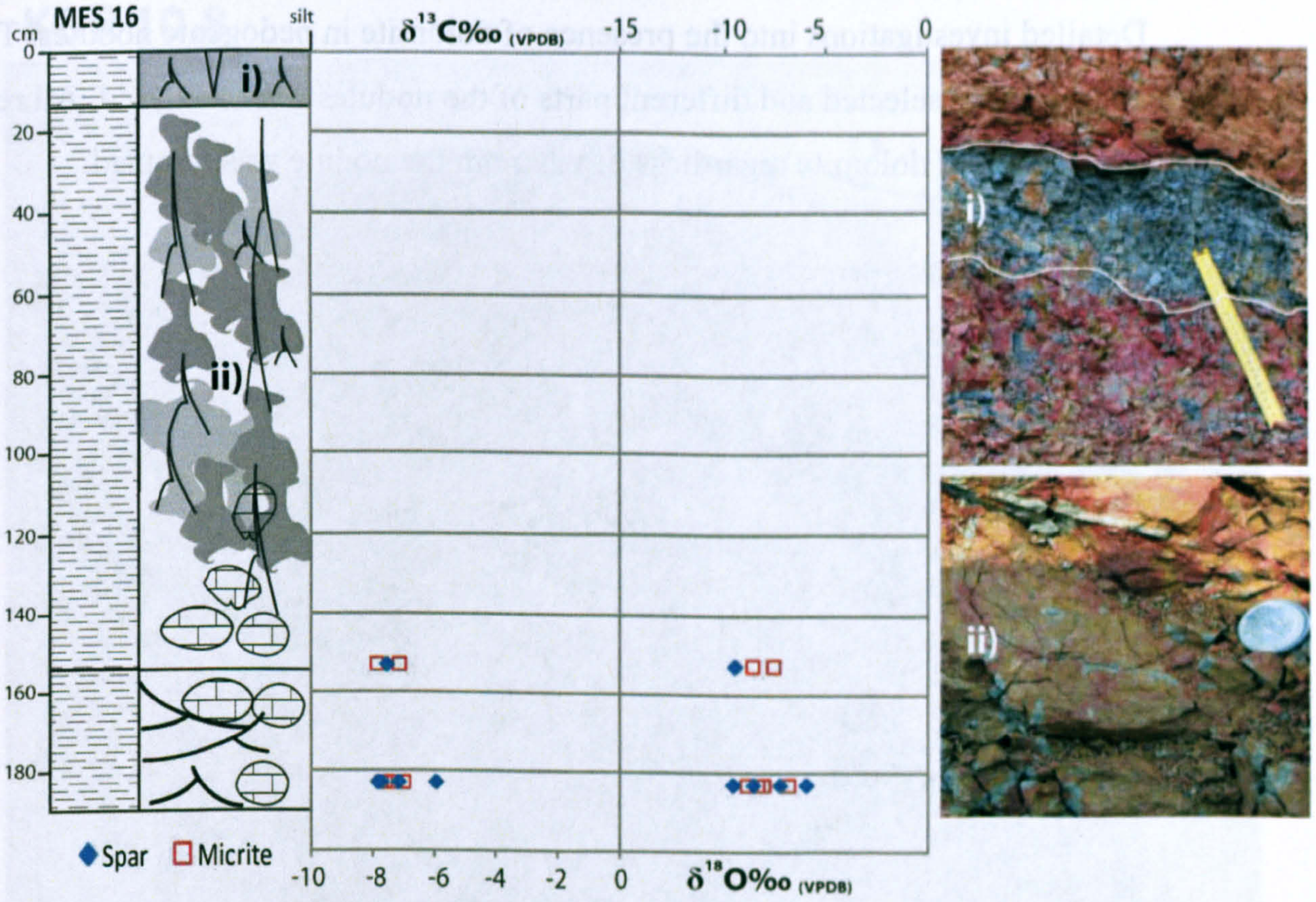


MES10

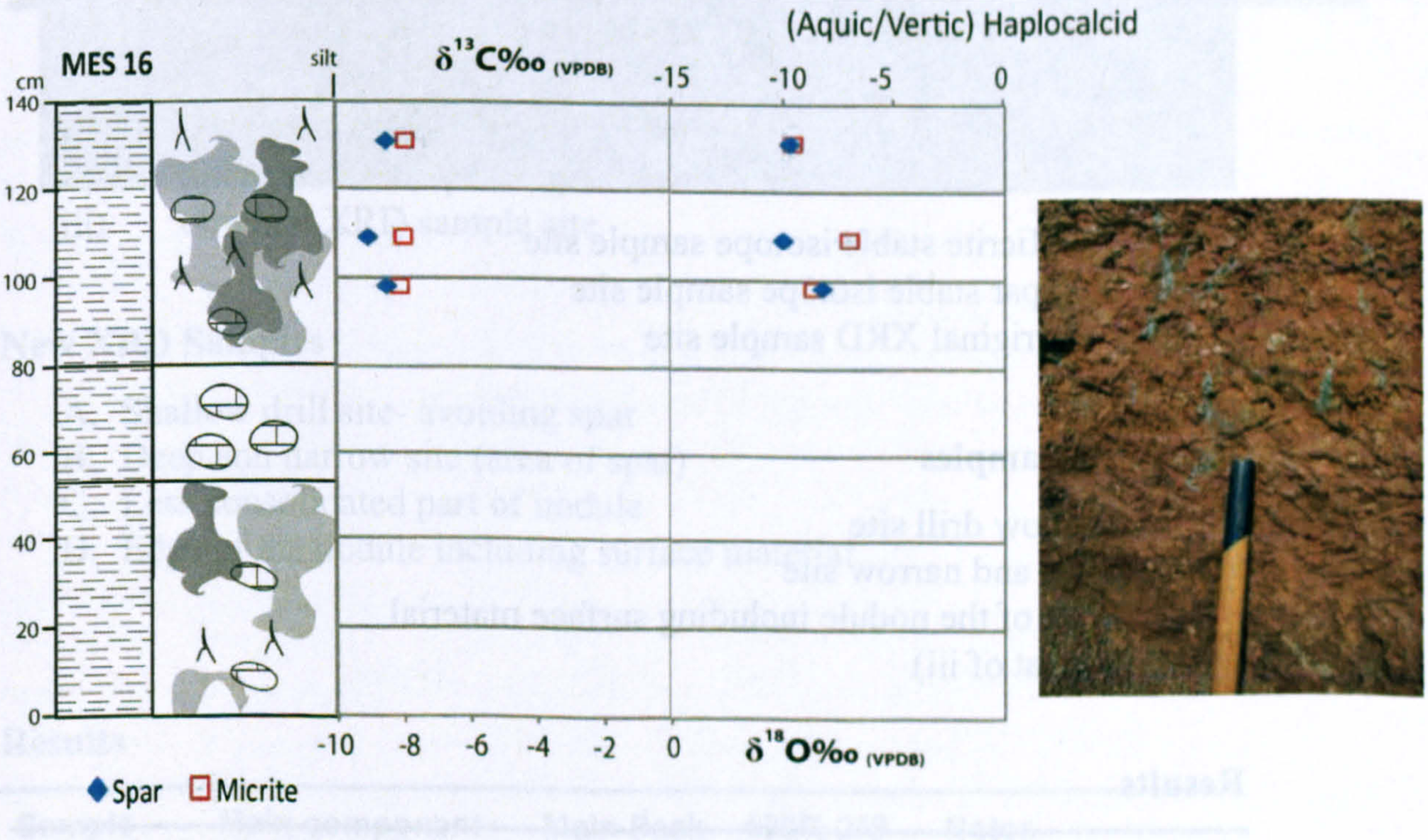
Petronodic Haplocalcid




(Aquic/Vertic) Haplocalcid
MES 16
silt
cm
0
20
40
60
80
100
120
140
160
180
i)
ii)
δ13C‰ (VPDB)
-15
-10
-5
0
Spar
Micrite
-10
-8
-6
-4
-2
0
δ18O‰ (VPDB)


i)

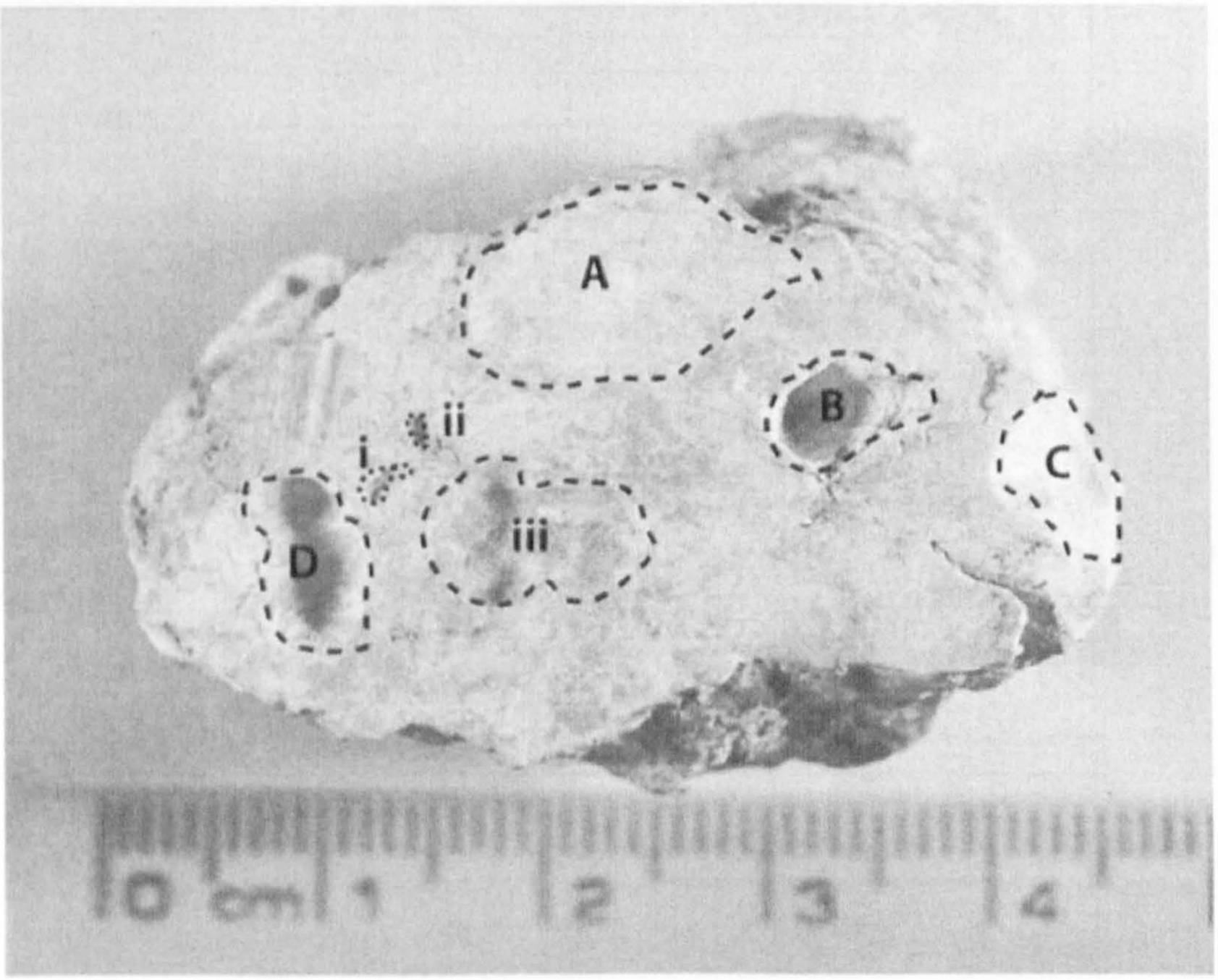

ii)


(Aquic/Vertic) Haplocalcid
MES 16
silt
cm
140
120
100
80
60
40
20
0
δ13C‰ (VPDB)
-15
-10
-5
0
Spar
Micrite
-10
-8
-6
-4
-2
0
δ18O‰ (VPDB)

## A2.3

Detailed investigations into the presence of dolomite in pedogenic nodules. Three nodules were selected and different parts of the nodules were analysed. All returned a XRD result of dolomite regardless of where in the nodule was sampled

### KOR 2.4



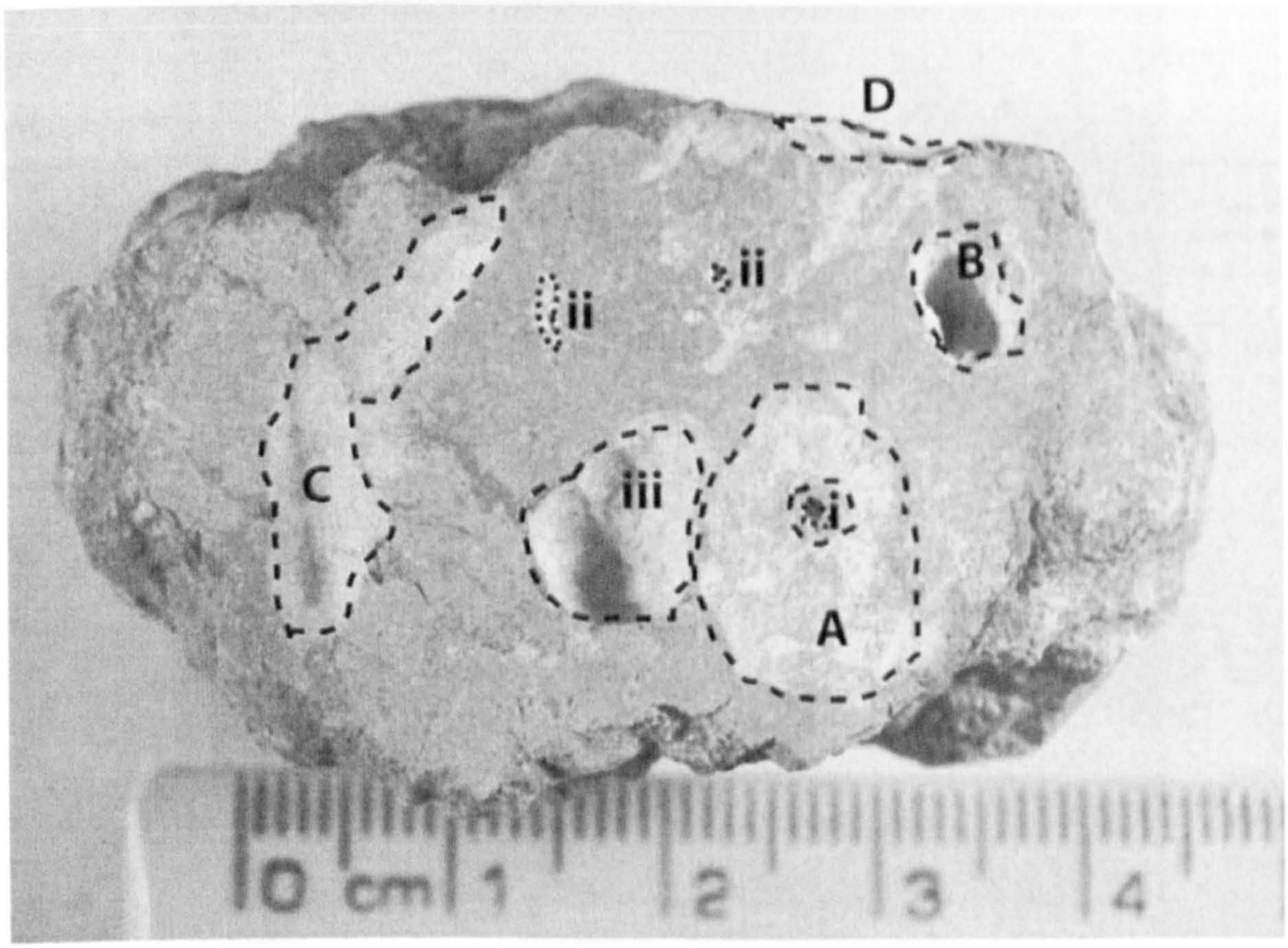

i) Micrite stable isotope sample site
ii) Spar stable isotope sample site
iii) Original XRD sample site

**New XRD Samples**

A. Shallow drill site
B. Deep and narrow site
C. Edge of the nodule including surface material
D. Repeat of iii)

**Results**

| Sample | Main component | Main Peak | 100% 2°θ | Notes |
|---|---|---|---|---|
| iii | Dolomite | 580 | 30.7749 | Calcite III (29.4016) |
| A | Dolomite | 796 | 30.7089 | |
| B | Dolomite | 298 | 30.8873 | Calcite III (29.5649) |
| C | Dolomite | 891 | 30.7478 | Calcite III (29.3763) |
| D | Dolomite | 933 | 30.8295 | |




i) Micrite stable isotope sample site
ii) Spar stable isotope sample site
iii) Original XRD sample site

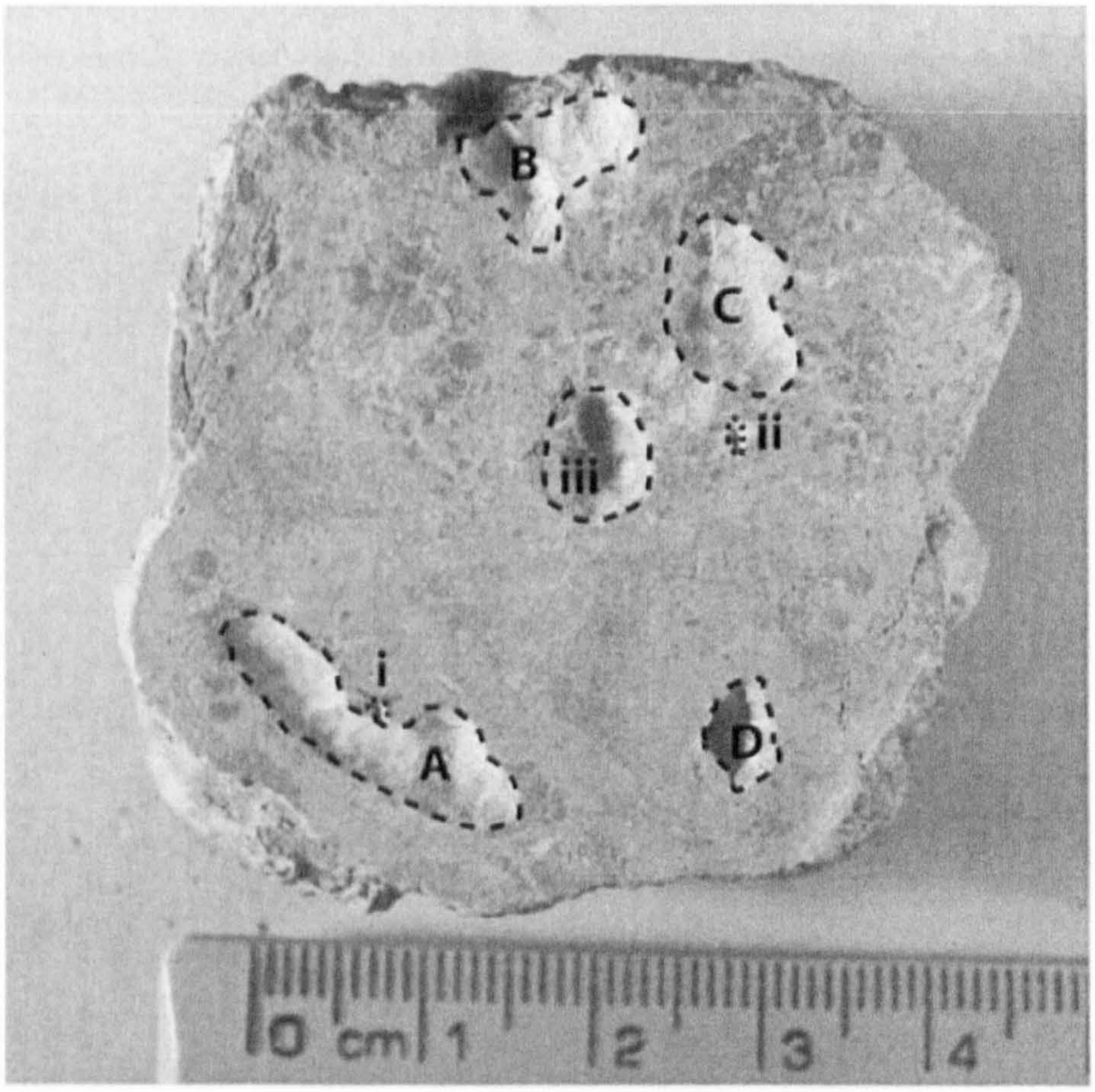
**New XRD Samples**

A. Shallow drill site- avoiding spar
B. Deep and narrow site (area of spar)
C. Less consolidated part of nodule
D. Edge of the nodule including surface material

**Results**

| Sample | Main component | Main Peak | 100% 2°θ | Notes |
|---|---|---|---|---|
| iii | Dolomite * | 874.84 | 30.6249 | Quartz High |
| A | Dolomite * | 1027.87 | 30.6143 | Quartz |
| B | Dolomite | 506 | 30.7588 | Quartz low |
| C | Dolomite | 626.26 | 30.5844 | Quartz |
| D | Dolomite | 579.23 | 30.5719 | |

## KOR 21.10




i) Micrite stable isotope sample site
ii) Spar stable isotope sample site
iii) Original XRD sample site

**New XRD Samples**

A. Shallow drill site
B. Redden less consolidated area of nodule (altered?)
C. In area of high amount of small spar cracks
D. Deep and narrow site

**Results**

| Sample | Main component | Main Peak | 100% 2°θ | Notes |
|---|---|---|---|---|
| iii | Dolomite | 896 | 30.7348 | |
| A | Dolomite | 636.92 | 30.6562 | |
| B* | Dolomite | 616.59 | 30.6596 | Quartz (50) |
| C | Dolomite | 510.2 | 30.7603 | Calcite (100% 2°θ= 29.3826)* |
| D | Dolomite | 777.8 | 30.6271 | Quartz (31) |

* only one with 'calcite' peak

# A2.4

X-ray diffraction results. Main component refers to the largest peak recorded in a sample. The 100% 2°θ is the 2°θ of the maximum peak in the sample. The second component is the second match after the main component had been removed.

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| KOR 1.7 | Boyevaya Gora | Dolomite | 1254 | 31.5633 | 2.83462 | - |
| KOR 1.8 | Boyevaya Gora | Dolomite | 1217 | 31.4403 | 2.84543 | - |
| KOR 1.9 | Boyevaya Gora | Dolomite | 512 | 31.8326 | 2.81125 | - |
| KOR 1.10 | Boyevaya Gora | Dolomite | 872 | 31.5266 | 2.83703 | - |
| KOR 1.8 | Boyevaya Gora | Dolomite | 1217 | 31.4403 | 2.84543 | - |
| KOR 2.1 | Boyevaya Gora | Dolomite | 779 | 31.8540 | 2.80941 | - |
| KOR 2.2 | Boyevaya Gora | Dolomite | 1709 | 31.5273 | 2.83777 | - |
| KOR 2.3 | Boyevaya Gora | Dolomite | 1233 | 31.6074 | 2.83076 | - |
| KOR 2.4 | Boyevaya Gora | Dolomite | 580 | 31.7748 | 2.81623 | Calcite |
| KOR 2.5 | Boyevaya Gora | Dolomite | 757 | 31.7169 | 2.82124 | - |
| KOR 2.6 | Boyevaya Gora | Dolomite | 1140 | 31.6193 | 2.82972 | - |
| KOR 2.7 | Boyevaya Gora | Dolomite | 1088 | 31.2852 | 2.85918 | Quartz |
| KOR 2.8 | Boyevaya Gora | Dolomite | 938 | 31.5512 | 2.83568 | Quartz |
| KOR 2.9 | Boyevaya Gora | Dolomite | 1304 | 31.5682 | 2.83490 | - |
| KOR 3.1 | Boyevaya Gora | Dolomite | 531 | 31.5412 | 2.83658 | Calcite, magnesian |
| KOR 4.1 | Boyevaya Gora | Dolomite | 1079 | 31.6145 | 2.83015 | - |
| KOR 5.1 | Boyevaya Gora | Quartz | 561 | 27.3632 | 3.25941 | Dolomite |
| KOR 5.2 | Boyevaya Gora | Dolomite | 955 | 31.5646 | 2.83450 | Quartz |
| KOR 5.3 | Boyevaya Gora | Dolomite | 798 | 31.7591 | 2.81759 | - |
| KOR 5.4 | Boyevaya Gora | Dolomite | 853 | 31.5276 | 2.83775 | Quartz |
| KOR 5.5 | Boyevaya Gora | Dolomite | 942 | 31.5960 | 2.83176 | Quartz |
| KOR 6.1 | Boyevaya Gora | Dolomite | 893 | 31.5059 | 2.83965 | - |
| KOR 6.2 | Boyevaya Gora | Dolomite | 439 | 31.6571 | 2.82643 | - |
| KOR 6.3 | Boyevaya Gora | Dolomite | 753 | 31.6416 | 2.82778 | Calcite III |
| KOR 6.4 | Boyevaya Gora | Dolomite | 938 | 31.6681 | 2.82541 | - |
| KOR 6.5 | Boyevaya Gora | Dolomite | 362 | 31.7096 | 2.82187 | Calcite III |
| KOR 6.6 | Boyevaya Gora | Dolomite | 750 | 31.6856 | 2.82396 | - |
| KOR 6.7 | Boyevaya Gora | Dolomite | 399 | 31.7531 | 2.81810 | Quartz |
| KOR 6.8 | Boyevaya Gora | Dolomite | 450 | 31.5936 | 2.83197 | - |
| KOR 7.1 | Boyevaya Gora | Dolomite | 807 | 31.5337 | 2.83686 | Quartz |
| KOR 9.1 | Boyevaya Gora | Dolomite | 701 | 31.5439 | 2.83631 | - |
| KOR 9.2 | Boyevaya Gora | Dolomite | 781 | 31.6584 | 2.82632 | - |
| KOR 9.3 | Boyevaya Gora | Dolomite | 645 | 31.5298 | 2.83755 | Quartz |
| KOR 9.4 | Boyevaya Gora | Dolomite | 612 | 31.6678 | 2.82550 | Quartz |
| KOR 10.2 | Boyevaya Gora | Dolomite | 689 | 31.6786 | 2.82457 | Quartz |
| KOR 10.3 | Boyevaya Gora | Dolomite | 1356 | 31.5795 | 2.83320 | - |
| KOR 10.4 | Boyevaya Gora | Dolomite | 974 | 31.4688 | 2.84292 | Quartz |
| KOR 10.5 | Boyevaya Gora | Dolomite | 471 | 31.8014 | 2.81394 | - |
| KOR 10.6 | Boyevaya Gora | Quartz | 484 | 27.3632 | 3.25941 | Dolomite |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| KOR 10.7 | Boyevaya Gora | Dolomite | 509 | 31.7508 | 2.81831 | – |
| KOR 10.8 | Boyevaya Gora | Dolomite | 875 | 31.6249 | 2.82924 | best match Kutnohorite |
| KOR 10.10 | Boyevaya Gora | Dolomite | 518 | 31.5156 | 2.83880 | Quartz |
| KOR 10.11 | Boyevaya Gora | Dolomite | 283 | 31.7619 | 2.81735 | – |
| KOR 10.12 | Boyevaya Gora | Dolomite | 434 | 31.6732 | 2.82504 | Quartz |
| KOR 10.B1 | Boyevaya Gora | Quartz | 764 | 31.6830 | 2.82418 | Dolomite |
| KOR 11.1 | Boyevaya Gora | Dolomite | 910 | 31.6244 | 2.82928 | – |
| KOR 12.1 | Boyevaya Gora | Dolomite | 525 | 31.6181 | 2.82983 | Quartz |
| KOR 12.2 | Boyevaya Gora | Dolomite | 785 | 31.5407 | 2.83660 | Quartz |
| KOR 12.3 | Boyevaya Gora | Dolomite | 769 | 31.6671 | 2.82557 | Quartz |
| KOR 13.1 | Boyevaya Gora | Dolomite | 963 | 31.5759 | 2.33510 | Quartz |
| KOR 14.1 | Boyevaya Gora | Dolomite | 1098 | 31.5750 | 2.83359 | – |
| KOR 14.2 | Boyevaya Gora | Dolomite | 810 | 31.5392 | 2.83673 | – |
| KOR 14.3 | Boyevaya Gora | Dolomite | 688 | 31.5683 | 2.83418 | – |
| KOR 14.7 | Boyevaya Gora | Dolomite | 860 | 31.6006 | 2.83133 | Quartz |
| KOR 14.6 | Boyevaya Gora | Dolomite | 773 | 31.5045 | 2.83977 | – |
| KOR 14.8 | Boyevaya Gora | Dolomite | 895 | 31.4686 | 2.84930 | Quartz |
| KOR 14.10 | Boyevaya Gora | Dolomite | 889 | 31.5506 | 2.83570 | Quartz |
| KOR 14.11 | Boyevaya Gora | Dolomite | 740 | 31.6716 | 2.82517 | – |
| KOR 14.14 | Boyevaya Gora | Dolomite | 768 | 31.5542 | 2.83542 | Quartz |
| KOR 14.15 | Boyevaya Gora | Dolomite | 1103 | 31.6730 | 2.82505 | – |
| KOR 15.2 | Boyevaya Gora | Dolomite | 519 | 31.8074 | 2.81345 | Quartz |
| KOR 15.3 | Boyevaya Gora | Dolomite | 527 | 31.4837 | 2.84161 | – |
| KOR 15.4 | Boyevaya Gora | Dolomite | 632 | 31.7288 | 2.82021 | – |
| KOR 15.5 | Boyevaya Gora | Dolomite | 718 | 31.6647 | 2.82577 | – |
| KOR 15.6 | Boyevaya Gora | Dolomite | 713 | 31.7108 | 2.82177 | Quartz |
| KOR 15.6 | Boyevaya Gora | Dolomite | 711 | 31.5483 | 2.83593 | – |
| KOR 15.7 | Boyevaya Gora | Dolomite | 642 | 31.6811 | 2.82435 | – |
| KOR 15.8 | Boyevaya Gora | Dolomite | 1964 | 31.7314 | 2.81999 | – |
| KOR 15.9 | Boyevaya Gora | Dolomite | 1173 | 31.5511 | 2.83569 | Quartz |
| KOR 15.B2 | Boyevaya Gora | Quartz | 834 | 27.4080 | 3.25419 | – |
| KOR 16.1 | Boyevaya Gora | Calcite, magnesian | 774 | 30.3301 | 2.94700 | – |
| KOR 16.2 | Boyevaya Gora | Calcite, magnesian | 456 | 30.4822 | 2.93264 | – |
| KOR 16.3 | Boyevaya Gora | Calcite | 1159 | 30.3550 | 2.94938 | – |
| KOR 16.4 | Boyevaya Gora | Calcite, magnesian | 990 | 30.4075 | 2.93968 | – |
| KOR 16.5 | Boyevaya Gora | Calcite, magnesian | 1178 | 30.2699 | 2.95273 | – |
| KOR 16.6 | Boyevaya Gora | Calcite, magnesian | 816 | 30.2943 | 2.95040 | – |
| KOR 16.7 | Boyevaya Gora | Calcite | 920 | 30.3167 | 2.94828 | – |
| KOR 16.8 | Boyevaya Gora | Calcite, magnesian | 871 | 30.3376 | 2.94629 | – |
| KOR 16.9 | Boyevaya Gora | Calcite, magnesian | 724 | 30.3077 | 2.94912 | – |
| KOR 17.2 | Boyevaya Gora | Calcite | 673 | 30.3557 | 2.94457 | – |
| KOR 17.3 | Boyevaya Gora | Dolomite | 397 | 31.6304 | 2.82875 | Quartz |
| KOR 17.4 | Boyevaya Gora | Dolomite | 557 | 31.7635 | 2.81721 | Quartz/ Calcite, magnesian |
| KOR 18.2 | Boyevaya Gora | Calcite | 491 | 30.5462 | 2.92665 | – |
| KOR 18.4 | Boyevaya Gora | Calcite | 404 | 30.4684 | 2.99339 | – |
| 04.8.1.I | Boyevaya Gora | Dolomite | 854 | 31.6494 | 2.82710 | – |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| 04.8.1.l.i | Boyevaya Gora | Dolomite | 641 | 31.7873 | 2.81516 | Quartz |
| 04.8.1.l.ii | Boyevaya Gora | Dolomite | 1110 | 31.5155 | 2.83881 | - |
| 04.8.1.l.iii | Boyevaya Gora | Dolomite | 964 | 31.4570 | 2.84396 | Quartz |
| KOR 21.1 | Boyevaya Gora | Calcite (Mg) | 620 | 30.2867 | 2.95112 | - |
| KOR 21.2 | Boyevaya Gora | Calcite, magnesian | 699 | 30.2624 | 2.95344 | - |
| KOR 21.3 | Boyevaya Gora | Calcite (CaCO3) | 621 | 30.3548 | 2.94466 | - |
| KOR 21.4 | Boyevaya Gora | Calcium Carbonate | 598 | 30.3825 | 2.94204 | - |
| KOR 21.5 | Boyevaya Gora | Dolomite | 309 | 31.8131 | 2.81293 | - |
| KOR 21.6 | Boyevaya Gora | Quartz | 498 | 30.3145 | 2.94848 | Calcite, magnesian |
| KOR 21.7 | Boyevaya Gora | Dolomite | 760 | 31.6952 | 2.82312 | - |
| KOR 21.8 | Boyevaya Gora | Dolomite | 482 | 31.8487 | 2.80987 | Quartz |
| KOR 21.9 | Boyevaya Gora | Dolomite | 625 | 31.6169 | 2.82994 | - |
| KOR 21.10 | Boyevaya Gora | Dolomite | 806 | 31.7348 | 2.81969 | - |
| 04.8.1.p | Boyevaya Gora | Dolomite | 1191 | 31.6651 | 2.82574 | - |
| KOR 22.1 | Boyevaya Gora | Calcite (CaCO3) | 401 | 30.3207 | 2.94786 | - |
| KOR 22.2a | Boyevaya Gora | Calcite (Mg, CaCO3) | 376 | 30.2494 | 2.95468 | - |
| KOR 22.2b | Boyevaya Gora | Calcite (Mg, CaCO3) | 961 | 30.2654 | 2.95316 | - |
| KOR 22.3 | Boyevaya Gora | Calcium Carbonate | 869 | 30.1836 | 2.96097 | - |
| KOR 22.4 | Boyevaya Gora | Calcite, magnesian | 901 | 30.3640 | 2.94379 | Quartz |
| KOR 22.5 | Boyevaya Gora | Quartz | 463 | 26.7236 | 3.33596 | - |
| KOR 22.6 | Boyevaya Gora | Calcite | 946 | 30.3095 | 2.94896 | - |
| KOR 22.7 | Boyevaya Gora | Calcite | 498 | 30.3949 | 2.94087 | - |
| KOR 22.8 | Boyevaya Gora | Calcite | 985 | 30.2524 | 2.95439 | - |
| KOR 22.9 | Boyevaya Gora | Calcite | 1045 | 30.2094 | 2.95853 | - |
| KOR 22.10 | Boyevaya Gora | Calcite | 1505 | 30.2863 | 2.95116 | - |
| KOR 22.11 | Boyevaya Gora | Calcite, magnesian | 948 | 30.2881 | 2.95099 | Calcite |
| KOR 22.12 | Boyevaya Gora | Calcite | 1102 | 30.1514 | 2.96406 | - |
| KOR 22.13 | Boyevaya Gora | Calcite | 683 | 30.2223 | 2.95727 | - |
| KOR 22.14 | Boyevaya Gora | Calcite, magnesian | 1277 | 30.2451 | 2.95509 | Calcite syn |
| KOR 23.1 | Boyevaya Gora | Calcite, magnesian | 525 | 30.4233 | 2.93815 | - |
| KOR 23.2 | Boyevaya Gora | Calcite, magnesian | 1090 | 30.2855 | 2.95124 | - |
| KOR 23.3 | Boyevaya Gora | Dolomite | 533 | 31.7121 | 2.82165 | - |
| KOR 23.4 | Boyevaya Gora | Dolomite | 468 | 31.6946 | 2.82318 | Calcite |
| 04.8.1.r | Boyevaya Gora | Dolomite | 404 | 31.4222 | 2.84614 | Calcite |
| 04.8.1.r.i | Boyevaya Gora | Dolomite | 499 | 31.4609 | 2.84361 | Calcite |
| 04.8.1.r.ii | Boyevaya Gora | Dolomite | 786 | 31.4327 | 2.83280 | Calcite |
| 04.8.1.r.iii | Boyevaya Gora | Dolomite | 810 | 31.5046 | 2.83977 | Calcite |
| KOR 24.6 | Boyevaya Gora | Calcite, magnesian | 1291 | 30.2714 | 2.95259 | - |
| KOR 24.5 | Boyevaya Gora | Calcite | 983 | 30.1801 | 2.92131 | - |
| KOR 25.1 | Boyevaya Gora | Calcite | 998 | 30.3554 | 2.94461 | - |
| KOR 25.5 | Boyevaya Gora | Calcite, magnesian | 1133 | 30.2963 | 2.95021 | - |
| KOR 25.3 | Boyevaya Gora | Calcite | 958 | 30.3564 | 2.94614 | - |
| 04.8.1.g | Boyevaya Gora | Calcite | 112 | 30.1714 | 2.96214 | - |
| KOR 27.2 | Boyevaya Gora | Quartz | 378 | 27.6516 | 3.22607 | Dolomite |
| KOR 27.3 | Boyevaya Gora | Quartz | 845 | 27.3539 | 3.29051 | Calcite |
| KOR 27.4 | Boyevaya Gora | Quartz | 386 | 27.4625 | 3.24786 | - |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| 04.8.1.f | Boyevaya Gora | Calcite | 312 | 30.1134 | 2.96772 | - |
| 04.8.1.e | Boyevaya Gora | Dolomite | 432 | 31.4767 | 2.84222 | Calcite |
| 04.8.1.c | Boyevaya Gora | Dolomite | 495 | 31.5352 | 2.83708 | - |
| 04.8.1.c.i | Boyevaya Gora | Dolomite | 582 | 31.6029 | 2.83116 | - |
| 04.8.1.c.ii | Boyevaya Gora | Dolomite | 519 | 31.5053 | 2.89700 | - |
| 04.8.1.c.iii | Boyevaya Gora | Dolomite | 418 | 31.4062 | 2.84844 | Calcite |
| KOR 31.1 | Boyevaya Gora | Calcite, magnesian | 810 | 30.3260 | 2.94740 | - |
| KOR 31.2 | Boyevaya Gora | Calcite | 526 | 30.4800 | 2.93285 | - |
| KOR 31.5 | Boyevaya Gora | Calcite | 590 | 30.2711 | 2.95261 | - |
| 04.8.1.b.ii | Boyevaya Gora | Calcite | 805 | 30.1484 | 2.96434 | - |
| 04.8.1.b.iii | Boyevaya Gora | Calcite | 423 | 30.1242 | 2.96667 | Quartz |
| KOR 32.2 | Boyevaya Gora | Calcite | 1200 | 30.1522 | 2.96398 | - |
| KOR 32.8 | Boyevaya Gora | Calcite | 621 | 30.3779 | 2.94247 | - |
| KOR 32.7 | Boyevaya Gora | Calcite | 829 | 30.1803 | 2.96129 | - |
| KOR 33.3 | Boyevaya Gora | Calcite | 1048 | 30.1523 | 2.96398 | Quartz |
| KOR 33.1 | Boyevaya Gora | Calcite, magnesian | 864 | 30.3867 | 2.41640 | - |
| KOR 33.2 | Boyevaya Gora | Calcite, magnesian | 1055 | 30.1724 | 2.96204 | Quartz |
| KOR 34.1 | Boyevaya Gora | Calcite | 1302 | 30.1462 | 2.96456 | - |
| KOR 34.2 | Boyevaya Gora | Calcite | 739 | 30.4058 | 2.93984 | - |
| KOR 34.3 | Boyevaya Gora | Calcite | 699 | 30.3990 | 2.94048 | - |
| KOR 34.4 | Boyevaya Gora | Calcite | 644 | 30.3535 | 2.94478 | - |
| KOR 34.5 | Boyevaya Gora | Calcite, magnesian | 876 | 30.3327 | 2.94676 | Quartz |
| KOR 34.6 | Boyevaya Gora | Calcite | 837 | 30.2202 | 2.95747 | - |
| KOR 34.7 | Boyevaya Gora | Calcite | 586 | 30.0209 | 2.97664 | - |
| KOR 35.1 | Boyevaya Gora | Calcite, magnesian | 821 | 30.2370 | 2.95507 | - |
| KOR 35.3 | Boyevaya Gora | Quartz | 391 | 27.6186 | 3.22986 | Calcite |
| KOR 35.4 | Boyevaya Gora | Quartz | 503 | 27.5255 | 3.24056 | Dolomite, High background |
| KOR 35.5 | Boyevaya Gora | Calcite, syn | 460 | 30.5144 | 2.92962 | - |
| KOR 36.1 | Boyevaya Gora | Calcium Carbonate | 1043 | 30.2186 | 2.95762 | Quartz |
| KOR 36.2 | Boyevaya Gora | Calcite | 1564 | 30.1481 | 2.96438 | Quartz |
| KOR 36.3 | Boyevaya Gora | Calcite | 428 | 30.5073 | 2.93081 | - |
| KOR 36.5 | Boyevaya Gora | Calcite | 939 | 30.0905 | 2.96992 | Quartz |
| KOR 36.6 | Boyevaya Gora | Quartz | 494 | 27.5600 | 3.24351 | - |
| KOR 36.4 | Boyevaya Gora | Quartz | 882 | 27.3167 | 3.26485 | - |
| KOR 37.2 | Boyevaya Gora | Quartz | 1032 | 27.3489 | 3.26109 | Calcite |
| KOR 37.3 | Boyevaya Gora | Calcite | 788 | 30.1765 | 2.96165 | Quartz |
| KOR 37.4 | Boyevaya Gora | Calcite | 679 | 30.1796 | 2.96135 | Quartz |
| KOR 37.5 | Boyevaya Gora | Calcite | 1523 | 30.2219 | 2.95730 | Allophane |
| KOR 37.1 | Boyevaya Gora | Quartz | 750 | 27.3036 | 3.26639 | - |
| KOR 39 | Boyevaya Gora | Quartz, low | 1027 | 26.6990 | 3.33897 | - |
| 04.8.2.a | Boyevaya Gora | Calcite | 389 | 30.4881 | 2.93209 | - |
| 04.8.2.e | Boyevaya Gora | Quartz | 594 | 27.5049 | 3.24940 | - |
| 04.8.2.f | Boyevaya Gora | Calcite, magnesian | 350 | 30.3946 | 2.94089 | - |
| 04.8.1.l | Boyevaya Gora | Calcite | 171 | 30.3734 | 2.94252 | - |
| SAM 1.1 | Sambullak | Calcite, magnesian | 506 | 30.5414 | 2.92709 | - |
| SAM 1.2 | Sambullak | Calcite | 767 | 30.4235 | 2.93817 | Quartz |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| SAM 1.3 | Sambullak | Calcite | 1142 | 30.3775 | 2.94252 | Quartz |
| SAM 1.4 | Sambullak | Calcite | 562 | 30.3061 | 2.94928 | - |
| SAM 1.5 | Sambullak | Calcite, magnesian | 1196 | 30.3067 | 2.94923 | Quartz |
| SAM 2.1 | Sambullak | Calcite, magnesian | 1374 | 30.2569 | 2.95396 | Quartz |
| SAM 2.2 | Sambullak | Dolomite | 1080 | 31.6675 | 2.82553 | Quartz |
| SAM 2.3 | Sambullak | Calcite, magnesian | 680 | 30.3760 | 2.94265 | - |
| SAM 2.4 | Sambullak | Calcite, magnesian | 984 | 30.4156 | 2.93891 | - |
| SAM 2.5 | Sambullak | Calcite, magnesian | 895 | 30.2868 | 2.95112 | Quartz |
| SAM 3.1 | Sambullak | Calcite, magnesian | 1385 | 30.3346 | 2.94657 | Calcite |
| SAM 3.2 | Sambullak | Calcite | 1114 | 30.1511 | 2.96409 | - |
| SAM 3.3 | Sambullak | Dolomite | 1647 | 31.7487 | 2.81849 | Calcite |
| SAM 3.4 | Sambullak | Dolomite | 608 | 31.6725 | 2.82509 | Calcite |
| SAM 3.5 | Sambullak | Dolomite | 550 | 31.9118 | 2.80446 | Quartz |
| SAM 4.2 | Sambullak | Calcite | 750 | 30.3658 | 2.94362 | Quartz |
| SAM 4.3 | Sambullak | Calcite, magnesian | 1204 | 30.2550 | 2.95415 | Calcite |
| SAM 4.4 | Sambullak | Calcite | 726 | 30.1257 | 2.96653 | Quartz |
| SAM 8.1 | Sambullak | Calcite, magnesian | 662 | 30.3793 | 2.94234 | - |
| SAM 8.2 | Sambullak | Calcite | 285 | 30.4847 | 2.93240 | - |
| SAM 8.3 | Sambullak | Calcite | 556 | 30.4441 | 2.93622 | - |
| SAM 8.4 | Sambullak | Calcite, magnesian | 494 | 30.3622 | 2.94396 | - |
| SAM 8.5 | Sambullak | Calcite | 860 | 30.1896 | 2.96040 | - |
| SAM 9.1 | Sambullak | Calcite, magnesian | 856 | 30.3107 | 2.94884 | - |
| SAM 9.2 | Sambullak | Dolomite | 833 | 31.7992 | 2.81413 | - |
| SAM 9.3 | Sambullak | Dolomite | 892 | 31.8439 | 2.81028 | - |
| SAM 9.4 | Sambullak | Dolomite | 911 | 31.6793 | 2.82450 | Quartz |
| SAM 10.1 | Sambullak | Dolomite | 1251 | 31.7161 | 2.82131 | - |
| SAM 10.2 | Sambullak | Dolomite | 443 | 31.8640 | 2.80855 | - |
| SAM 10.3 | Sambullak | Dolomite | 788 | 31.7021 | 2.82252 | Quartz |
| SAM 10.4 | Sambullak | Dolomite | 401 | 31.9494 | 2.79868 | Quartz |
| SAM 10.5 | Sambullak | Dolomite | 605 | 31.8401 | 2.81060 | Quartz |
| SAM 10.6 | Sambullak | Dolomite | 183 | 32.0066 | 2.79636 | Quartz |
| SAM 10.7 | Sambullak | Dolomite | 128 | 31.6293 | 2.82886 | - |
| SAM 10.8 | Sambullak | Dolomite | 337 | 31.7830 | 2.81552 | Quartz |
| SAM 10.9 | Sambullak | Calcite, magnesian | 239 | 30.3818 | 2.94210 | Quartz |
| SAM 12.1 | Sambullak | Calcite | 566 | 30.2255 | 2.95696 | - |
| SAM 12.2 | Sambullak | Dolomite | 645 | 31.7125 | 2.82162 | Quartz |
| SAM 13.1 | Sambullak | Calcite | 522 | 30.0544 | 2.97340 | Quartz |
| SAM 13.2 | Sambullak | Calcite, magnesian | 901 | 30.3296 | 2.94705 | Calcite |
| SAM 13.3 | Sambullak | Calcite, magnesian | 507 | 30.2293 | 2.95659 | - |
| SAM 13.4 | Sambullak | Calcite, magnesian | 654 | 30.2192 | 2.95757 | - |
| SAM 13.5 | Sambullak | Calcite, magnesian | 424 | 30.3089 | 2.94901 | - |
| SAM 14.1 | Sambullak | Calcite, magnesian | 452 | 30.3387 | 2.94619 | - |
| SAM 14.2 | Sambullak | Calcite, magnesian | 805 | 30.3818 | 2.94210 | - |
| SAM 17.1 | Sambullak | Calcite | 548 | 30.4738 | 2.93343 | Quartz |
| SAM 17.3 | Sambullak | Calcite | 688 | 30.0765 | 2.97127 | - |
| SAM 17.4 | Sambullak | Calcium Carbonate | 426 | 30.2520 | 2.95444 | - |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| SAM 19.5 | Sambullak | Dolomite | 1085 | 31.6440 | 2.82757 | – |
| SAM 20.2 | Sambullak | Dolomite | 549 | 31.7059 | 2.82220 | Quartz |
| SAM 20.3 | Sambullak | Dolomite | 856 | 31.6440 | 2.82758 | Quartz |
| SAM 20.4 | Sambullak | Dolomite | 487 | 31.7537 | 2.88050 | – |
| SAM 20.5 | Sambullak | Dolomite | 579 | 31.7278 | 2.82030 | – |
| SAM 21. 1 | Sambullak | Calcite | 330 | 30.4106 | 2.93987 | – |
| SAM 21. 2 | Sambullak | Calcite, magnesian | 541 | 30.1148 | 2.96758 | – |
| SAM 21.3 | Sambullak | Calcite, magnesian | 375 | 30.4091 | 2.93953 | – |
| SAM 21.4 | Sambullak | Calcite | 417 | 30.3825 | 2.94204 | – |
| SAM 21.4 | Sambullak | Calcium Carbonate | 819 | 30.1894 | 2.96042 | Ankerite (25) |
| SAM 22. 1 | Sambullak | Calcite, magnesian | 279 | 30.3487 | 2.94523 | – |
| SAM 23.3 | Sambullak | Calcite | 540 | 30.2155 | 2.95792 | – |
| SAM 23. 2 | Sambullak | Dolomite | 202 | 30.2578 | 2.95388 | – |
| SAM 24.1 | Sambullak | Calcite | 500 | 30.1662 | 2.96264 | – |
| SAM 24.10 | Sambullak | Calcite | 403 | 30.2323 | 2.95631 | Quartz |
| SAM 24.11 | Sambullak | Calcite, magnesian | 203 | 30.2341 | 2.95614 | – |
| SAM 24.12 | Sambullak | Calcite | 257 | 30.3315 | 2.94687 | – |
| SAM 24.13 | Sambullak | Calcite | 481 | 30.1737 | 2.96192 | – |
| SAM 24.14 | Sambullak | Calcite | 424 | 30.1941 | 2.95996 | – |
| SAM 24.3 | Sambullak | calcite | 314 | 30.3813 | 2.94215 | – |
| SAM 24.5 | Sambullak | Calcite, magnesian | 448 | 30.2659 | 2.95311 | – |
| SAM 24.6 | Sambullak | Calcite | 333 | 30.1427 | 2.96490 | – |
| SAM 24.7 | Sambullak | Calcite | 673 | 30.3330 | 2.94672 | – |
| SAM 24.8 | Sambullak | Calcite, magnesian | 703 | 30.2977 | 2.95008 | – |
| SAM 24.9 | Sambullak | Calcite | 424 | 30.1213 | 2.96660 | – |
| 04.7.23.i II | Sambullak | Dolomite | 650 | 31.3528 | 2.85316 | Quartz |
| 04.7.23.k I | Sambullak | Dolomite | 378 | 31.3802 | 2.85074 | Quartz |
| 04.7.24.a | Sambullak | Dolomite | 553 | 31.4085 | 2.84824 | Quartz |
| 04.7.24.c | Sambullak | Dolomite | 416 | 31.6863 | 2.82390 | – |
| 04.7.24.d | Sambullak | Calcite, magnesian | 468 | 30.1377 | 2.96537 | – |
| 04.7.24.i | Sambullak | Dolomite | 782 | 31.8124 | 2.81299 | – |
| 04.7.24.j | Sambullak | Dolomite | 890 | 31.6129 | 2.83029 | – |
| 04.7.24.p | Sambullak | Calcite | 668 | 30.1627 | 2.96298 | – |
| 04.7.24s | Sambullak | Calcite | 605 | 30.1208 | 2.96700 | – |
| 04.7.23.f | Sambullak | Dolomite | 647 | 31.6873 | 2.82380 | – |
| 04.7.23.h | Sambullak | Dolomite | 702 | 31.6503 | 2.82700 | Quartz |
| 04.7.23.n | Sambullak | Dolomite | 300 | 31.5383 | 2.83681 | – |
| 04.7.23.o | Sambullak | Quartz | 626 | 27.5465 | 3.23814 | Dolomite |
| 04.7.23.J 2 | Sambullak | Dolomite | 1048 | 31.5622 | 2.83472 | – |
| 04.7.23.o | Sambullak | Dolomite | 380 | 31.6562 | 2.82265 | Calcite |
| 04.7.23.o2 | Sambullak | Quartz | 896 | 27.4778 | 3.24608 | – |
| 04.7.24.e | Sambullak | Calcite | 487 | 30.3680 | 2.94341 | – |
| 04.7.23.J | Sambullak | Dolomite | 796 | 31.5708 | 2.83397 | – |
| 04.7.24.h | Sambullak | Dolomite | 429 | 31.3834 | 2.85046 | – |
| 04.7.24.k | Sambullak | Dolomite | 374 | 31.4229 | 2.84696 | – |
| 04.7.24.a I | Sambullak | Dolomite | 316 | 31.3727 | 2.85140 | – |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| 04.7.24.a II | Sambullak | Dolomite | 489 | 31.4796 | 2.84197 | Quartz |
| 04.7.24.k.II | Sambullak | Dolomite | 326 | 31.3886 | 2.84999 | - |
| 04.7.24.j | Sambullak | Dolomite | 890 | 31.6129 | 2.83029 | - |
| 04.7.24.b | Sambullak | Dolomite | 646 | 31.3641 | 2.85217 | - |
| 04.7.23.e | Sambullak | Dolomite | 632 | 31.3332 | 2.85491 | - |
| 04.7.23.g | Sambullak | Quartz | 1425 | 27.1899 | 3.27979 | Dolomite |
| 04.7.23.i.II | Sambullak | Dolomite | 588 | 31.5330 | 2.83728 | - |
| 04.7.23.a | Sambullak | Dolomite | 390 | 31.3659 | 2.85201 | - |
| 04.7.23.l | Sambullak | Calcite | 632 | 30.1510 | 2.96410 | - |
| 04.7.23.k | Sambullak | Dolomite | 1084 | 31.5045 | 2.83977 | - |
| 04.7.24.f | Sambullak | Dolomite | 301 | 31.3417 | 2.85416 | - |
| 04.7.24.l | Sambullak | Dolomite | 360 | 31.4178 | 2.84741 | - |
| 04.7.24.m | Sambullak | Dolomite | 294 | 31.2950 | 2.85830 | Quartz |
| 04.7.24.q | Sambullak | Calcite, magnesian | 764 | 30.1841 | 2.96092 | - |
| 04.7.26.a | Tuyembetka | Calcite | 461 | 30.4611 | 2.93403 | Montmorillinite |
| 04.7.26.b | Tuyembetka | Dolomite | 797 | 31.7620 | 2.81753 | - |
| 04.7.26.c | Tuyembetka | Dolomite | 497 | 31.5522 | 2.83559 | - |
| 04.7.26.c I | Tuyembetka | Dolomite | 493 | 31.6619 | 2.82602 | Quartz |
| 04.7.26.d | Tuyembetka | Dolomite | 478 | 31.5555 | 2.83530 | - |
| 04.7.26.e | Tuyembetka | Dolomite | 860 | 31.6734 | 2.82501 | - |
| 04.7.26.f | Tuyembetka | Dolomite | 528 | 31.6151 | 2.83009 | Quartz |
| 04.7.26.g | Tuyembetka | Dolomite | 361 | 31.5103 | 2.83926 | - |
| 04.7.26.h | Tuyembetka | Dolomite | 631 | 31.5564 | 2.83522 | - |
| 04.7.26.i | Tuyembetka | Dolomite | 534 | 31.6875 | 2.82379 | - |
| 04.7.26.j | Tuyembetka | Dolomite | 753 | 31.6573 | 2.82641 | - |
| 04.7.26.k | Tuyembetka | Dolomite | 664 | 31.5175 | 2.83864 | Quartz |
| 04.7.26.l | Tuyembetka | Dolomite | 647 | 31.5893 | 2.83234 | - |
| 04.7.26.m | Tuyembetka | Dolomite | 591 | 31.6520 | 2.82688 | Quartz |
| 04.7.26.n | Tuyembetka | Dolomite | 635 | 31.5491 | 2.83586 | Quartz |
| 04.7.26.o | Tuyembetka | Dolomite | 568 | 31.5989 | 2.83150 | Quartz |
| 04.7.26.p | Tuyembetka | Dolomite | 686 | 31.3230 | 2.83815 | - |
| 04.7.26.q | Tuyembetka | Dolomite | 1036 | 31.5145 | 2.83889 | - |
| 04.7.26.q III | Tuyembetka | Dolomite | 675 | 31.5029 | 2.83994 | Quartz |
| 04.7.26.r | Tuyembetka | Dolomite | 771 | 31.6828 | 2.82420 | Quartz |
| 04.7.26.s | Tuyembetka | Dolomite | 1016 | 31.6048 | 2.83094 | Quartz |
| 04.7.26.t | Tuyembetka | Dolomite | 680 | 31.6400 | 2.82792 | - |
| 04.7.26.u | Tuyembetka | Halite? | 283 | 31.1337 | 2.87274 | - |
| TUY 23.4 | Tuyembetka | Dolomite | 368 | 31.4838 | 2.84159 | - |
| TUY 23.3 | Tuyembetka | Dolomite | 778 | 31.5982 | 2.83156 | - |
| TUY 27.7 | Tuyembetka | Dolomite | 513 | 31.5084 | 2.89430 | - |
| TUY 31.3 | Tuyembetka | Dolomite | 580 | 31.5931 | 2.83202 | - |
| TUY 23.2 | Tuyembetka | Dolomite | 446 | 31.4409 | 2.84538 | - |
| TUY 27.3 | Tuyembetka | Dolomite | 782 | 31.5895 | 2.83233 | - |
| TUY 31.4 | Tuyembetka | Dolomite | 351 | 31.5872 | 2.83253 | Calcite |
| TUY 38.1 | Tuyembetka | Calcium Carbonate | 316 | 30.1841 | 2.96930 | - |
| TUY 23.4 | Tuyembetka | Dolomite | 368 | 31.4838 | 2.84159 | - |

| Sample | Section | Main Component | Max Number of counts | 100% 2°θ | 100% d-spacing (Å) | Second Component |
|---|---|---|---|---|---|---|
| KRA 2.2 | Krasnogor | Quartz | 321 | 27.5015 | 3.24329 | calcite |
| KRA 1.1 | Krasnogor | Calcite | 673 | 30.1927 | 2.82769 | Quartz |
| KRA 5.14 | Krasnogor | Dolomite | 633 | 31.6426 | 3.25639 | Quartz |
| MES 7.2 | Mescheryakovka | Calcite | 568 | 30.1447 | 2.96470 | - |
| MES 3.3 | Mescheryakovka | Calcite | 607 | 30.3145 | 2.94890 | - |
| MES 1.2 | Mescheryakovka | Calcite (mg) | 642 | 30.3456 | 2.94556 | - |
| MES 1.4 | Mescheryakovka | Calcite | 162 | 30.1230 | 2.96732 | Quartz |
| MES 8.4 | Mescheryakovka | Calcite | 419 | 30.2348 | 2.95607 | - |
| MES 8.5 | Mescheryakovka | Calcite (mg) | 691 | 30.1606 | 2.96318 | - |
| MES 8.2 | Mescheryakovka | Calcite | 634 | 30.1933 | 2.95966 | Quartz |
| MES 8.1 | Mescheryakovka | Calcium Carbonate | 1061 | 30.2335 | 2.95619 | - |
| MES 10.3 | Mescheryakovka | Calcite | 773 | 30.2110 | 2.95834 | - |
| MES 10.5 | Mescheryakovka | Calcite | 643 | 30.2414 | 2.95544 | - |
| MES 16.5 | Mescheryakovka | Calcite | 344 | 30.4718 | 2.93362 | Quartz |
| MES 16.6 | Mescheryakovka | Calcite | 200 | 30.2641 | 2.95703 | - |
| MES 16.1 | Mescheryakovka | Calcite (mg) | 529 | 30.2972 | 2.95013 | - |

# A2.5

Statistical treatment paleosols from Boyevaya Gora and Sambullak to ascertain whether the excursions identified represent true variation from the background values. The Mann-Whitney was used as this is a nonparametric test which does not assume a normal distribution within the data. The test assumes uses as a null hypothesis that the two datasets, in this case two paleosols, are from the same population (Conover 1971). Below a $p \leq 0.1$ it is statistically likely that the null hypothesis is invalid (to a 90% confidence interval) and the two datasets are from separate populations (Dr R. Moyced *pers. comm.*; Conover 1971).

## Boyevaya Gora

All data - *Results*

| Test | $\delta^{13}C$ (p values) | $\delta^{18}O$ (p values) |
|---|---|---|
| P1 v 'Background' | 0.0022 | 0.0011 |
| P2 v 'Background' | 0.0007 | 0.0000 |
| P3 v 'Background' | 0.0000 | 0.0000 |
| Triassic v 'Background Permian' | 0.6073 | 0.0000 |

*Input values*

| | $\delta^{13}C$ | $\delta^{18}O$ |
|---|---|---|
| P1 | | |
| *Median (‰)* | -5.85 | -7.79 |
| *number of values* | 4 | 4 |
| P2 | | |
| *Median (‰)* | -10.04 | -8.03 |
| *number of values* | 4 | 4 |
| P3 | | |
| *Median (‰)* | -6.59 | -7.67 |
| *number of values* | 24 | 24 |
| Background | | |
| *Median (‰)* | -1.29 | -0.40 |
| *number of values* | 119 | 119 |
| Triassic | | |
| *Median (‰)* | -1.23 | -0.40 |
| *number of values* | 42 | 42 |

Pedogenic calcite only- *Results*

| Test | $\delta^{13}C$ (p values) | $\delta^{18}O$ (p values) |
|---|---|---|
| P1 v 'Background' | 0.0803 | 0.1064 |
| P2 v 'Background' | 0.0693 | 0.2528 |
| P3 v 'Background' | 0.0000 | 0.0005 |
| Triassic v 'Background Permian' | 0.4757 | 0.0003 |

*Input values*

| | $\delta^{13}C$ | $\delta^{18}O$ |
|---|---|---|
| P1 | | |
| *Median (‰)* | -4.62 | -6.79 |
| *number of values* | 3 | 3 |
| P2 | | |
| *Median (‰)* | 0.36 | -8.85 |
| *number of values* | 3 | 3 |
| P3 | | |
| *Median (‰)* | -10.43 | -11.00 |
| *number of values* | 14 | 14 |
| Background Permian | | |
| *Median (‰)* | -2.47 | -5.15 |
| *number of values* | 13 | 13 |
| Triassic | | |
| *Median (‰)* | -2.76 | -9.88 |
| *number of values* | 10 | 10 |

## Sambullak

All data - *Results*

| Test | $\delta^{13}C$ (p values) | $\delta^{18}O$ (p values) |
|---|---|---|
| P3 v 'Background' | 0.0000 | 0.0000 |
| P4 v 'Background' | 0.0004 | 0.0000 |

*Input values*

| | $\delta^{13}C$ | $\delta^{18}O$ |
|---|---|---|
| P3 | | |
| *Median (‰)* | -5.6 | -8.2 |
| *number of values* | 31 | 31 |
| P4 | | |
| *Median (‰)* | -5.0 | -9.4 |
| *number of values* | 34 | 34 |
| Background | | |
| *Median (‰)* | -3.7 | -4.3 |
| *number of values* | 49 | 49 |

Pedogenic calcite only- *Results*

| Test | $\delta^{13}C$ (p values) | $\delta^{18}O$ (p values) |
|---|---|---|
| P3 v 'Background' | 1.0000 | 0.5160 |
| P4 v 'Background' | 0.2703 | 0.0200 |

*Input values*

| | $\delta^{13}C$ | $\delta^{18}O$ |
|---|---|---|
| P3 | | |
| *Median (‰)* | -5.509 | -8.08 |
| *number of values* | 7 | 7 |
| P4 | | |
| *Median (‰)* | -6.054 | -12.944 |
| *number of values* | 4 | 4 |
| Background permian | | |
| *Median (‰)* | -5.57 | -7.446 |
| *number of values* | 5 | 5 |

# A2.6

Calibrated values for NBS 19 for all stable isotope runs undertaken as part of this project with the deviation from the published values for that standard (National Bureau of Standards 19 published values; $\delta^{13}C = 1.95‰$ $\delta^{18}O = -2.20‰$).

| Date | $\delta^{13}C$ (‰,VPDB) | *difference from given values* | $\delta^{18}O$ (‰,VPDB) | *difference from given values* | Field Area |
|---|---|---|---|---|---|
| 15/07/2008 | 1.95 | 0.00 | -2.83 | -0.63 | Russia |
| 15/07/2008 | 1.95 | 0.00 | -2.83 | -0.63 | Russia |
| 15/07/2008 | 1.95 | 0.00 | -2.83 | -0.63 | Russia |
| 14/07/2008 | 2.12 | 0.17 | -2.46 | -0.26 | Russia |
| 14/07/2008 | 2.04 | 0.09 | -2.42 | -0.22 | Russia |
| 14/07/2008 | 2.00 | 0.05 | -2.21 | -0.01 | Russia |
| 14/07/2008 | 2.01 | 0.06 | -2.01 | 0.19 | Russia |
| 14/07/2008 | 1.51 | -0.44 | -1.15 | 1.05 | Russia |
| 09/07/2008 | 2.04 | 0.09 | -2.64 | -0.44 | Russia |
| 09/07/2008 | 2.04 | 0.09 | -2.64 | -0.44 | Russia |
| 09/07/2008 | 2.13 | 0.18 | -2.09 | 0.11 | Russia |
| 09/07/2008 | 2.13 | 0.18 | -2.09 | 0.11 | Russia |
| 09/07/2008 | 2.07 | 0.12 | -2.03 | 0.17 | Russia |
| 09/07/2008 | 2.07 | 0.12 | -2.03 | 0.17 | Russia |
| 09/07/2008 | 2.09 | 0.14 | -1.97 | 0.23 | Russia |
| 09/07/2008 | 2.09 | 0.14 | -1.97 | 0.23 | Russia |
| 18/06/2008 | 2.16 | 0.21 | -2.26 | -0.06 | Russia |
| 18/06/2008 | 2.28 | 0.33 | -2.21 | -0.01 | Russia |
| 18/06/2008 | 2.29 | 0.34 | -1.95 | 0.25 | Russia |
| 18/06/2008 | 2.05 | 0.10 | -1.72 | 0.48 | Russia |
| 18/06/2008 | 2.33 | 0.38 | -1.64 | 0.56 | Russia |
| 02/06/2008 | 1.99 | 0.04 | -2.59 | -0.39 | Russia |
| 02/06/2008 | 1.98 | 0.03 | -2.11 | 0.09 | Russia |
| 02/06/2008 | 2.19 | 0.24 | -1.96 | 0.24 | Russia |
| 02/06/2008 | 1.93 | -0.02 | -1.90 | 0.30 | Russia |
| 02/06/2008 | 2.01 | 0.06 | -1.86 | 0.34 | Russia |
| 21/05/2008 | 2.24 | 0.29 | -2.26 | -0.06 | Russia |
| 21/05/2008 | 2.24 | 0.29 | -2.26 | -0.06 | Russia |
| 21/05/2008 | 2.24 | 0.29 | -2.26 | -0.06 | Russia |
| 21/05/2008 | 2.24 | 0.29 | -2.26 | -0.06 | Russia |
| 21/05/2008 | 2.03 | 0.08 | -1.97 | 0.23 | Russia |
| 21/05/2008 | 2.03 | 0.08 | -1.97 | 0.23 | Russia |
| 21/05/2008 | 2.03 | 0.08 | -1.97 | 0.23 | Russia |
| 21/05/2008 | 2.03 | 0.08 | -1.97 | 0.23 | Russia |
| 21/05/2008 | 2.09 | 0.14 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.09 | 0.14 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.09 | 0.14 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.09 | 0.14 | -1.80 | 0.40 | Russia |

| Date | $\delta^{13}C$ (‰,VPDB) | *difference from given values* | $\delta^{18}O$ (‰,VPDB) | *difference from given values* | Field Area |
|---|---|---|---|---|---|
| 21/05/2008 | 2.20 | 0.25 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.20 | 0.25 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.20 | 0.25 | -1.80 | 0.40 | Russia |
| 21/05/2008 | 2.20 | 0.25 | -1.80 | 0.40 | Russia |
| 28/11/2007 | 2.05 | 0.10 | -2.72 | -0.52 | Russia |
| 28/11/2007 | 1.90 | -0.05 | -2.44 | -0.24 | Russia |
| 28/11/2007 | 1.92 | -0.03 | -2.38 | -0.18 | Russia |
| 28/11/2007 | 2.07 | 0.12 | -2.23 | -0.03 | Russia |
| 28/11/2007 | 2.02 | 0.07 | -2.18 | 0.02 | Russia |
| 18/11/2007 | 2.02 | 0.07 | -2.56 | -0.36 | Russia |
| 17/11/2007 | 2.17 | 0.22 | -2.16 | 0.04 | Russia |
| 16/11/2007 | 2.06 | 0.11 | -2.16 | 0.04 | Russia |
| 15/11/2007 | 2.05 | 0.10 | -2.37 | -0.17 | Russia |
| 14/11/2007 | 2.20 | 0.25 | -3.05 | -0.85 | Russia |
| 14/11/2007 | 2.02 | 0.07 | -2.35 | -0.15 | Russia |
| 14/11/2007 | 2.04 | 0.09 | -2.19 | 0.01 | Russia |
| 14/11/2007 | 2.20 | 0.25 | -2.03 | 0.17 | Russia |
| 11/11/2007 | 1.99 | 0.04 | -2.34 | -0.14 | Russia |
| 11/11/2007 | 1.99 | 0.04 | -2.34 | -0.14 | Russia |
| 11/11/2007 | 2.15 | 0.20 | -2.28 | -0.08 | Russia |
| 11/11/2007 | 2.15 | 0.20 | -2.28 | -0.08 | Russia |
| 11/11/2007 | 2.02 | 0.07 | -2.21 | -0.01 | Russia |
| 11/11/2007 | 2.02 | 0.07 | -2.21 | -0.01 | Russia |
| 10/11/2007 | 1.73 | -0.22 | -2.57 | -0.37 | Russia |
| 10/11/2007 | 1.73 | -0.22 | -2.57 | -0.37 | Russia |
| 10/11/2007 | 1.95 | 0.00 | -2.53 | -0.33 | Russia |
| 10/11/2007 | 1.95 | 0.00 | -2.53 | -0.33 | Russia |
| 10/11/2007 | 2.03 | 0.08 | -2.34 | -0.14 | Russia |
| 10/11/2007 | 2.03 | 0.08 | -2.34 | -0.14 | Russia |
| 10/11/2007 | 2.02 | 0.07 | -2.26 | -0.06 | Russia |
| 10/11/2007 | 2.02 | 0.07 | -2.26 | -0.06 | Russia |
| 19/09/2007 | 2.41 | 0.46 | -2.46 | -0.26 | Russia |
| 19/09/2007 | 2.41 | 0.46 | -2.46 | -0.26 | Russia |
| 19/09/2007 | 2.41 | 0.46 | -2.46 | -0.26 | Russia |
| 19/09/2007 | 2.41 | 0.46 | -2.46 | -0.26 | Russia |
| 10/09/2007 | 2.08 | 0.13 | -3.01 | -0.81 | Russia |
| 10/09/2007 | 2.14 | 0.19 | -2.88 | -0.68 | Russia |
| 10/09/2007 | 2.29 | 0.34 | -2.24 | -0.04 | Russia |
| 10/09/2007 | 2.26 | 0.31 | -2.20 | 0.00 | Russia |
| 10/09/2007 | 2.28 | 0.33 | -2.11 | 0.09 | Russia |
| 10/09/2007 | 1.78 | -0.17 | -2.08 | 0.12 | Russia |
| 05/09/2007 | 2.11 | 0.16 | -3.21 | -1.01 | Russia |
| 05/09/2007 | 2.00 | 0.05 | -2.58 | -0.38 | Russia |
| 05/09/2007 | 2.12 | 0.17 | -2.54 | -0.34 | Russia |
| 05/09/2007 | 2.07 | 0.12 | -2.17 | 0.03 | Russia |
| 05/09/2007 | 2.15 | 0.20 | -1.95 | 0.25 | Russia |

| Date | $\delta^{13}C$ (‰,VPDB) | *difference from given values* | $\delta^{18}O$ (‰,VPDB) | *difference from given values* | Field Area |
|---|---|---|---|---|---|
| 25/08/2007 | 1.71 | -0.24 | -2.84 | -0.64 | Russia |
| 25/08/2007 | 1.71 | -0.24 | -2.84 | -0.64 | Russia |
| 25/08/2007 | 1.85 | -0.10 | -2.79 | -0.59 | Russia |
| 25/08/2007 | 1.85 | -0.10 | -2.79 | -0.59 | Russia |
| 25/08/2007 | 1.99 | 0.04 | -2.45 | -0.25 | Russia |
| 25/08/2007 | 1.99 | 0.04 | -2.45 | -0.25 | Russia |
| 12/11/2006 | 1.93 | -0.02 | -2.63 | -0.43 | Russia |
| 12/11/2006 | 1.96 | 0.01 | -2.35 | -0.15 | Russia |
| 12/11/2006 | 1.99 | 0.04 | -2.04 | 0.16 | Russia |
| 12/11/2006 | 1.99 | 0.04 | -2.00 | 0.20 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -2.50 | -0.30 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -2.50 | -0.30 | Russia |
| 10/05/2006 | 1.96 | 0.01 | -2.34 | -0.14 | Russia |
| 10/05/2006 | 1.96 | 0.01 | -2.34 | -0.14 | Russia |
| 10/05/2006 | 2.12 | 0.17 | -2.34 | -0.14 | Russia |
| 10/05/2006 | 2.12 | 0.17 | -2.34 | -0.14 | Russia |
| 10/05/2006 | 2.28 | 0.33 | -2.27 | -0.07 | Russia |
| 10/05/2006 | 2.28 | 0.33 | -2.27 | -0.07 | Russia |
| 10/05/2006 | 2.02 | 0.07 | -2.27 | -0.07 | Russia |
| 10/05/2006 | 2.02 | 0.07 | -2.27 | -0.07 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -2.18 | 0.02 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -2.18 | 0.02 | Russia |
| 10/05/2006 | 1.96 | 0.01 | -2.07 | 0.13 | Russia |
| 10/05/2006 | 1.96 | 0.01 | -2.07 | 0.13 | Russia |
| 10/05/2006 | 2.02 | 0.07 | -2.02 | 0.18 | Russia |
| 10/05/2006 | 2.02 | 0.07 | -2.02 | 0.18 | Russia |
| 10/05/2006 | 2.01 | 0.06 | -2.00 | 0.20 | Russia |
| 10/05/2006 | 2.01 | 0.06 | -2.00 | 0.20 | Russia |
| 10/05/2006 | 1.95 | 0.00 | -1.98 | 0.22 | Russia |
| 10/05/2006 | 1.95 | 0.00 | -1.98 | 0.22 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -1.95 | 0.25 | Russia |
| 10/05/2006 | 2.11 | 0.16 | -1.95 | 0.25 | Russia |
| 10/05/2006 | 1.99 | 0.04 | -1.94 | 0.26 | Russia |
| 10/05/2006 | 1.99 | 0.04 | -1.94 | 0.26 | Russia |
| 10/05/2006 | 2.05 | 0.10 | -1.84 | 0.36 | Russia |
| 10/05/2006 | 2.05 | 0.10 | -1.84 | 0.36 | Russia |
| 08/05/2006 | 2.11 | 0.16 | -2.40 | -0.20 | Russia |
| 08/05/2006 | 2.19 | 0.24 | -2.35 | -0.15 | Russia |
| 08/05/2006 | 2.02 | 0.07 | -2.34 | -0.14 | Russia |
| 08/05/2006 | 2.03 | 0.08 | -2.25 | -0.05 | Russia |
| 08/05/2006 | 2.05 | 0.10 | -2.21 | -0.01 | Russia |
| 08/05/2006 | 2.00 | 0.05 | -2.18 | 0.02 | Russia |
| 08/05/2006 | 2.05 | 0.10 | -2.17 | 0.03 | Russia |
| 08/05/2006 | 2.06 | 0.11 | -2.11 | 0.09 | Russia |
| 08/05/2006 | 2.08 | 0.13 | -2.10 | 0.10 | Russia |
| 08/05/2006 | 2.02 | 0.07 | -2.04 | 0.16 | Russia |

| Date | $\delta^{13}C$ (‰,VPDB) | *difference from given values* | $\delta^{18}O$ (‰,VPDB) | *difference from given values* | Field Area |
|---|---|---|---|---|---|
| 08/05/2006 | 2.22 | 0.27 | -2.04 | 0.16 | Russia |
| 08/05/2006 | 2.15 | 0.20 | -2.03 | 0.17 | Russia |
| 08/05/2006 | 1.96 | 0.01 | -1.87 | 0.33 | Russia |
| 05/04/2006 | 1.05 | -0.90 | -2.91 | -0.71 | Russia |
| 05/04/2006 | 1.05 | -0.90 | -2.91 | -0.71 | Russia |
| 05/04/2006 | 1.06 | -0.89 | -2.73 | -0.53 | Russia |
| 05/04/2006 | 1.06 | -0.89 | -2.73 | -0.53 | Russia |
| 05/04/2006 | 1.23 | -0.72 | -2.56 | -0.36 | Russia |
| 05/04/2006 | 1.23 | -0.72 | -2.56 | -0.36 | Russia |
| 29/03/2006 | 0.81 | -1.14 | -3.27 | -1.07 | Russia |
| 29/03/2006 | 0.81 | -1.14 | -3.27 | -1.07 | Russia |
| 29/03/2006 | 0.81 | -1.14 | -3.27 | -1.07 | Russia |
| 29/03/2006 | 1.08 | -0.87 | -3.26 | -1.06 | Russia |
| 29/03/2006 | 1.08 | -0.87 | -3.26 | -1.06 | Russia |
| 29/03/2006 | 1.08 | -0.87 | -3.26 | -1.06 | Russia |
| 29/03/2006 | 1.19 | -0.76 | -3.16 | -0.96 | Russia |
| 29/03/2006 | 1.19 | -0.76 | -3.16 | -0.96 | Russia |
| 29/03/2006 | 1.19 | -0.76 | -3.16 | -0.96 | Russia |
| 29/03/2006 | 1.05 | -0.90 | -3.11 | -0.91 | Russia |
| 29/03/2006 | 1.05 | -0.90 | -3.11 | -0.91 | Russia |
| 29/03/2006 | 1.05 | -0.90 | -3.11 | -0.91 | Russia |
| 29/03/2006 | 1.12 | -0.83 | -3.04 | -0.84 | Russia |
| 29/03/2006 | 1.12 | -0.83 | -3.04 | -0.84 | Russia |
| 29/03/2006 | 1.12 | -0.83 | -3.04 | -0.84 | Russia |
| 29/03/2006 | 0.95 | -1.00 | -2.70 | -0.50 | Russia |
| 29/03/2006 | 0.95 | -1.00 | -2.70 | -0.50 | Russia |
| 29/03/2006 | 0.95 | -1.00 | -2.70 | -0.50 | Russia |
| 29/03/2006 | 1.11 | -0.84 | -2.51 | -0.31 | Russia |
| 29/03/2006 | 1.11 | -0.84 | -2.51 | -0.31 | Russia |
| 29/03/2006 | 1.11 | -0.84 | -2.51 | -0.31 | Russia |
| 29/03/2006 | 1.27 | -0.68 | -2.23 | -0.03 | Russia |
| 29/03/2006 | 1.27 | -0.68 | -2.23 | -0.03 | Russia |
| 29/03/2006 | 1.27 | -0.68 | -2.23 | -0.03 | Russia |
| 24/03/2006 | 1.44 | -0.51 | -3.39 | -1.19 | Russia |
| 24/03/2006 | 1.52 | -0.43 | -3.13 | -0.93 | Russia |
| 24/03/2006 | 1.17 | -0.78 | -3.04 | -0.84 | Russia |
| 24/03/2006 | 1.22 | -0.73 | -2.89 | -0.69 | Russia |
| 24/03/2006 | 1.22 | -0.73 | -2.81 | -0.61 | Russia |
| 24/03/2006 | 1.15 | -0.80 | -2.74 | -0.54 | Russia |
| 21/03/2006 | 1.12 | -0.83 | -3.36 | -1.16 | Russia |
| 21/03/2006 | 1.12 | -0.83 | -3.36 | -1.16 | Russia |
| 21/03/2006 | 0.99 | -0.96 | -3.29 | -1.09 | Russia |
| 21/03/2006 | 0.99 | -0.96 | -3.29 | -1.09 | Russia |
| 21/03/2006 | 0.91 | -1.04 | -3.20 | -1.00 | Russia |
| 21/03/2006 | 0.91 | -1.04 | -3.20 | -1.00 | Russia |
| 21/03/2006 | 1.05 | -0.90 | -3.08 | -0.88 | Russia |

| Date | $\delta^{13}C$ (‰,VPDB) | *difference from given values* | $\delta^{18}O$ (‰,VPDB) | *difference from given values* | Field Area |
|---|---|---|---|---|---|
| 21/03/2006 | 1.05 | -0.90 | -3.08 | -0.88 | Russia |
| 21/03/2006 | 1.19 | -0.76 | -3.07 | -0.87 | Russia |
| 21/03/2006 | 1.19 | -0.76 | -3.07 | -0.87 | Russia |
| 21/03/2006 | 1.19 | -0.76 | -2.99 | -0.79 | Russia |
| 21/03/2006 | 1.19 | -0.76 | -2.99 | -0.79 | Russia |
| 21/03/2006 | 1.20 | -0.75 | -2.94 | -0.74 | Russia |
| 21/03/2006 | 1.20 | -0.75 | -2.94 | -0.74 | Russia |
| 21/03/2006 | 1.18 | -0.77 | -2.89 | -0.69 | Russia |
| 21/03/2006 | 1.18 | -0.77 | -2.89 | -0.69 | Russia |
| 21/03/2006 | 0.95 | -1.00 | -2.89 | -0.69 | Russia |
| 21/03/2006 | 0.95 | -1.00 | -2.89 | -0.69 | Russia |
| 21/03/2006 | 0.95 | -1.00 | -2.88 | -0.68 | Russia |
| 21/03/2006 | 0.95 | -1.00 | -2.88 | -0.68 | Russia |
| 12/07/2007 | 1.66 | -0.29 | -3.44 | -1.24 | Italy |
| 12/07/2007 | 2.04 | 0.09 | -3.82 | -1.62 | Italy |
| 12/07/2007 | 2.03 | 0.08 | -2.50 | -0.30 | Italy |
| 02/03/2007 | 2.20 | 0.25 | -2.98 | -0.78 | Italy |
| 02/03/2007 | 2.17 | 0.22 | -2.56 | -0.36 | Italy |
| 02/03/2007 | 2.02 | 0.07 | -3.48 | -1.28 | Italy |
| 02/03/2007 | 2.16 | 0.21 | -2.23 | -0.03 | Italy |
| 02/03/2007 | 2.22 | 0.27 | -2.47 | -0.27 | Italy |
| 21/01/2007 | 2.01 | 0.06 | -2.98 | -0.78 | Italy |
| 21/01/2007 | 1.98 | 0.03 | -3.65 | -1.45 | Italy |
| 21/01/2007 | 1.99 | 0.04 | -3.36 | -1.16 | Italy |
| 21/01/2007 | 1.99 | 0.04 | -3.76 | -1.56 | Italy |
| 18/01/2007 | 1.86 | -0.09 | -2.56 | -0.36 | Italy |
| 18/01/2007 | 2.08 | 0.13 | -3.88 | -1.68 | Italy |
| 18/01/2007 | 2.17 | 0.22 | -3.62 | -1.42 | Italy |
| 18/01/2007 | 2.05 | 0.10 | -2.33 | -0.13 | Italy |

# Appendix 3

## Palaeoprecipitation, Palaeotemperature, and $pCO_2$calculations

## (Chapter 5 and 7)

# A3.1

Palaeoprecipitation estimates from Chapter 5 from Boyevaya Gora, Sambullak, Tuyembetka, and Mescheryakovka.

| Paleosol Horizon | Location | Strat Height (m) | Height from palaeo surface (cm) | De-compressed height (cm) | MAP Calculation | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Equation 5.2 (mm) | Equation 5.3 (mm) | Equation 5.3a (mm) | Equation 5.4 (mm) |
| KOR 33 | Boyevaya Gora | 199 | 3 | 3.3 | 159 | 418 | 1043 | 177 |
| KOR 32 | Boyevaya Gora | 198 | 8 | 8.7 | 195 | 395 | 1035 | 181 |
| KOR 37 | Boyevaya Gora | 196 | 9 | 9.8 | 202 | 390 | 1034 | 183 |
| KOR 01 | Boyevaya Gora | 171 | 49 | 53.5 | 521 | 204 | 965 | 284 |
| KOR 06 | Boyevaya Gora | 169 | 34 | 37.1 | 395 | 274 | 992 | 233 |
| KOR 10 | Boyevaya Gora | 163 | 27 | 29.5 | 339 | 307 | 1004 | 215 |
| KOR 11 | Boyevaya Gora | 160 | 18 | 19.6 | 269 | 349 | 1019 | 196 |
| KOR 12 | Boyevaya Gora | 158 | 36 | 39.3 | 411 | 265 | 989 | 239 |
| KOR 02 | Boyevaya Gora | 157 | 25 | 27.3 | 323 | 316 | 1008 | 210 |
| KOR 14 | Boyevaya Gora | 155 | 26 | 28.4 | 331 | 311 | 1006 | 212 |
| KOR 14 | Boyevaya Gora | 154 | 18 | 19.6 | 269 | 349 | 1019 | 196 |
| KOR 23 | Boyevaya Gora | 145 | 28 | 30.6 | 347 | 302 | 1003 | 217 |
| KOR 22 | Boyevaya Gora | 142 | 64.5 | 70.4 | 658 | 132 | 936 | 354 |
| KOR 21 | Boyevaya Gora | 142 | 23 | 25.1 | 308 | 325 | 1011 | 206 |
| KOR 15 | Boyevaya Gora | 140 | 17 | 18.6 | 262 | 353 | 1021 | 194 |
| KOR 16 | Boyevaya Gora | 136 | 13 | 14.2 | 231 | 372 | 1027 | 188 |
| KOR 17 | Boyevaya Gora | 136 | 24 | 26.2 | 315 | 321 | 1010 | 208 |
| KOR 16 | Boyevaya Gora | 136 | 14 | 15.3 | 239 | 367 | 1026 | 189 |
| KOR 25 | Boyevaya Gora | 105 | 21 | 22.9 | 292 | 335 | 1014 | 201 |
| KOR 26 | Boyevaya Gora | 99 | 41 | 44.8 | 453 | 242 | 980 | 255 |
| KOR 27 | Boyevaya Gora | 99 | 26 | 28.4 | 331 | 311 | 1006 | 212 |
| KOR 30 | Boyevaya Gora | 79 | 18 | 19.6 | 269 | 349 | 1019 | 196 |
| SAM 01 | Sambullak | 131.13 | 31 | 33.84 | 371 | 288 | 998 | 225 |
| SAM 10 | Sambullak | 123.28 | 42 | 45.85 | 461 | 237 | 978 | 259 |
| SAM 03 | Sambullak | 122.62 | 49 | 53.49 | 521 | 204 | 965 | 284 |
| SAM 10 | Sambullak | 122.6 | 24 | 26.20 | 315 | 321 | 1010 | 208 |
| SAM 12 | Sambullak | 114.38 | 14 | 15.28 | 239 | 367 | 1026 | 189 |
| SAM 11 | Sambullak | 113.45 | 28 | 30.56 | 347 | 302 | 1003 | 217 |
| SAM 09 | Sambullak | 102.48 | 80 | 87.33 | 803 | 60 | 904 | 439 |
| SAM 08 | Sambullak | 98.61 | 18 | 19.65 | 269 | 349 | 1019 | 196 |
| SAM 05 | Sambullak | 91.48 | 37 | 40.39 | 420 | 260 | 987 | 242 |
| SAM 20 | Sambullak | 87.76 | 27 | 29.47 | 339 | 307 | 1004 | 215 |
| SAM 17 | Sambullak | 80.435 | 39 | 42.57 | 436 | 251 | 984 | 249 |

| Paleosol Horizon | Location | Strat Height (m) | Height from palaeo surface (cm) | De-compressed height (cm) | MAP Calculation | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Equation 5.2 (mm) | Equation 5.3 (mm) | Equation 5.3a (mm) | Equation 5.4 (mm) |
| SAM 19 | Sambullak | 80.14 | 33 | 36.02 | 387 | 279 | 994 | 230 |
| SAM 18 | Sambullak | 79.116 | 17 | 18.56 | 262 | 353 | 1021 | 194 |
| SAM 15 | Sambullak | 73.965 | 27 | 29.47 | 339 | 307 | 1004 | 215 |
| SAM 16 | Sambullak | 69.2225 | 37 | 40.39 | 420 | 260 | 987 | 242 |
| SAM 14 | Sambullak | 68.205 | 15 | 16.37 | 246 | 363 | 1024 | 191 |
| SAM 13 | Sambullak | 66.8 | 14 | 15.28 | 239 | 367 | 1026 | 189 |
| SAM 21 | Sambullak | 62.44 | 19 | 20.74 | 277 | 344 | 1018 | 198 |
| SAM 22 | Sambullak | 60.97 | 27 | 29.47 | 339 | 307 | 1004 | 215 |
| SAM 23 | Sambullak | 60.15 | 47 | 51.31 | 503 | 214 | 969 | 277 |
| SAM 24 | Sambullak | 57.44 | 51 | 55.67 | 538 | 195 | 962 | 292 |
| SAM 24 | Sambullak | 57.02 | 31 | 33.84 | 371 | 288 | 998 | 225 |
| SAM 24 | Sambullak | 56.29 | 54 | 58.95 | 564 | 181 | 956 | 305 |
| SAM 24 | Sambullak | 56.28 | 88 | 96.06 | 880 | 22 | 887 | 490 |
| MES 1 | Mescheryakovka | 10 | 24 | 26.36 | 317 | 320 | 1009 | 208 |
| MES 8 | Mescheryakovka | 140 | 44 | 48.33 | 480 | 226 | 974 | 267 |
| MES 4 | Mescheryakovka | 8 | 43 | 47.23 | 472 | 231 | 976 | 263 |
| MES 6 | Mescheryakovka | 8 | 38 | 41.74 | 430 | 255 | 985 | 246 |
| MES 16 | Mescheryakovka | 183 | 100 | 109.83 | 1007 | | 859 | 579 |
| TUY 56 | Tuyembetka | 107 | 3 | 3 | 159 | 418 | 1043 | 177 |
| TUY 58 | Tuyembetka | 104 | 54 | 59 | 567 | 180 | 955 | 306 |
| TUY 2 | Tuyembetka | 95 | 62 | 68 | 639 | 142 | 940 | 343 |
| TUY 46 | Tuyembetka | 95 | 10 | 11 | 210 | 386 | 1032 | 184 |
| TUY 4 | Tuyembetka | 93 | 26 | 29 | 332 | 311 | 1006 | 213 |
| TUY 5 | Tuyembetka | 93 | 18 | 20 | 270 | 348 | 1019 | 196 |
| TUY 6 | Tuyembetka | 91 | 62 | 68 | 639 | 142 | 940 | 343 |
| TUY 7 | Tuyembetka | 90 | 26 | 29 | 332 | 311 | 1006 | 213 |
| TUY 8 | Tuyembetka | 89 | 21 | 23 | 293 | 334 | 1014 | 202 |
| TUY 13 | Tuyembetka | 74 | 33 | 36 | 389 | 278 | 994 | 231 |
| TUY 15 | Tuyembetka | 71 | 18 | 20 | 270 | 348 | 1019 | 196 |
| TUY 16 | Tuyembetka | 66 | 32 | 35 | 380 | 283 | 996 | 228 |
| TUY 18 | Tuyembetka | 61 | 40 | 44 | 446 | 245 | 981 | 253 |
| TUY 23 | Tuyembetka | 56 | 58 | 64 | 603 | 161 | 948 | 324 |
| TUY 24 | Tuyembetka | 55 | 48 | 53 | 515 | 208 | 967 | 282 |
| TUY 25 | Tuyembetka | 49 | 100 | 110 | 1007 | -37 | 859 | 579 |
| TUY 28 | Tuyembetka | 43 | 34 | 37 | 397 | 273 | 992 | 234 |
| TUY 31 | Tuyembetka | 34 | 20 | 22 | 285 | 339 | 1016 | 200 |
| TUY 39 | Tuyembetka | 21 | 25 | 27 | 324 | 315 | 1008 | 210 |
| TUY 40 | Tuyembetka | 18 | 22 | 24 | 301 | 329 | 1013 | 204 |
| TUY 41 | Tuyembetka | 16 | 23 | 25 | 309 | 325 | 1011 | 206 |

| Paleosol Horizon | Location | Strat. Height (m) | Height from palaeo surface (cm) | De-compressed height (cm) | MAP Calculation | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Equation 5.2 (mm) | Equation 5.3 (mm) | Equation 5.3a (mm) | Equation 5.4 (mm) |
| TUY 42 | Tuyembetka | 16 | 34 | 37 | 397 | 273 | 992 | 234 |
| TUY 45 | Tuyembetka | 0 | 28 | 31 | 348 | 301 | 1002 | 218 |

# A3.2

Mean annual range precipitation estimates from Chapter 5 from Boyevaya Gora, Sambullak, Tuyembetka, and Mescheryakovka.

| Paleosol Horizon | Location | Strat. Height (m) | Thickness of nodule horizon (cm) | Decompressed Thickness (cm) | Equation 5.5 (mm) |
|---|---|---|---|---|---|
| KOR 36 | Boyevaya Gora | 211 | 37 | 40.39 | 45.62 |
| KOR 33 | Boyevaya Gora | 199 | 29 | 31.66 | 38.72 |
| KOR 37 | Boyevaya Gora | 196 | 71 | 77.50 | 74.94 |
| KOR 34 | Boyevaya Gora | 199 | 22 | 24.02 | 32.68 |
| KOR 32 | Boyevaya Gora | 198 | 43 | 46.94 | 50.79 |
| KOR 1 | Boyevaya Gora | 173 | 10 | 10.92 | 22.33 |
| KOR 1a | Boyevaya Gora | 171 | 45 | 49.12 | 52.52 |
| KOR 2 | Boyevaya Gora | 170 | 58 | 63.31 | 63.73 |
| KOR 9 | Boyevaya Gora | 165 | 20 | 21.83 | 30.96 |
| KOR 6 | Boyevaya Gora | 163 | 44 | 48.03 | 51.65 |
| KOR 10 | Boyevaya Gora | 159 | 69 | 75.32 | 73.21 |
| KOR 11 | Boyevaya Gora | 158 | 40 | 43.66 | 48.20 |
| KOR 12 | Boyevaya Gora | 157 | 6 | 6.55 | 18.88 |
| KOR 14 | Boyevaya Gora | 155 | 24 | 26.20 | 34.41 |
| KOR 14a | Boyevaya Gora | 154 | 40 | 43.66 | 48.20 |
| KOR 14b | Boyevaya Gora | 154 | 9 | 9.82 | 21.47 |
| KOR 22 | Boyevaya Gora | 144 | 76 | 82.96 | 79.25 |
| KOR 21a | Boyevaya Gora | 142 | 19 | 20.74 | 30.09 |
| KOR 21 | Boyevaya Gora | 142 | 38 | 41.48 | 46.48 |
| KOR 15 | Boyevaya Gora | 140 | 38 | 41.48 | 46.48 |
| KOR 16 | Boyevaya Gora | 136 | 6 | 6.55 | 18.88 |

| Paleosol Horizon | Location | Strat. Height (m) | Thickness of nodule horizon (cm) | Decompressed Thickness (cm) | Equation 5.5 (mm) |
|---|---|---|---|---|---|
| KOR 16a | Boyevaya Gora | 136 | 13 | 14.19 | 24.92 |
| KOR 18 | Boyevaya Gora | 128 | 7 | 7.64 | 19.75 |
| KOR 25 | Boyevaya Gora | 105 | 8 | 8.73 | 20.61 |
| KOR 26 | Boyevaya Gora | 99 | 5 | 5.46 | 18.02 |
| KOR 27 | Boyevaya Gora | 99 | 4 | 4.37 | 17.16 |
| KOR 28 | Boyevaya Gora | 96 | 15 | 16.37 | 26.65 |
| KOR 31 | Boyevaya Gora | 80 | 11 | 12.01 | 23.20 |
| KOR 35 | Boyevaya Gora | 79 | 5 | 5.46 | 18.02 |
| SAM 1 | Sambullak | 131 | 35 | 38.21 | 43.89 |
| SAM 4 | Sambullak | 131 | 82 | 89.51 | 84.42 |
| SAM 10 | Sambullak | 123 | 43 | 46.94 | 50.79 |
| SAM 10a | Sambullak | 122 | 38 | 41.48 | 46.48 |
| SAM 12 | Sambullak | 114 | 6 | 6.55 | 18.88 |
| SAM 11 | Sambullak | 113 | 6 | 6.55 | 18.88 |
| SAM 9 | Sambullak | 102 | 85 | 92.79 | 87.01 |
| SAM 8 | Sambullak | 98 | 65 | 70.95 | 69.76 |
| SAM 20 | Sambullak | 88 | 20 | 21.83 | 30.96 |
| SAM 17 | Sambullak | 80 | 13 | 14.19 | 24.92 |
| SAM 16 | Sambullak | 76 | 18 | 19.65 | 29.23 |
| SAM 15 | Sambullak | 73 | 42 | 45.85 | 49.93 |
| SAM 14 | Sambullak | 68 | 25 | 27.29 | 35.27 |
| SAM 13 | Sambullak | 67 | 69 | 75.32 | 73.21 |
| SAM 21 | Sambullak | 62 | 23 | 25.11 | 33.54 |
| SAM 22 | Sambullak | 61 | 11 | 12.01 | 23.20 |
| SAM 24a | Sambullak | 57 | 10 | 10.92 | 22.33 |
| SAM 24b | Sambullak | 57 | 71 | 77.50 | 74.94 |
| SAM 24c | Sambullak | 57 | 6 | 6.55 | 18.88 |
| SAM 24d | Sambullak | 56 | 18 | 19.65 | 29.23 |
| SAM 24e | Sambullak | 53 | 14 | 15.28 | 29.23 |
| 04.7.24.d | Sambullak | 51 | 25 | 27.29 | 35.27 |
| 04.7.23.o | Sambullak | 33 | 20 | 21.83 | 30.96 |
| 04.7.23.j | Sambullak | 11 | 15 | 16.37 | 26.65 |
| 04.7.23.h | Sambullak | 10 | 35 | 38.21 | 43.89 |
| TUY 56 | Tuyembetka | 107 | 52 | 56.76 | 58.55 |
| TUY 58 | Tuyembetka | 104 | 88 | 96.06 | 89.60 |
| TUY 46 | Tuyembetka | 95 | 70 | 76.41 | 74.08 |
| TUY 4 | Tuyembetka | 93 | 8 | 8.73 | 20.61 |
| TUY 5 | Tuyembetka | 93 | 45 | 49.12 | 52.52 |
| TUY 7 | Tuyembetka | 90 | 98 | 106.98 | 98.22 |
| TUY 13 | Tuyembetka | 74 | 58 | 63.31 | 63.73 |
| TUY 15 | Tuyembetka | 71 | 11 | 12.01 | 23.20 |
| TUY 16 | Tuyembetka | 66 | 20 | 21.83 | 30.96 |

| Paleosol Horizon | Location | Strat. Height (m) | Thickness of nodule horizon (cm) | Decompressed Thickness (cm) | Equation 5.5 (mm) |
|---|---|---|---|---|---|
| TUY 18 | Tuyembetka | 61 | 50 | 54.58 | 56.83 |
| TUY 23 | Tuyembetka | 56 | 5 | 5.46 | 18.02 |
| TUY 24 | Tuyembetka | 55 | 49 | 53.49 | 55.97 |
| TUY 31 | Tuyembetka | 34 | 67 | 73.14 | 71.49 |
| TUY 39 | Tuyembetka | 21 | 10 | 10.92 | 22.33 |
| TUY 41 | Tuyembetka | 16 | 23 | 25.11 | 33.54 |
| TUY 42 | Tuyembetka | 16 | 7 | 7.64 | 19.75 |
| TUY 45 | Tuyembetka | 0 | 9 | 9.82 | 21.47 |
| MES 5 | Mescheryakovka | 7 | 70 | 76.41 | 74.08 |
| MES 7 | Mescheryakovka | 7 | 5 | 5.46 | 18.02 |
| MES 6 | Mescheryakovka | 8 | 76 | 82.96 | 79.25 |
| MES 4 | Mescheryakovka | 8 | 13 | 14.19 | 24.92 |
| MES 3 | Mescheryakovka | 9 | 43 | 46.94 | 50.79 |
| MES 2 | Mescheryakovka | 9 | 6 | 6.55 | 18.88 |
| MES 1 | Mescheryakovka | 10 | 10 | 10.92 | 22.33 |
| MES 10 | Mescheryakovka | 137 | 23 | 25.11 | 33.54 |
| MES 9 | Mescheryakovka | 140 | 37 | 40.39 | 45.62 |
| MES 8 | Mescheryakovka | 140 | 39 | 42.57 | 47.34 |
| MES 12 | Mescheryakovka | 142 | 23 | 25.11 | 33.54 |
| MES 11 | Mescheryakovka | 142 | 10 | 10.92 | 22.33 |
| MES 13 | Mescheryakovka | 178 | 20 | 21.83 | 30.96 |
| MES 14 | Mescheryakovka | 180 | 46 | 50.21 | 53.38 |
| MES 15 | Mescheryakovka | 183 | 15 | 16.37 | 26.65 |
| MES 16 | Mescheryakovka | 183 | 37 | 40.39 | 45.62 |
| MES 17 | Mescheryakovka | 186 | 140 | 152.82 | 134.44 |

# A3.3

Palaeotemperature estimates from Chapter 5 from Boyevaya Gora, Sambullak, and Mescheryakovka. For method by which these equations are generated is by using the methods described in Chapter 2.

| | | | | Equations (°C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Section height (m) | Section | $\delta^{18}O$ (‰, VPDB) | 6 | 8a | 8b | 8c | 9 | 10 |
| SU06 KOR 36.1 | 79 | Boyevaya Gora | -6.79 | 21 | 11 | 142 | 32 | 10 | 38 |
| SU06 KOR 36.4 | 79 | Boyevaya Gora | -8.79 | 31 | 3 | 79 | -409 | 3 | 44 |
| SU06 KOR 36.5 | 79 | Boyevaya Gora | -6.00 | 18 | 14 | -436 | -410 | 2 | 45 |
| SU06 KOR 36.6 | 80 | Boyevaya Gora | -2.64 | 4 | 27 | 83 | -409 | 3 | 44 |
| 04.8.2.f | 80 | Boyevaya Gora | -5.85 | 17 | 15 | 132 | 22 | 9 | 37 |
| 04.8.2.f | 99 | Boyevaya Gora | -4.10 | 10 | 21 | 146 | 36 | 11 | 42 |
| 04.8.2.f | 99 | Boyevaya Gora | -8.84 | 31 | 2 | 145 | 35 | 11 | 42 |
| SU06 KOR 33.1 | 99 | Boyevaya Gora | -9.26 | 34 | 0 | 108 | -409 | 6 | 39 |
| SU06 KOR 37.4 | 105 | Boyevaya Gora | -11.31 | 45 | -10 | 109 | -409 | 6 | 42 |
| SU06 KOR 37.5 | 105 | Boyevaya Gora | -11.24 | 45 | -9 | 149 | 39 | 12 | 41 |
| SU06 KOR 34.7 | 105 | Boyevaya Gora | -11.29 | 45 | -9 | 115 | -409 | 6 | 37 |
| 04.8.2.e.i | 105 | Boyevaya Gora | -11.01 | 43 | -8 | 119 | -408 | 7 | 41 |
| 04.8.2.e.iii | 136 | Boyevaya Gora | -5.51 | 16 | 16 | 118 | -408 | 7 | 41 |
| 04.8.2.e.iv | 136 | Boyevaya Gora | -5.08 | 14 | 18 | 147 | 37 | 11 | 41 |
| SU06 KOR 32.2 | 136 | Boyevaya Gora | -6.16 | 18 | 14 | 107 | -409 | 5 | 37 |
| SU06 KOR 32.7 | 136 | Boyevaya Gora | -5.64 | 16 | 16 | 114 | -409 | 6 | 37 |
| SU06 KOR 23.1 | 136 | Boyevaya Gora | -5.15 | 14 | 17 | 66 | -409 | 2 | 45 |
| SU06 KOR 23.2 | 141 | Boyevaya Gora | 0.73 | -9 | 38 | 84 | -409 | 3 | 44 |
| 04.8.1.q.I | 141 | Boyevaya Gora | 1.03 | -10 | 39 | 71 | -409 | 2 | 46 |
| 04.8.1.q.II | 141 | Boyevaya Gora | 0.64 | -8 | 38 | 123 | 7 | 8 | 44 |
| SU06 KOR 22.10 | 142 | Boyevaya Gora | -1.09 | -2 | 32 | 86 | -409 | 3 | 44 |
| SU06 KOR 22.11 | 142 | Boyevaya Gora | -1.81 | 0 | 30 | 105 | -409 | 5 | 42 |
| SU06 KOR 22.12 | 142 | Boyevaya Gora | -5.27 | 14 | 17 | 165 | 52 | 14 | 44 |
| SU06 KOR 22.14 | 142 | Boyevaya Gora | -4.10 | 9 | 21 | -437 | -410 | 1 | 40 |
| SU06 KOR 22.2 | 143 | Boyevaya Gora | -11.30 | 45 | -10 | 77 | -409 | 3 | 44 |
| SU06 KOR 22.4 | 143 | Boyevaya Gora | -11.00 | 43 | -8 | 175 | 60 | 16 | 44 |
| SU06 KOR 22.5 | 143 | Boyevaya Gora | -5.60 | 16 | 16 | 97 | -409 | 4 | 34 |
| SU06 KOR 22.6 | 143 | Boyevaya Gora | -4.66 | 12 | 19 | 77 | -409 | 3 | 33 |
| SU06 KOR 22.7 | 143 | Boyevaya Gora | -10.49 | 40 | -5 | 86 | -409 | 3 | 43 |
| SU06 KOR 22.8 | 144 | Boyevaya Gora | -12.14 | 50 | -14 | 165 | 52 | 14 | 34 |
| SU06 KOR 21.10 | 144 | Boyevaya Gora | -11.30 | 45 | -10 | 169 | 55 | 15 | 24 |
| SU06 KOR 21.5 | 144 | Boyevaya Gora | -5.57 | 16 | 16 | 181 | 64 | 17 | 28 |
| SU06 KOR 21.7 | 144 | Boyevaya Gora | -10.99 | 43 | -8 | 203 | 81 | 22 | 27 |

| Sample | Section height (m) | Section | $\delta^{18}O$ (‰, VPDB) | Equations (°C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 6 | 8a | 8b | 8c | 9 | 10 |
| SU06 KOR 21.8 | 144 | Boyevaya Gora | -10.12 | 38 | -4 | 210 | 85 | 24 | 23 |
| SU06 KOR 21.9 | 144 | Boyevaya Gora | -11.45 | 46 | -10 | 227 | 97 | 27 | 24 |
| SU06 KOR 21.1 | 144 | Boyevaya Gora | -8.96 | 32 | 2 | 229 | 98 | 28 | 34 |
| SU06 KOR 21.2 | 145 | Boyevaya Gora | -11.55 | 47 | -11 | 226 | 96 | 27 | 32 |
| 04.8.1.n* | 145 | Boyevaya Gora | -11.05 | 44 | -8 | 165 | 52 | 14 | 35 |
| SU06 KOR 16.5 | 196 | Boyevaya Gora | -10.01 | 38 | -3 | 170 | 56 | 15 | 34 |
| SU06 KOR 16.6 | 196 | Boyevaya Gora | -9.54 | 35 | -1 | 159 | 47 | 13 | 34 |
| SU06 KOR 16.3 | 198 | Boyevaya Gora | -7.15 | 23 | 10 | 166 | 53 | 15 | 34 |
| SU06 KOR 16.4 | 198 | Boyevaya Gora | -9.48 | 35 | -1 | 171 | 57 | 15 | 34 |
| SU06 KOR 25.1 | 198 | Boyevaya Gora | -9.21 | 33 | 1 | 76 | -409 | 3 | 44 |
| SU06 KOR 25.3 | 198 | Boyevaya Gora | -9.31 | 34 | 0 | 79 | -409 | 3 | 44 |
| SU06 KOR 25.4 | 198 | Boyevaya Gora | -7.01 | 22 | 10 | 77 | -409 | 3 | 44 |
| SU06 KOR 25.5 | 199 | Boyevaya Gora | -7.36 | 24 | 9 | 85 | -409 | 3 | 44 |
| 04.8.1.f* | 199 | Boyevaya Gora | -9.92 | 37 | -3 | 181 | 64 | 17 | 32 |
| SU06 KOR 27.2 | 199 | Boyevaya Gora | -9.84 | 37 | -2 | 125 | 11 | 8 | 40 |
| SU06 KOR 27.4 | 199 | Boyevaya Gora | -7.21 | 23 | 9 | 119 | -408 | 7 | 41 |
| 04.8.1.b* | 199 | Boyevaya Gora | -8.32 | 29 | 5 | 195 | 75 | 20 | 29 |
| 04.8.1.b.I | 211 | Boyevaya Gora | -11.25 | 45 | -9 | 162 | 50 | 14 | 35 |
| 04.8.1.a | 211 | Boyevaya Gora | -11.77 | 48 | -12 | 161 | 48 | 14 | 35 |
| SU06 KOR 35.1 | 211 | Boyevaya Gora | -11.09 | 44 | -8 | 151 | 41 | 12 | 36 |
| SU06 KOR 35.5 | 211 | Boyevaya Gora | -7.60 | 25 | 8 | 126 | 12 | 8 | 40 |
| 04.7.24.u.I | 131 | Sambullak | -14.15 | 67 | -28 | -438 | -411 | -3 | 49 |
| 04.7.24.u.II | 131 | Sambullak | -12.82 | 57 | -18 | -437 | -410 | 0 | 47 |
| SU06 SAM 1.3 | 131 | Sambullak | -13.07 | 59 | -20 | -437 | -410 | -1 | 47 |
| SU06 SAM 1.5 | 131 | Sambullak | -11.38 | 48 | -10 | 74 | -409 | 3 | 44 |
| 04.7.24.t | 131 | Sambullak | -9.50 | 37 | -1 | 115 | -409 | 6 | 41 |
| 04.7.24.t.I | 131 | Sambullak | -7.95 | 29 | 6 | 137 | 27 | 10 | 38 |
| 04.7.24.t.II | 131 | Sambullak | -7.99 | 29 | 6 | 137 | 27 | 9 | 38 |
| 04.7.24.t.III | 131 | Sambullak | -7.57 | 27 | 8 | 142 | 32 | 10 | 38 |
| SU06 SAM 4.3 | 130 | Sambullak | -12.98 | 59 | -19 | -437 | -410 | -1 | 47 |
| SU06 SAM 4.4 | 130 | Sambullak | -12.77 | 57 | -18 | -437 | -410 | 0 | 47 |
| SU06 SAM 12.1 | 114 | Sambullak | -9.78 | 39 | -2 | 110 | -409 | 6 | 42 |
| SU06 SAM 8.3 | 98 | Sambullak | -8.32 | 31 | 5 | 132 | 22 | 9 | 39 |
| SU06 SAM 8.1 | 98 | Sambullak | -7.45 | 27 | 8 | 143 | 34 | 11 | 38 |
| SU06 SAM 17.2 | 80 | Sambullak | -7.46 | 27 | 8 | 143 | 34 | 11 | 38 |
| SU06 SAM 13.2 | 67 | Sambullak | -8.08 | 30 | 6 | 135 | 25 | 9 | 39 |
| SU06 SAM 13.1 | 66 | Sambullak | -8.18 | 30 | 5 | 134 | 24 | 9 | 39 |
| SU06 SAM 21.5 | 62 | Sambullak | -7.00 | 25 | 10 | 149 | 39 | 12 | 37 |
| SU06 SAM 22.1 | 61 | Sambullak | -7.79 | 28 | 7 | 139 | 29 | 10 | 38 |
| SU06 SAM 24.3 | 57 | Sambullak | -9.49 | 37 | -1 | 115 | -409 | 6 | 41 |
| SU06 SAM 24.4 | 57 | Sambullak | -8.62 | 33 | 3 | 128 | 16 | 8 | 40 |

| Sample | Section height (m) | Section | $\delta^{18}O$ (‰, VPDB) | Equations (°C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 6 | 8a | 8b | 8c | 9 | 10 |
| 04.7.24.d | 51 | Sambullak | -4.98 | 15 | 18 | 172 | 57 | 16 | 33 |
| 04.7.24.d | 51 | Sambullak | -6.27 | 21 | 13 | 157 | 46 | 13 | 36 |
| MES 8.2 | 80 | Mescheryakovka | -9.85 | 39 | -2 | -275 | -409 | 6 | 42 |
| MES 16.6 | 183 | Mescheryakovka | -8.12 | 30 | 5 | -268 | 25 | 9 | 39 |
| MES 16.1 | 184 | Mescheryakovka | -7.64 | 28 | 8 | -265 | 31 | 9 | 38 |
| MES 17.9 | 186 | Mescheryakovka | -7.00 | 25 | 10 | -263 | 39 | 10 | 37 |

# A3.4

Atmospheric carbon dioxide ($pCO_2$ ppmV) estimates for those pedogenic carbonate isotope results which passed all screening tests laid out in Chapter 4 and thus most likely to represent pedogenic calcite and represent a fractionation from meteoric water. All other variables were generated as described in Chapter 7.

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| MES 7.2 | 5 | Calcite | Olenekian | -10 | 44 | 715 | 953 | 716 | 954 | – | – |
| MES 8.4 | 80 | Calcite | Olenekian | -9 | 54 | 1292 | 1722 | 1233 | 1643 | – | – |
| MES 8.2 | 80 | Calcite | Olenekian | -8 | 42 | 1375 | 1834 | 1316 | 1755 | – | – |
| MES 8.1 | 80 | Calcite | Olenekian | -9 | 55 | 1412 | 1883 | 1339 | 1786 | – | – |
| MES 10.3 | 137 | Calcite | Olenekian | -8 | 53 | 1767 | 2356 | 1654 | 2205 | – | – |
| MES 10.4 | 137 | Calcite | Olenekian | -9 | 54 | 1670 | 2226 | 1568 | 2091 | – | – |
| MES 10.5 | 137 | Calcite | Olenekian | -9 | 50 | 1429 | 1905 | 1357 | 1810 | – | – |
| MES 16.6 | 183 | Calcite | Olenekian | -7 | 39 | 1438 | 1918 | 1375 | 1833 | – | – |
| MES 16.1 | 184 | Calcite | Olenekian | -8 | 38 | 1149 | 1531 | 1115 | 1487 | – | – |
| MES 17.9 | 186 | Calcite | Olenekian | -8 | 37 | 1058 | 1411 | 1034 | 1379 | – | – |
| SU06 KOR 36.1 | 211 | Calcite | Induan | -2 | 38 | 10755 | 14340 | 8437 | 11250 | – | – |
| SU06 KOR 36.4 | 211 | Calcite | Induan | -5 | 44 | 5847 | 7795 | 5042 | 6722 | – | – |
| SU06 KOR 36.5 | 211 | Calcite | Induan | -6 | 45 | 3932 | 5243 | 3543 | 4724 | – | – |
| SU06 KOR 36.6 | 211 | Calcite | Induan | -6 | 44 | 3592 | 4789 | 3266 | 4355 | – | – |
| 04.8.2.f | 199 | Calcite | Induan | -2 | 37 | 10476 | 13969 | 8263 | 11017 | – | – |

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| 04.8.2.f | 199 | Calcite | Induan | -3 | 42 | 10537 | 14050 | 8287 | 11049 | – | – |
| 04.8.2.f | 199 | Calcite | Induan | -3 | 42 | 9843 | 13123 | 7842 | 10456 | – | – |
| SU06 KOR 33.1 | 199 | Calcite | Induan | -3 | 39 | 8582 | 11443 | 7011 | 9349 | – | – |
| SU06 KOR 37.1 | 197 | Calcite | Induan | -1 | 41 | 3297 | 4396 | 3079 | 4105 | – | – |
| SU06 KOR 37.2 | 197 | Calcite | Induan | -1 | 43 | 2927 | 3903 | 2764 | 3686 | – | – |
| SU06 KOR 37.3 | 197 | Calcite | Induan | -2 | 41 | 2812 | 3749 | 2665 | 3554 | – | – |
| SU06 KOR 37.4 | 196 | Calcite | Induan | -1 | 42 | 46269 | 61692 | 22135 | 29513 | – | – |
| SU06 KOR 37.5 | 196 | Calcite | Induan | 0 | 41 | 56152 | 74869 | 24262 | 32350 | – | – |
| SU06 KOR 23.1 | 145 | Calcite | Changhsingian | -11 | 45 | 351 | 468 | 374 | 498 | 277 | 369 |
| SU06 KOR 23.2 | 145 | Calcite | Changhsingian | -11 | 44 | 392 | 522 | 412 | 549 | 309 | 411 |
| 04.8.1.q.I | 144 | Calcite | Changhsingian | -11 | 46 | 415 | 553 | 432 | 576 | 326 | 434 |
| 04.8.1.q.II | 144 | Calcite | Changhsingian | -10 | 44 | 563 | 751 | 571 | 761 | 440 | 587 |
| SU06 KOR 22.10 | 144 | Calcite | Changhsingian | -11 | 44 | 262 | 349 | 291 | 388 | 207 | 277 |
| SU06 KOR 22.11 | 144 | Calcite | Changhsingian | -11 | 42 | 347 | 463 | 371 | 495 | 275 | 367 |
| SU06 KOR 22.12 | 144 | Calcite | Changhsingian | -11 | 44 | 279 | 373 | 307 | 409 | 221 | 294 |
| SU06 KOR 22.14 | 144 | Calcite | Changhsingian | -10 | 40 | 516 | 688 | 529 | 706 | 406 | 541 |
| SU06 KOR 22.2 | 143 | Calcite | Changhsingian | -10 | 44 | 583 | 777 | 589 | 785 | 455 | 607 |
| SU06 KOR 22.4 | 143 | Calcite | Changhsingian | -11 | 44 | 334 | 445 | 358 | 478 | 264 | 352 |
| SU06 KOR 22.5 | 143 | Calcite | Changhsingian | -5 | 34 | 2426 | 3235 | 2235 | 2980 | 1720 | 2293 |
| SU06 KOR 22.6 | 143 | Calcite | Changhsingian | -5 | 33 | 2250 | 3000 | 2085 | 2780 | 1611 | 2149 |
| SU06 KOR 22.7 | 143 | Calcite | Changhsingian | -10 | 43 | 422 | 563 | 441 | 588 | 333 | 443 |
| SU06 KOR 22.8 | 144 | Calcite | Changhsingian | -5 | 34 | 2423 | 3231 | 2232 | 2976 | 1718 | 2291 |
| SU06 KOR 21.10 | 141 | Calcite | Changhsingian | -1 | 24 | 4801 | 6402 | 4185 | 5580 | 3026 | 4035 |
| SU06 KOR 21.5 | 142 | Calcite | Changhsingian | -2 | 28 | 3960 | 5280 | 3514 | 4685 | 2598 | 3464 |
| SU06 KOR 21.7 | 142 | Calcite | Changhsingian | -1 | 27 | 5391 | 7188 | 4635 | 6180 | 3302 | 4403 |

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| SU06 KOR 21.8 | 141 | Calcite | Changhsingian | 0 | 23 | 6379 | 8505 | 5378 | 7171 | 3739 | 4985 |
| SU06 KOR 21.9 | 141 | Calcite | Changhsingian | -2 | 24 | 4577 | 6103 | 4010 | 5347 | 2916 | 3889 |
| SU06 KOR 21.1 | 142 | Calcite | Changhsingian | -4 | 34 | 3058 | 4078 | 2769 | 3692 | 2097 | 2796 |
| SU06 KOR 21.2 | 142 | Calcite | Changhsingian | -2 | 32 | 4758 | 6344 | 4140 | 5520 | 2998 | 3998 |
| 04.8.1.n* | 136 | Calcite | Changhsingian | -2 | 35 | 5637 | 7515 | 4807 | 6409 | 3405 | 4540 |
| SU06 KOR 16.5 | 136 | Calcite | Changhsingian | -4 | 34 | 2912 | 3883 | 2646 | 3528 | 2012 | 2682 |
| SU06 KOR 16.6 | 136 | Calcite | Changhsingian | -4 | 34 | 3177 | 4237 | 2868 | 3824 | 2165 | 2887 |
| SU06 KOR 16.3 | 136 | Calcite | Changhsingian | -5 | 34 | 2678 | 3571 | 2449 | 3266 | 1873 | 2498 |
| SU06 KOR 16.4 | 136 | Calcite | Changhsingian | -5 | 34 | 2506 | 3342 | 2304 | 3072 | 1770 | 2360 |
| SU06 KOR 25.1 | 105 | Calcite | Changhsingian | -10 | 44 | 518 | 691 | 529 | 705 | 406 | 541 |
| SU06 KOR 25.3 | 105 | Calcite | Changhsingian | -10 | 44 | 513 | 685 | 525 | 700 | 402 | 536 |
| SU06 KOR 25.4 | 105 | Calcite | Changhsingian | -10 | 44 | 604 | 806 | 609 | 812 | 471 | 628 |
| SU06 KOR 25.5 | 105 | Calcite | Changhsingian | -10 | 44 | 592 | 790 | 598 | 797 | 462 | 617 |
| 04.8.1.f* | 99 | Calcite | Changhsingian | -1 | 32 | 7201 | 9602 | 5954 | 7939 | 4063 | 5417 |
| SU06 KOR 27.2 | 99 | Calcite | Changhsingian | 0 | 40 | 23429 | 31239 | 14696 | 19594 | 7783 | 10378 |
| SU06 KOR 27.4 | 99 | Calcite | Changhsingian | 0 | 41 | 23186 | 30914 | 14591 | 19455 | 7749 | 10332 |
| 04.8.1.b* | 80 | Calcite | Changhsingian | -3 | 29 | 3953 | 5271 | 3507 | 4676 | 2593 | 3458 |
| 04.8.1.b.I | 80 | Calcite | Changhsingian | -4 | 35 | 3102 | 4136 | 2804 | 3739 | 2121 | 2829 |
| 04.8.1.a | 79 | Calcite | Changhsingian | -3 | 35 | 4255 | 5673 | 3741 | 4987 | 2745 | 3660 |
| SU06 KOR 35.1 | 79 | Calcite | Changhsingian | -5 | 36 | 2828 | 3771 | 2573 | 3431 | 1961 | 2614 |
| SU06 KOR 35.5 | 79 | Calcite | Changhsingian | -7 | 40 | 1519 | 2025 | 1439 | 1919 | 1129 | 1505 |
| 04.7.24.u.I | 131 | Calcite | Changhsingian | -6 | 49 | 3055 | 4074 | 2750 | 3667 | 2084 | 2779 |
| 04.7.24.u.II | 131 | Calcite | Changhsingian | -5 | 47 | 3640 | 4854 | 3233 | 4310 | 2412 | 3216 |
| SU06 SAM 1.3 | 131 | Calcite | Changhsingian | -6 | 47 | 2580 | 3440 | 2354 | 3138 | 1805 | 2407 |
| SU06 SAM 1.5 | 131 | Calcite | Changhsingian | -7 | 44 | 2029 | 2706 | 1884 | 2512 | 1464 | 1952 |

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| 04.7.24.t | 131 | Calcite | Changhsingian | -3 | 41 | 4928 | 6571 | 4259 | 5679 | 3072 | 4096 |
| 04.7.24.t.I | 131 | Calcite | Changhsingian | -5 | 38 | 2926 | 3901 | 2653 | 3538 | 2017 | 2689 |
| 04.7.24.t.II | 131 | Calcite | Changhsingian | -3 | 38 | 5396 | 7194 | 4620 | 6160 | 3293 | 4391 |
| SU06 SAM 4.3 | 130 | Calcite | Changhsingian | -6 | 47 | 2747 | 3663 | 2495 | 3326 | 1905 | 2540 |
| SU06 SAM 4.4 | 130 | Calcite | Changhsingian | -6 | 47 | 3089 | 4118 | 2780 | 3707 | 2105 | 2807 |
| SU06 SAM 12.1 | 114 | Calcite | Changhsingian | -6 | 42 | 2374 | 3165 | 2183 | 2911 | 1683 | 2244 |
| SU06 SAM 8.3 | 98 | Calcite | Changhsingian | -6 | 39 | 2063 | 2751 | 1917 | 2557 | 1489 | 1985 |
| SU06 SAM 8.1 | 98 | Calcite | Changhsingian | -6 | 38 | 2222 | 2963 | 2056 | 2742 | 1591 | 2121 |
| SU06 SAM 17.2 | 80 | Calcite | Changhsingian | -5 | 38 | 2430 | 3240 | 2235 | 2980 | 1720 | 2294 |
| SU06 SAM 13.2 | 67 | Calcite | Changhsingian | -6 | 39 | 2325 | 3100 | 2144 | 2859 | 1655 | 2206 |
| SU06 SAM 13.1 | 66 | Calcite | Changhsingian | -5 | 39 | 2422 | 3229 | 2227 | 2969 | 1714 | 2286 |
| SU06 SAM 21.5 | 62 | Calcite | Changhsingian | -7 | 37 | 1201 | 1601 | 1157 | 1543 | 911 | 1214 |
| SU06 SAM 22.1 | 61 | Calcite | Changhsingian | -6 | 38 | 2311 | 3081 | 2132 | 2843 | 1646 | 2195 |
| SU06 SAM 24.3 | 57 | Calcite | Changhsingian | -6 | 41 | 2515 | 3353 | 2304 | 3072 | 1770 | 2360 |
| SU06 SAM 24.4 | 57 | Calcite | Changhsingian | -5 | 40 | 2615 | 3487 | 2391 | 3187 | 1832 | 2442 |
| 04.7.24.d | 51 | Calcite | Changhsingian | -3 | 33 | 3649 | 4865 | 3256 | 4341 | 2427 | 3237 |
| 04.7.24.d | 51 | Calcite | Changhsingian | -5 | 36 | 2280 | 3040 | 2108 | 2810 | 1628 | 2171 |
| 04.8.1.ac* | 171 | Dolomite | Changhsingian | 0 | 49 | 38417 | 51222 | 19694 | 26258 | 9238 | 12317 |
| 04.8.1.ac.I | 171 | Dolomite | Changhsingian | 0 | 49 | 33490 | 44653 | 18246 | 24328 | 8852 | 11803 |
| 04.8.1.ac.II | 171 | Dolomite | Changhsingian | 0 | 49 | 49013 | 65351 | 22294 | 29725 | 9869 | 13159 |
| SU06 KOR 1.10 | 170 | Dolomite | Changhsingian | 0 | 49 | 45421 | 60561 | 21480 | 28640 | 9679 | 12906 |
| SU06 KOR 1.8 | 170 | Dolomite | Changhsingian | 0 | 49 | 37269 | 49693 | 19372 | 25829 | 9154 | 12206 |
| SU06 KOR 1.9 | 170 | Dolomite | Changhsingian | 0 | 49 | 31396 | 41862 | 17575 | 23433 | 8664 | 11552 |
| SU06 KOR 2.1 | 170 | Dolomite | Changhsingian | 0 | 49 | 34657 | 46209 | 18605 | 24807 | 8950 | 11933 |
| SU06 KOR 9.1 | 165 | Dolomite | Changhsingian | 0 | 49 | 27068 | 36091 | 16063 | 21418 | 8217 | 10957 |

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| SU06 KOR 9.2 | 165 | Dolomite | Changhsingian | -1 | 49 | 23304 | 31072 | 14593 | 19458 | 7749 | 10333 |
| SU06 KOR 9.3 | 165 | Dolomite | Changhsingian | 0 | 49 | 29566 | 39422 | 16957 | 22609 | 8485 | 11314 |
| 04.8.1.z | 163 | Dolomite | Changhsingian | -1 | 49 | 20934 | 27911 | 13582 | 18109 | 7406 | 9875 |
| SU06 KOR 5.1 | 163 | Dolomite | Changhsingian | 0 | 49 | 27676 | 36901 | 16286 | 21715 | 8285 | 11047 |
| SU06 KOR 5.3 | 163 | Dolomite | Changhsingian | -1 | 49 | 19036 | 25381 | 12718 | 16958 | 7098 | 9464 |
| SU06 KOR 5.4 | 163 | Dolomite | Changhsingian | -2 | 49 | 13066 | 17422 | 9635 | 12846 | 5867 | 7822 |
| SU06 KOR 5.5 | 163 | Dolomite | Changhsingian | -1 | 49 | 18189 | 24252 | 12316 | 16422 | 6949 | 9266 |
| SU06 KOR 6.2 | 163 | Dolomite | Changhsingian | -1 | 49 | 15388 | 20518 | 10906 | 14542 | 6401 | 8535 |
| SU06 KOR 6.3 | 163 | Dolomite | Changhsingian | -1 | 49 | 17051 | 22734 | 11759 | 15678 | 6738 | 8983 |
| SU06 KOR 6.4 | 163 | Dolomite | Changhsingian | -2 | 49 | 13600 | 18134 | 9936 | 13248 | 5997 | 7996 |
| SU06 KOR 6.5 | 163 | Dolomite | Changhsingian | -1 | 49 | 14959 | 19946 | 10679 | 14238 | 6308 | 8411 |
| SU06 KOR 6.6 | 163 | Dolomite | Changhsingian | -1 | 49 | 15537 | 20716 | 10984 | 14646 | 6432 | 8577 |
| SU06 KOR 6.7 | 163 | Dolomite | Changhsingian | -1 | 49 | 16235 | 21647 | 11346 | 15128 | 6577 | 8769 |
| SU06 KOR 6.8 | 163 | Dolomite | Changhsingian | -1 | 49 | 17548 | 23398 | 12005 | 16006 | 6832 | 9109 |
| SU06 KOR 14.8 | 154 | Dolomite | Changhsingian | -1 | 49 | 15645 | 20860 | 11041 | 14721 | 6455 | 8607 |
| SU06 KOR 14.9 | 154 | Dolomite | Changhsingian | -1 | 49 | 14555 | 19407 | 10462 | 13949 | 6219 | 8291 |
| 04.8.1.s | 154 | Dolomite | Changhsingian | -2 | 49 | 12886 | 17182 | 9532 | 12709 | 5822 | 7762 |
| 04.8.1.o | 140 | Dolomite | Changhsingian | -1 | 49 | 19371 | 25827 | 12874 | 17166 | 7155 | 9539 |
| SU06 KOR 15.3 | 140 | Dolomite | Changhsingian | -1 | 49 | 22558 | 30077 | 14283 | 19044 | 7646 | 10195 |
| SU06 KOR 15.4 | 140 | Dolomite | Changhsingian | -1 | 49 | 25336 | 33782 | 15407 | 20542 | 8013 | 10684 |
| SU06 KOR 15.5 | 140 | Dolomite | Changhsingian | -1 | 49 | 21371 | 28494 | 13774 | 18365 | 7473 | 9964 |
| SU06 KOR 15.7 | 140 | Dolomite | Changhsingian | -1 | 49 | 22086 | 29448 | 14082 | 18777 | 7578 | 10104 |
| SU06 KOR 15.9 | 140 | Dolomite | Changhsingian | 0 | 49 | 26155 | 34874 | 15721 | 20962 | 8112 | 10816 |
| SU06 SAM 12.2 | 114 | Dolomite | Changhsingian | -5 | 49 | 3404 | 4539 | 3038 | 4050 | 2281 | 3041 |
| SU06 SAM 10.6 | 123 | Dolomite | Changhsingian | -4 | 49 | 5455 | 7274 | 4649 | 6199 | 3310 | 4414 |

| Sample | Section height | Mineral composition | Age | $\delta^{13}C$ (‰,VPDB) | Temp (°C)[a] | Method 1 | | Method 2 | | Method 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV | Sz= 3000 ppmV | Sz= 4000 ppmV |
| SU06 SAM 10.5 | 123 | Dolomite | Changhsingian | -4 | 49 | 5774 | 7699 | 4888 | 6517 | 3453 | 4604 |
| SU06 SAM 10.4 | 122 | Dolomite | Changhsingian | -3 | 49 | 6524 | 8698 | 5437 | 7250 | 3773 | 5030 |
| SU06 SAM 10.2 | 122 | Dolomite | Changhsingian | -4 | 49 | 5458 | 7277 | 4651 | 6201 | 3311 | 4415 |
| SU06 SAM 10.1 | 122 | Dolomite | Changhsingian | -4 | 49 | 5329 | 7106 | 4554 | 6071 | 3253 | 4337 |
| 04.7.24.m | 102 | Dolomite | Changhsingian | -2 | 49 | 12352 | 16470 | 9223 | 12297 | 5685 | 7580 |
| SU06 SAM 9.3 | 102 | Dolomite | Changhsingian | -5 | 49 | 4505 | 6006 | 3919 | 5225 | 2859 | 3812 |
| 04.7.24.l | 98 | Dolomite | Changhsingian | -2 | 49 | 10060 | 13413 | 7829 | 10439 | 5034 | 6712 |
| 04.7.24.j | 88 | Dolomite | Changhsingian | -2 | 49 | 9099 | 12132 | 7210 | 9614 | 4726 | 6302 |
| SU06 SAM 20.2 | 88 | Dolomite | Changhsingian | -4 | 49 | 5744 | 7659 | 4865 | 6487 | 3440 | 4587 |
| SU06 SAM 20.5 | 88 | Dolomite | Changhsingian | -4 | 49 | 5866 | 7822 | 4956 | 6608 | 3494 | 4658 |
| 04.7.23.o | 33 | Dolomite | Changhsingian | -2 | 49 | 11826 | 15768 | 8913 | 11884 | 5545 | 7393 |
| 04.7.23.j | 11 | Dolomite | Changhsingian | -2 | 49 | 13592 | 18122 | 9931 | 13242 | 5995 | 7993 |
| 04.7.23.h | 10 | Dolomite | Changhsingian | -3 | 49 | 8442 | 11256 | 6774 | 9032 | 4502 | 6003 |
| 04.7.23.i | 10 | Dolomite | Changhsingian | -2 | 49 | 12381 | 16508 | 9240 | 12320 | 5692 | 7590 |

# Appendix 4

## Italian dolomite brachiopods and bulk rock isotope results and palaeotemperature estimates

## (Chapter 6)

# A4.1

Isotope results and palaeotemperature estimates for brachiopods recovered from Val Brutta and Tesero in the Italian Dolomites. Material refers to the part of the specimen sampled: p= prismatic layer of the shell; f = fibrous layer of the shell; m = micrite associated with the shell. Cl luminescence: NL= Non-Luminescent; NL+SL= Non-Luminescent with Slightly Luminescent; L+SNL= Luminescent and Slightly Non- Luminescent shells; L= those areas that were completely luminescent (see Chapter 2 for fuller description) Palaeotemperature A was calculated using equation 6.1 and Palaeotemperature B was calculated using equation 6.2 (see Chapter 6). All collations were performed at a $\delta^{18}O$ seawater of 0.0‰ (VSMOW). Fossil identifications based on Posenato (2001) for Val Brutta and Chen *et al.* (2006) for Tesero. Note that the CL analysis for TS1 was undertaken by Nikita Jacobsen (unpublished data).

| Fossil | Taxon | Drill site | From outer to inner part of the shell (mm) | Material | CL luminescence | Discounted because | Date run | $\delta^{13}C$ (‰,VPDB) | $\delta^{18}O$ (‰,VPDB) | Temp A (°C) | Temp B (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VB1 | *Comelicania? Sp.* | Bulk | | m | L | CL | 02/03/07 | 2.18 | -5.68 | | |
| VB1 | | ii | 4 | p | NL+SNL | CL | 02/03/07 | 4.22 | -2.33 | | |
| VB1 | | iii | 3 | p | NL+SNL | CL | 02/03/07 | 3.19 | -2.82 | | |
| VB1 | | iv | 1.9 | p | NL+SNL | CL | 02/03/07 | 4.09 | -2.31 | | |
| VB1 | | v | 0.6 | f | L+SNL | CL | 02/03/07 | 3.19 | -4.30 | | |
| VB1 | | vi | 2.1 | p | NL | | 02/03/07 | 3.96 | -2.83 | 30 | 29 |
| VB1 | | vii | 1.4 | p | NL | | 02/03/07 | 4.38 | -1.87 | 25 | 24 |
| VB1 | | viii | 0.6 | f | NL | | 02/03/07 | 3.25 | -2.73 | 29 | 28 |
| VB1 | | ix | 1.4 | p | NL | | 02/03/07 | 3.82 | -2.80 | 30 | 29 |
| VB1 | | x | 0.9 | p | NL | | 02/03/07 | 4.35 | -1.95 | 25 | 25 |
| VB2 | *Janiceps aff.paracuta.* | Bulk | | m | L | CL | 12/07/07 | 2.02 | -6.16 | | |
| VB2 | | i | 0.4 | f | NL | | 12/07/07 | 0.96 | -2.64 | 29 | 28 |
| VB2 | | ii | 1.5 | p | NL+SNL | CL | 12/07/07 | 4.27 | -2.20 | | |
| VB2 | | iii | 2 | p | NL+SNL | CL | 12/07/07 | 4.09 | -1.81 | | |
| VB2 | | iv | 1.8 | p | NL | | 12/07/07 | 1.94 | -2.48 | 28 | 27 |
| VB2 | | v | 1.1 | p | NL | | 12/07/07 | 3.45 | -1.81 | 25 | 24 |
| VB2 | | vi | 0.4 | f | NL | | 12/07/07 | 3.63 | -2.33 | 27 | 26 |
| VB2 | | vii | 0.4 | f | NL | | 12/07/07 | 1.48 | -3.29 | 32 | 31 |
| VB2 | | viii | 1 | f | NL | | 12/07/07 | 2.82 | -3.63 | 34 | 33 |
| VB3 | *Comelicania? Sp.* | Bulk | | m | L | CL + TRACE | 02/03/07 | 2.49 | -5.62 | | |

| Fossil | Taxon | Drill site | From outer to inner part of the shell (mm) | Material | CL luminescence | Discounted because | Date run | $\delta^{13}C$ (‰,VPDB) | $\delta^{18}O$ (‰,VPDB) | Temp A (°C) | Temp B (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VB3 | | i | 7.8 | p | L+SNL | CL + TRACE | 02/03/07 | 3.79 | -1.86 | | |
| VB3 | | ii | 6.8 | p | L+SNL | CL + TRACE | 02/03/07 | 4.18 | -1.47 | | |
| VB3 | | iii | 5.4 | p | L+SNL | CL + TRACE | 02/03/07 | 3.60 | -1.96 | | |
| VB3 | | iv | 3.7 | p | L+SNL | CL + TRACE | 02/03/07 | 2.15 | -2.30 | | |
| VB3 | | v | 2.2 | p | L+SNL | CL + TRACE | 02/03/07 | 4.32 | -2.29 | | |
| VB3 | | vi | 0.9 | p | L+SNL | CL + TRACE | 02/03/07 | 4.07 | -1.91 | | |
| VB3 | | viii | 7.1 | p | NL+SNL | CL + TRACE | 02/03/07 | 3.29 | -1.74 | | |
| VB3 | | x | 3.7 | p | NL+SNL | CL + TRACE | 02/03/07 | 2.79 | -2.02 | | |
| VB3 | | xi | 2.5 | p | NL+SNL | CL + TRACE | 02/03/07 | 3.43 | -3.76 | | |
| VB3 | | xii | 1.4 | p | NL+SNL | CL + TRACE | 02/03/07 | 3.74 | -2.03 | | |
| VB4 | *Comelicania? Sp.* | Bulk | | m | L | CL | 12/07/07 | 2.00 | -4.35 | | |
| VB4 | | i | 0.5 | p | L+SNL | CL | 12/07/07 | 4.01 | -1.68 | | |
| VB4 | | ii | 1.6 | f | NL+SNL | CL | 12/07/07 | 3.36 | -2.09 | | |
| VB4 | | iii | 1.1 | p | NL+SNL | CL | 12/07/07 | 4.04 | -2.13 | | |
| VB4 | | iv | 0.6 | p | NL+SNL | CL | 12/07/07 | 3.67 | -2.03 | | |
| VB4 | | v | 0.7 | p | NL+SNL | CL | 12/07/07 | 3.82 | -2.14 | | |
| VB4 | | vi | 0.4 | p | NL+SNL | CL | 12/07/07 | 3.38 | -2.20 | | |
| VB5 | *Janiceps sp.* | Bulk | | m | L | CL | 12/07/07 | 2.50 | -6.74 | | |
| VB5 | | i | 4.8 | p | NL+SNL | CL | 12/07/07 | 5.05 | -2.12 | | |
| VB5 | | ii | 1.1 | p | L+SNL | CL | 12/07/07 | 4.40 | -3.42 | | |
| VB5 | | iii | 2.5 | p | NL+SNL | CL | 12/07/07 | 5.12 | -1.73 | | |
| VB5 | | iv | 0.8 | f | NL | | 12/07/07 | 4.26 | -2.17 | 27 | 26 |
| VB5 | | v | 4.1 | p | NL | | 12/07/07 | 5.13 | -1.91 | 25 | 24 |
| VB5 | | vii | 7.1 | p | NL | | 12/07/07 | 4.78 | -2.31 | 27 | 26 |
| VB5 | | viii | 10.2 | p | NL | | 12/07/07 | 4.17 | -2.67 | 29 | 28 |
| VB5 | | ix | 12.9 | p | NL | | 12/07/07 | 4.28 | -2.64 | 29 | 28 |
| VB6 | *Comelicania? Sp* | Bulk | | | L | CL + TRACE | 02/03/07 | 2.58 | -4.67 | | |
| VB6 | | i | 0.6 | p | NL | | 02/03/07 | 2.63 | -3.17 | 31 | 30 |
| VB6 | | ii | 2 | p | NL | | 02/03/07 | 2.97 | -1.93 | 25 | 24 |
| VB6 | | iii | 1 | p | NL | | 02/03/07 | 3.63 | -1.97 | 26 | 25 |
| VB6 | | iv | 2 | p | NL | | 02/03/07 | 3.27 | -1.77 | 25 | 24 |
| VB6 | | v | 3.5 | p | NL+SNL | CL | 02/03/07 | 2.63 | -3.17 | | |

| Fossil | Taxon | Drill site | From outer to inner part of the shell (mm) | Material | CL luminescence | Discounted because | Date run | $\delta^{13}C$ (‰,VPDB) | $\delta^{18}O$ (‰,VPDB) | Temp A (°C) | Temp B (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| VB6 | | vii | 1.8 | p | NL+SNL | CL | 02/03/07 | 3.84 | -1.74 | | |
| VB6 | | viii | 0.6 | p | NL+SNL | CL | 02/03/07 | 3.02 | -2.11 | | |
| VB6 | | ix | 0.4 | f | NL+SNL | CL | 02/03/07 | 2.96 | -2.15 | | |
| TS1 | *Orbicoelia dolomitensis.* | Bulk | | | L | | 12/07/07 | 1.09 | -6.86 | | |
| TS1 | | i | 2.8 | p | NL | | 12/07/07 | 1.29 | -3.82 | 35 | 34 |
| TS1 | | ii | 4.1 | p | NL | | 12/07/07 | 1.31 | -4.59 | 39 | 38 |
| TS1 | | iii | 5.5 | p | NL+SNL | | 12/07/07 | 1.13 | -5.25 | | |
| TS1 | | v | 8.3 | p | NL | | 12/07/07 | 1.74 | -3.74 | 34 | 33 |
| TS1 | | vii | 11.0 | p | NL+SNL | | 12/07/07 | 1.25 | -5.93 | | |

# A4.2

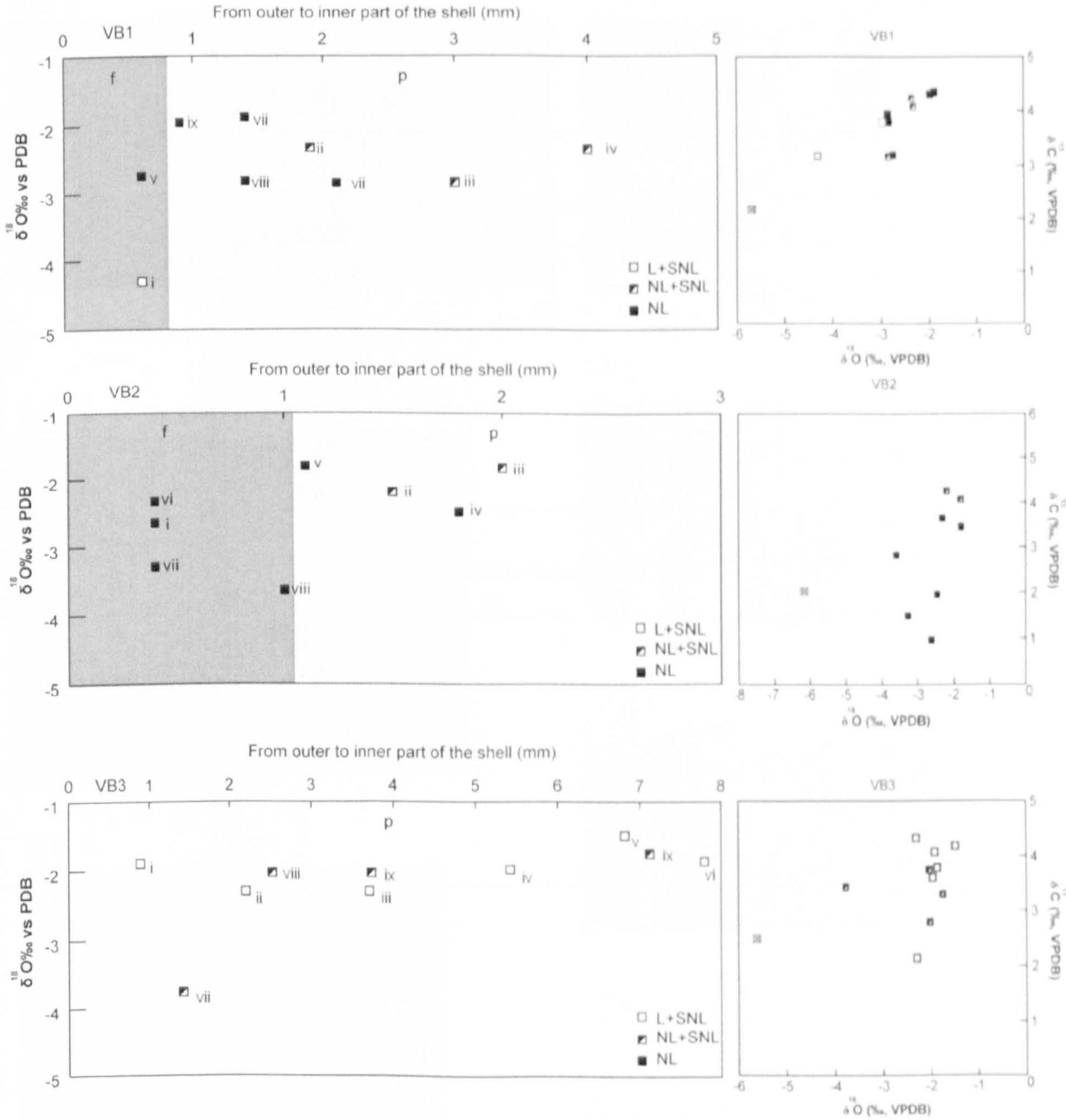
Bulk rock isotope results from Val Brutta results from across the P/Tr boundary.

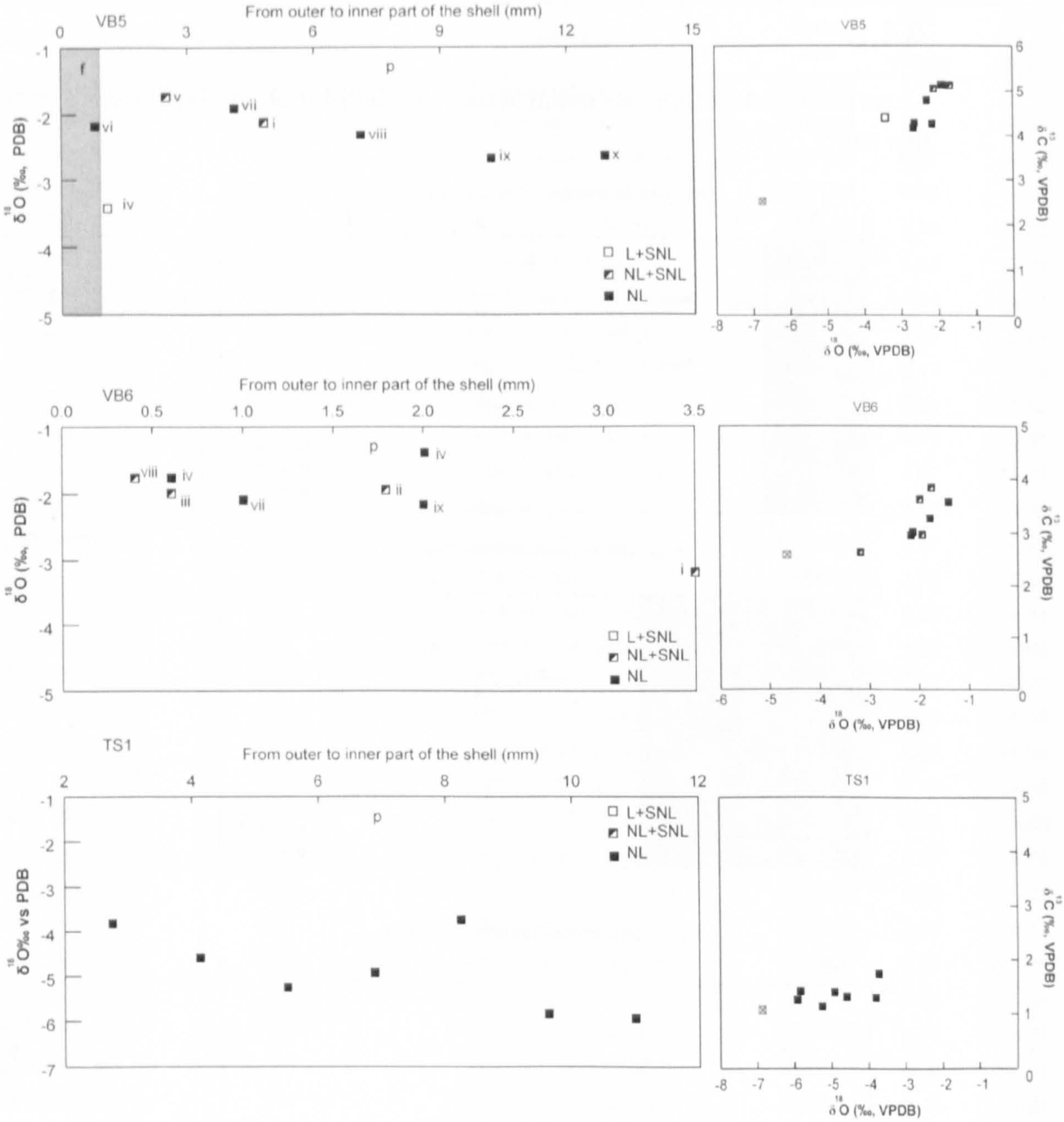
| Sample number | Strat. height with respect to the PTB (m) | Lithology | Date run | $\delta^{13}C$ (‰, VPDB) | $\delta^{18}O$ (‰, VPDB) |
|---|---|---|---|---|---|
| TKD_VB_2_35 | -6.86 | Grey blocky micrite | 18/01/07 | 3.51 | -0.68 |
| TKD_VB_2_36 | -6.76 | Grey blocky micrite | 18/01/07 | 3.09 | -0.77 |
| TKD_VB_2_37 | -6.66 | Grey blocky micrite | 18/01/07 | 2.87 | -1.35 |
| TKD_VB_2_38 | -6.56 | Blocky white micrite | 18/01/07 | 2.97 | -0.68 |
| TKD_VB_2_39 | -6.46 | Blocky white micrite | 18/01/07 | 3.23 | -1.01 |
| TKD_VB_2_40 | -6.36 | Blocky white micrite | 18/01/07 | 3.31 | -0.76 |
| TKD_VB_2_41 | -6.26 | Burrowed mottled wackestone | 18/01/07 | 3.54 | -0.88 |
| TKD_VB_2_42 | -6.16 | Burrowed mottled wackestone | 18/01/07 | 3.35 | -1.00 |
| TKD_VB_2_43 | -6.06 | Burrowed mottled wackestone | 18/01/07 | 3.35 | -0.77 |
| TKD_VB_2_44 | -5.96 | Burrowed mottled wackestone | 18/01/07 | 3.39 | -0.94 |
| TKD_VB_2_45 | -5.86 | Burrowed mottled wackestone | 18/01/07 | 3.45 | -0.90 |
| TKD_VB_2_46 | -5.14 | Grey clay | 18/01/07 | 3.30 | -1.35 |
| TKD_VB_2_47 | -5.04 | Recrystallised micrite | 18/01/07 | 3.44 | -1.85 |
| TKD_VB_2_48 | -3.98 | Grey burrowed recrystallised micrite | 18/01/07 | 3.12 | -1.53 |
| TKD_VB_2_49 | -3.88 | Grey burrowed recrystallised micrite | 18/01/07 | 2.94 | -1.17 |
| TKD_VB_2_50 | -3.8 | Grey burrowed recrystallised micrite | 18/01/07 | 2.91 | -1.25 |
| TKD_VB_2_51 | -3.7 | Grey burrowed recrystallised micrite | 18/01/07 | 2.70 | -1.26 |
| TKD_VB_2_52 | -3.6 | Grey burrowed recrystallised micrite | 18/01/07 | 2.09 | -1.87 |
| TKD_VB_2_53 | -3.5 | Grey burrowed recrystallised micrite | 18/01/07 | 2.04 | -1.69 |
| TKD_VB_2_54 | -3.4 | Grey burrowed recrystallised micrite | 18/01/07 | 2.52 | -1.36 |
| TKD_VB_2_55 | -3.3 | Cream recrystallised micrite | 18/01/07 | 2.81 | -1.64 |
| TKD_VB_2_56 | -3.2 | White blocky burrowed micrite | 18/01/07 | 2.91 | -1.63 |
| TKD_VB_2_57 | -3.1 | Grey with plant fragments | 18/01/07 | 2.88 | -1.31 |
| TKD_VB_2_58 | -3 | White recrystallised micrite | 18/01/07 | 3.09 | -1.29 |
| TKD_VB_2_59 | -2.9 | White recrystallised micrite | 18/01/07 | 2.91 | -1.53 |
| TKD_VB_2_60 | -2.83 | White recrystallised micrite | 18/01/07 | 2.35 | -1.11 |
| TKD_VB_2_61 | -2.71 | White recrystallised micrite | 18/01/07 | 2.36 | -0.93 |
| TKD_VB_2_63 | -2.62 | Thinly bedded clay rich micrite | 18/01/07 | 2.45 | -0.91 |
| TKD_VB_2_62 | -2.61 | White recrystallised micrite | 18/01/07 | 1.99 | -1.69 |
| TKD_VB_2_64 | -2.43 | Thinly bedded clay rich micrite | 18/01/07 | 2.32 | -0.91 |
| TKD_VB_2_87 | -1.33 | Bioturbated, recrystallised wackestone | 18/01/07 | 2.11 | -2.49 |
| TKD_VB_2_65 | -1.19 | Bioturbated, recrystallised wackestone | 18/01/07 | 2.13 | -1.25 |
| TKD_VB_2_66 | -0.99 | Clay micrite | 18/01/07 | 2.61 | -1.93 |
| TKD_VB_2_67 | -0.91 | Dark grey clay | 18/01/07 | 2.82 | -1.18 |
| TKD_VB_2_68 | -0.81 | Grey recrystallised wackestone | 18/01/07 | 2.87 | -0.74 |
| TKD_VB_2_69 | -0.68 | Nodular grey recrystallised wackestone | 18/01/07 | 1.55 | -1.29 |
| TKD_VB_2_89 | -0.68 | Nodular grey recrystallised wackestone | 18/01/07 | 1.64 | -1.53 |
| TKD_VB_2_90 | -0.61 | Recrystallised wackestone/packstone | 18/01/07 | 0.83 | -3.62 |
| TKD_VB_2_70 | -0.59 | Recrystallised wackestone/packstone | 18/01/07 | 1.69 | -1.95 |
| TKD_VB_2_71 | -0.5 | Recrystallised wackestone/packstone | 18/01/07 | 0.49 | -4.02 |
| TKD_VB_2_91 | -0.43 | Recrystallised wackestone/packstone | 18/01/07 | 2.17 | -3.87 |
| TKD_VB_2_72 | -0.4 | Recrystallised wackestone/packstone | 18/01/07 | -2.14 | -4.39 |
| TKD_VB_2_73 | -0.31 | Bioclastic 'wavy' packstone | 18/01/07 | 1.78 | -3.97 |
| TKD_VB_2_74 | -0.2 | Bioclastic 'wavy' packstone | 18/01/07 | 2.96 | -4.45 |
| TKD_VB_2_78 | -0.1 | Bioclastic 'wavy' packstone | 18/01/07 | 1.89 | -3.60 |
| TKD_VB_2_76 | -0.01 | Bioclastic 'wavy' packstone | 18/01/07 | 2.10 | -3.86 |
| TKD_VB_2_92 | -0.01 | Oolitic stylolitic packstone | 18/01/07 | 1.45 | -4.27 |

| Sample number | Strat. height with respect to the PTB (m) | Lithology | Date run | $\delta^{13}C$ (‰, VPDB) | $\delta^{18}O$ (‰, VPDB) |
|---|---|---|---|---|---|
| TKD_VB_2_82 | 0.05 | Oolitic stylolitic packstone | 18/01/07 | 1.16 | -3.91 |
| TKD_VB_2_84 | 0.14 | Oolitic stylolitic packstone | 18/01/07 | 1.14 | -4.08 |
| TKD_VB_2_94 | 0.16 | Oolitic stylolitic packstone | 18/01/07 | 0.97 | -5.41 |
| TKD_VB_2_85 | 0.23 | Oolitic packstone | 18/01/07 | 0.66 | -2.95 |
| TKD_VB_2_86 | 0.34 | Oolitic stylolitic packstone | 18/01/07 | 1.78 | -3.29 |
| TKD_VB_2_95 | 0.36 | Oolitic packstone | 18/01/07 | 1.53 | -3.89 |
| TKD_VB_2_96 | 0.41 | Oolitic stylolitic packstone | 18/01/07 | 1.01 | -4.21 |
| TKD_VB_2_97 | 0.51 | Oolitic stylolitic packstone | 18/01/07 | 0.69 | -5.70 |
| TKD_VB_2_98 | 0.61 | Oolitic stylolitic packstone | 18/01/07 | 0.17 | -4.75 |
| TKD_VB_2_99 | 0.71 | Oolitic stylolitic packstone | 21/01/07 | 0.29 | -4.43 |
| TKD_VB_2_100 | 0.79 | Oolitic stylolitic packstone | 21/01/07 | 0.71 | -4.67 |
| TKD_VB_2_101 | 0.91 | Oolitic stylolitic packstone | 21/01/07 | 1.07 | -4.27 |
| TKD_VB_2_102 | 1.01 | Oolitic stylolitic packstone | 21/01/07 | 0.78 | -3.93 |
| TKD_VB_2_103 | 1.11 | Oolitic stylolitic packstone | 21/01/07 | 0.67 | -4.41 |
| TKD_VB_2_104 | 1.21 | Oolitic stylolitic packstone | 21/01/07 | 0.72 | -4.49 |
| TKD_VB_2_105 | 1.29 | Oolitic stylolitic packstone | 21/01/07 | 0.96 | -4.41 |
| TKD_VB_2_106 | 1.37 | Oolitic stylolitic packstone | 21/01/07 | 0.96 | -4.68 |
| TKD_VB_2_107 | 1.47 | Oolitic stylolitic packstone | 21/01/07 | 0.85 | -4.97 |
| TKD_VB_2_108 | 1.61 | Oolitic stylolitic packstone | 21/01/07 | 0.84 | -4.50 |
| TKD_VB_2_109 | 1.71 | Oolitic stylolitic packstone | 21/01/07 | 0.97 | -4.83 |
| TKD_VB_2_110 | 1.81 | Oolitic stylolitic packstone | 21/01/07 | 1.11 | -4.56 |
| TKD_VB_2_111 | 1.91 | Oolitic stylolitic packstone | 21/01/07 | 0.98 | -4.96 |
| TKD_VB_2_112 | 1.94 | Oolitic stylolitic packstone | 21/01/07 | 0.77 | -4.74 |
| TKD_VB_2_113 | 2.05 | Oolitic stylolitic packstone | 21/01/07 | 1.02 | -5.22 |
| TKD_VB_2_114 | 2.21 | Oolitic stylolitic packstone | 21/01/07 | 0.54 | -5.11 |
| TKD_VB_2_115 | 2.29 | Oolitic stylolitic packstone | 21/01/07 | 0.91 | -5.78 |
| TKD_VB_2_116 | 2.45 | Oolitic stylolitic packstone | 21/01/07 | 0.62 | -5.35 |
| TKD_VB_2_117 | 2.52 | Oolitic stylolitic packstone | 21/01/07 | 0.74 | -5.77 |
| TKD_VB_2_118 | 2.73 | Oolitic stylolitic packstone | 21/01/07 | 0.26 | -5.92 |
| TKD_VB_2_119 | 2.8 | Oolitic stylolitic packstone | 21/01/07 | 0.30 | -4.92 |
| TKD_VB_2_120 | 2.9 | Oolitic stylolitic packstone | 21/01/07 | 0.81 | -4.76 |
| TKD_VB_2_121 | 3.01 | Oolitic stylolitic packstone | 21/01/07 | -0.41 | -5.15 |
| TKD_VB_2_122 | 3.11 | Oolitic stylolitic packstone | 21/01/07 | -0.14 | -5.48 |
| TKD_VB_2_123 | 3.18 | Oolitic stylolitic packstone | 21/01/07 | 0.07 | -4.86 |
| TKD_VB_2_124 | 3.3 | Oolitic stylolitic packstone | 21/01/07 | 0.62 | -5.33 |
| TKD_VB_2_125 | 3.4 | Oolitic stylolitic packstone | 21/01/07 | 0.20 | -5.67 |
| TKD_VB_2_126 | 3.5 | Oolitic stylolitic packstone | 21/01/07 | 0.38 | -5.39 |
| TKD_VB_2_127 | 3.6 | Oolitic stylolitic packstone | 21/01/07 | 0.21 | -5.80 |
| TKD_VB_2_128 | 3.7 | Oolitic stylolitic packstone | 21/01/07 | 0.58 | -5.64 |
| TKD_VB_2_129 | 3.79 | Oolitic stylolitic packstone | 21/01/07 | 0.16 | -5.53 |
| TKD_VB_2_130 | 3.89 | Oolitic stylolitic packstone | 21/01/07 | 0.20 | -5.42 |
| TKD_VB_2_131 | 3.99 | Oolitic stylolitic packstone | 21/01/07 | 0.35 | -4.93 |
| TKD_VB_2_132 | 4.07 | Oolitic stylolitic packstone | 21/01/07 | 0.51 | -5.33 |
| TKD_VB_2_133 | 4.17 | Oolitic stylolitic packstone | 21/01/07 | 0.65 | -5.58 |
| TKD_VB_2_134 | 4.27 | Oolitic stylolitic packstone | 21/01/07 | 0.38 | -5.60 |

# A4.3

Cross plots and isotopic variation across the shell for all the brachiopods analyzed in this study

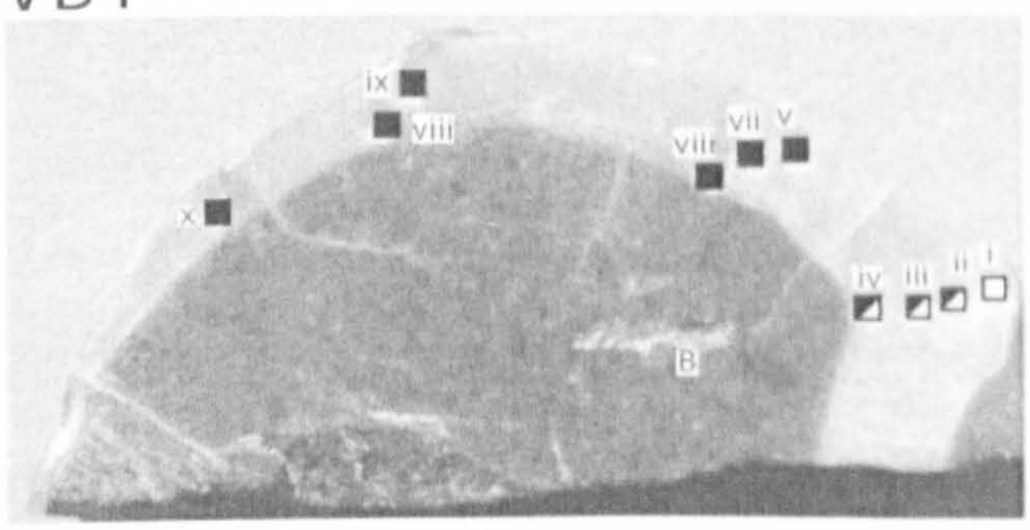



VB5
From outer to inner part of the shell (mm)
f
p
vi
v
vii
i
viii
ix
x
iv
L+SNL
NL+SNL
NL
δ18O (‰, PDB)
δ13C (‰, VPDB)
δ18O (‰, VPDB)
VB6
From outer to inner part of the shell (mm)
p
viii
iv
iii
vii
ii
iv
ix
i
L+SNL
NL+SNL
NL
δ18O (‰, PDB)
δ13C (‰, VPDB)
δ18O (‰, VPDB)
TS1
From outer to inner part of the shell (mm)
p
L+SNL
NL+SNL
NL
δ18O‰ vs PDB
δ13C (‰, VPDB)
δ18O (‰, VPDB)

# A4.4

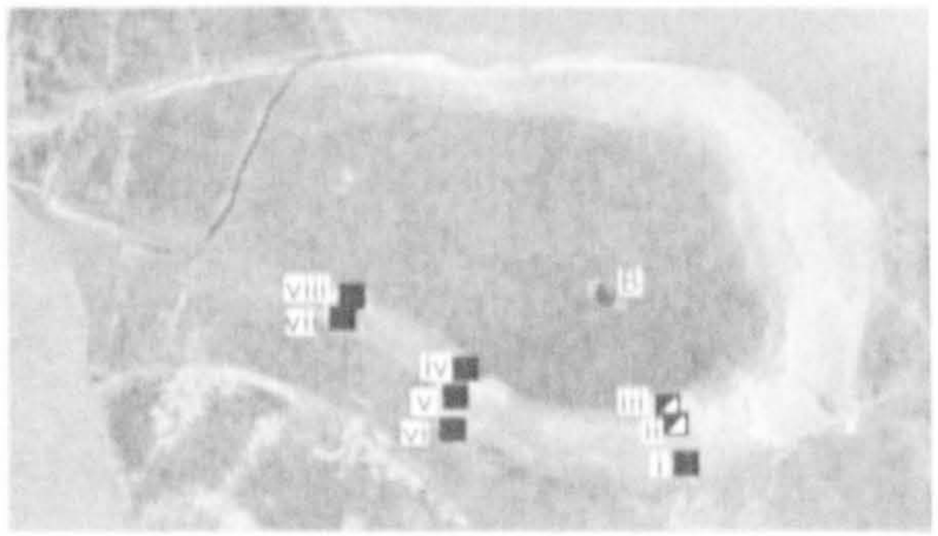
Isotope drill sites, with ornament showing the CL results from each drill site.

VB1



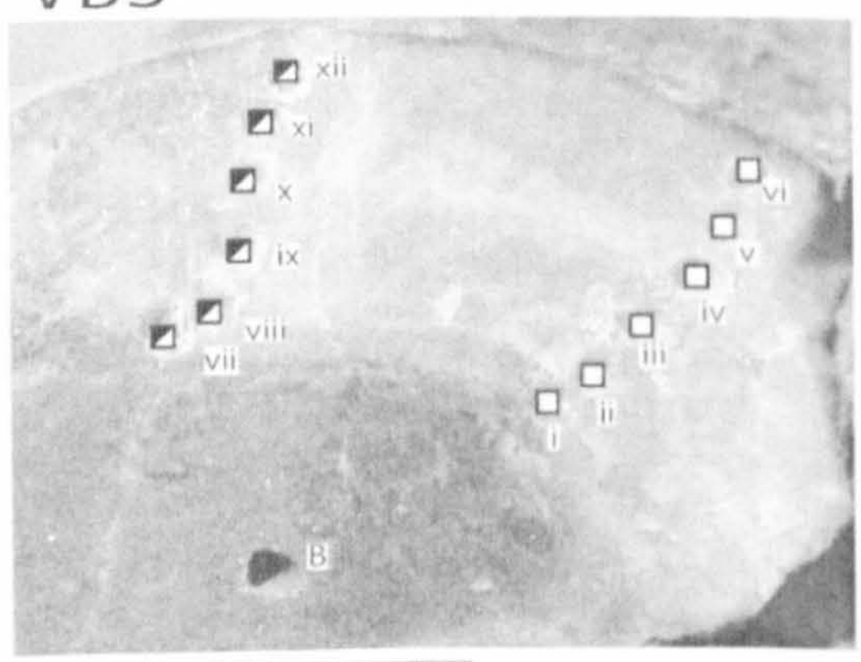

10mm

VB2



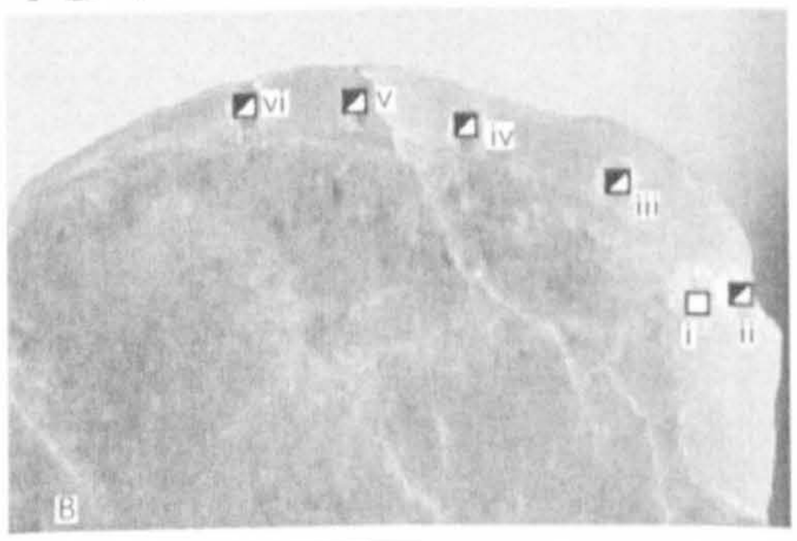

10mm

VB3



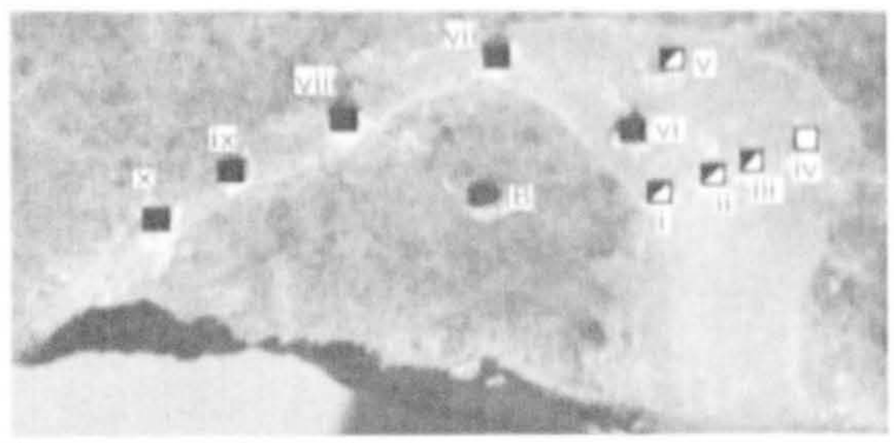

10mm

VB4




10mm

VB5

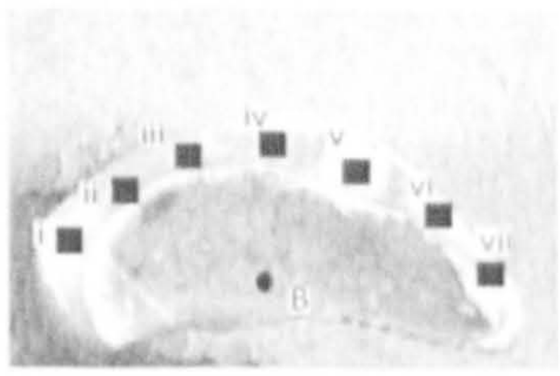



10mm

VB6


10mm

TS1




10mm

# Appendix 5

## A study of the effects of diagenetic dolomitisation on the isotopic composition of paleosols from the Italian Dolomites (Chapter 4)

## 1.1 Introduction

To investigate the effect diagenetic dolomitisation on pedogenic carbonates and their isotopic composition diagenetically altered paleosols from the Italian Dolomites were studied. This locality is close to Sass di Putia at Rü D'Antermeia (N 46°40.320', E011°49.366'). The section investigated is a Permian section of paleosols from the Val Grade formation and sits unconformably on the Hercynian metamorphic basement (Broglio Loriga *et al.* 1986). The Italian Dolomites region has been affected by a low-pressure-high-temperature metamorphic regime (Schuster and Stüwe 2008) and thus an excellent case study for as studying the effects of alteration on the isotopic signal of a paleosol. This provides also a direct comparison to the pedogenic and lacustrine dolomites from the South Urals of Russia.

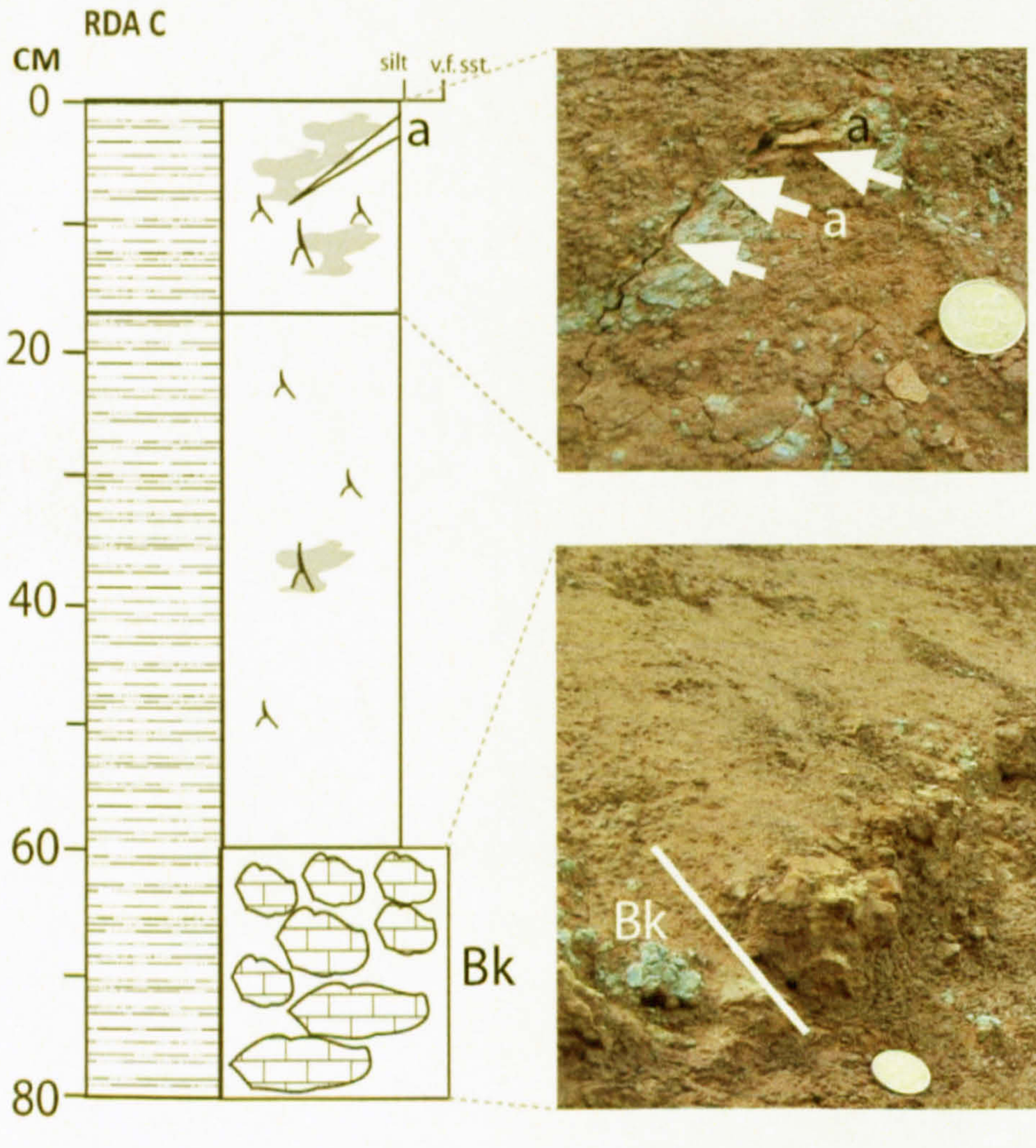



**Figure 1 Typical paleosol from Rü D'Antermeia. (a) is a thin 2mm thick calcite vain cutting though the top of the soil.**

## 1.2 Paleosols

In total 10 paleosols were identified at this locality. All contained pedogenic carbonate at stage II nodule development. The paleosols were all pale reddish brown (10R 5/4) in colour although many of the soils had pale blue green (5BG 7/2) mottled A horizons. These gleys are concentrated in the very top of the paleosols although some are drab root halos (Figure 1). The only field evidence of later alteration or recrystallisation are occasional fine carbonate veins 2mm in width. Which are filled with a fibrous calcite spar and are only present in the very top of the paleosols (Figure 1). Bases on the depth to the Bk horizon and the presence of nodular carbonate they classified as Aridisols or Petronodic Haplocalcids (see Chapter 3 for classification scheme).

## 1.3 Petrographic evidence of recrystallisation

Although the paleosols in the field do not appear to be intensely altered by later diagenesis, when the nodules are petrographically thin sectioned it is evident that the majority of the carbonate has been recrystallised.

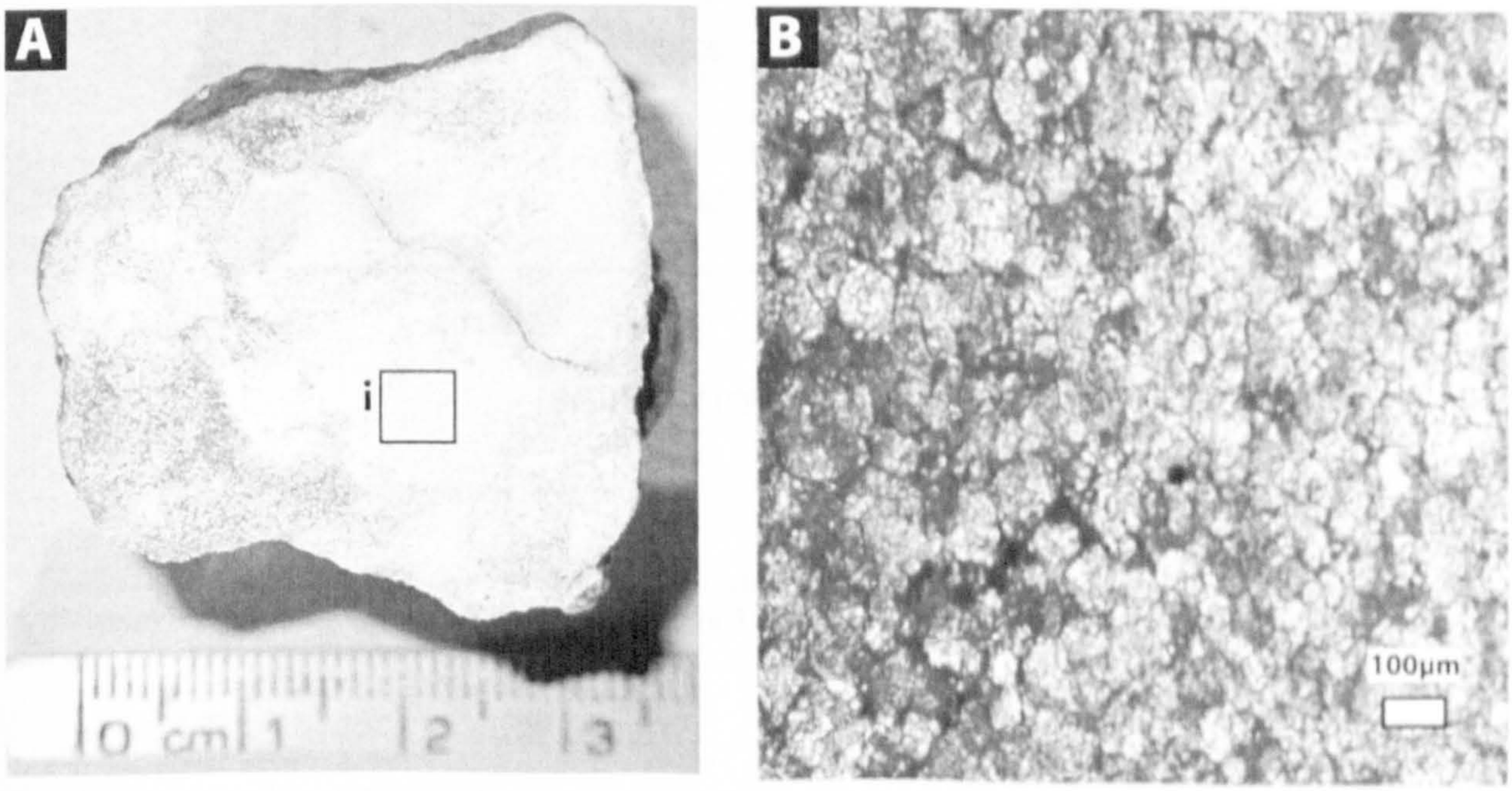



**Figure 2 (A) shows the saccharoidal texture of the carbonate material within a nodule. (B) shows a petrographic thin section of area (i) showing the equigranular nature of the crystals (B has been stained with Dixons stain and shows no reaction suggesting it is dolomite).**

Figure 2 shows the extent of the recrystallisation in the nodules. The dolomite crystals all are equigranular and show interlocking structures. This is similar to the Micro- to coarsely

crystalline, rhombohedral dolomites described by Quast *et al.* (2006) which they ascribe to burial and recrystallisation textures.

## 1.4 Isotopic results

Stable isotope analysis was carried out on 30 carbonate nodules. The carbonate material was divided into microcrystalline (crystal size ≤100μm) and spar (crystal size >100 μm). Figure 3 shows the results from the analysis (values see Table 1). Unlike the pedogenic carbonates from Russia there is no positive correlation between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ (compare with Chapter 4, Figure 4.16) also while there is a wide range of $\delta^{18}O_{carb}$ values the $\delta^{13}C_{carb}$ values are restricted to a 2‰ range.

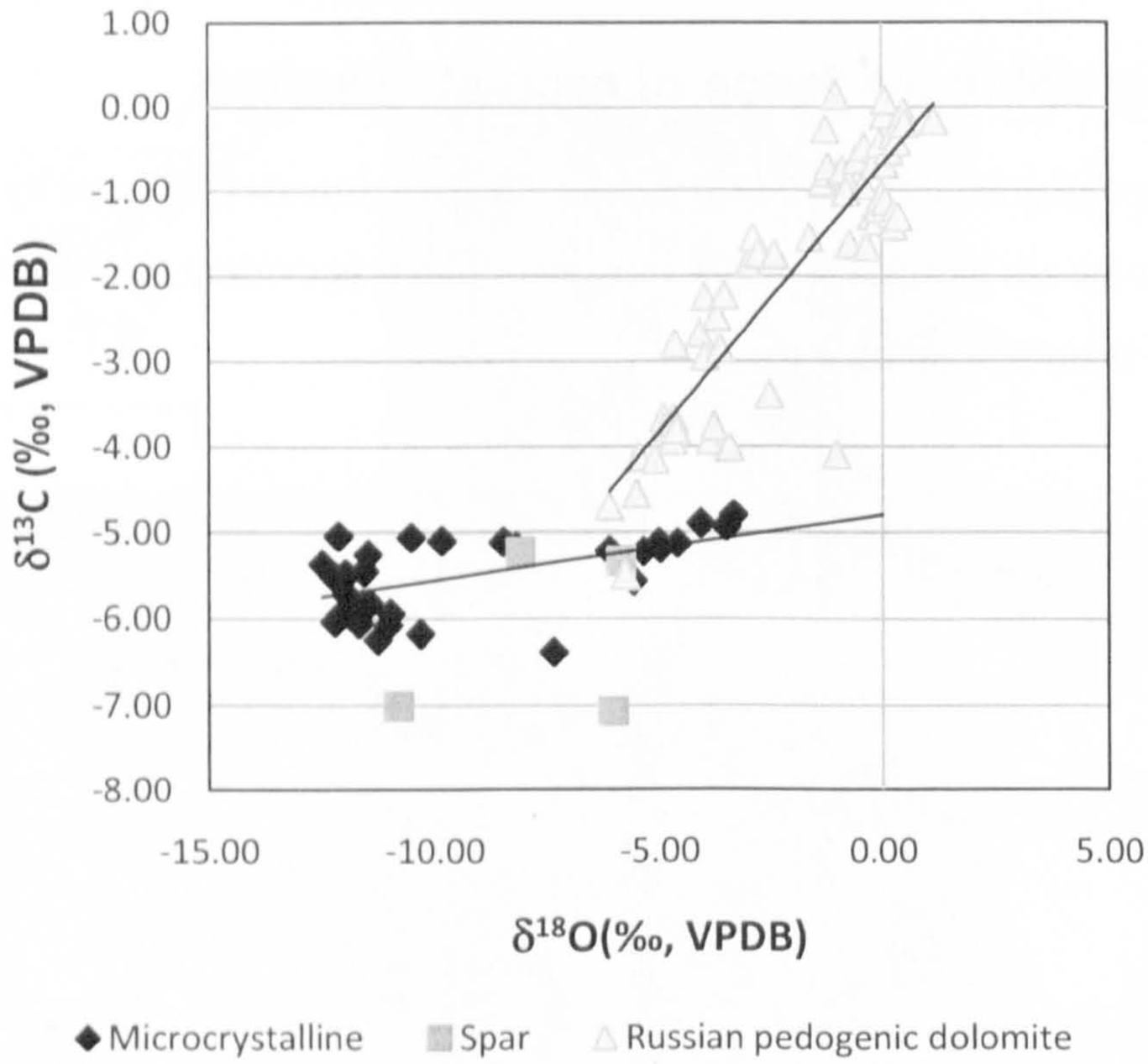



**Figure 3 Cross plot of the isotopic results from Rü D'Antermeia. Microcrystalline (crystal size ≤100μm, blue diamonds) and spar (crystal size >100 μm, red squares). Compared against the pedogenic dolomite values from the Russian sections (in grey triangles).**

There is no distinct difference between the fine (microcrystalline) dolomite and the large spar crystals suggesting the recrystallisation event effected different grain sizes in the similar ways. Other studies into recrystallisation in paleosols (e.g. Quast *et al.* 2006) have observed that diagenetically altered paleosol carbonates show little isotopic difference between the microcrystalline and spar component of a paleosol. Equally it appears that recrystallisation destroys the positive correlation between oxygen and carbon, restricting the carbon range, and

although the oxygen range is still similar to that from modern soils (Cerling and Quade 1993) there is no way of determining if these too have altered from their original composition.

**Table 1 Isotopic and classification of paleosols from Rü D'Antermeia**

| Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | Texture | microcrystalline areas ≤100µm | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB | $\delta^{13}C‰$ VPDB | $\delta^{18}O‰$ VPDB |
| Aridisol | II / III | eroded | 07RDA A.2 | 16.36 | 8 | MCR | -5.18 | -8.17 | – | – |
| | | | 07RDA A.3 | 16.22 | 22 | MCR | -6.38 | -7.34 | – | – |
| | | | 07RDA A.4 | 16.04 | 40 | MCR | -5.19 | -4.96 | – | – |
| Vertisol? | II | 70 | 07RDA C.1 | 22.07 | 258 | MCR | – | – | -5.24 | -8.07 |
| | | | 07RDA C.2 | 22.83 | 182 | MCR | -6.17 | -10.30 | – | – |
| | | | 07RDA C.3 | 22.83 | 182 | MCR | -6.07 | -11.02 | – | – |
| | | | 07RDA C.4 | 23.18 | 147 | MCR | -5.13 | -4.58 | – | – |
| Aridisol | II | 59 | 07RDA D.1 | 23.98 | 67 | MCR | -5.12 | -4.98 | -5.34 | -5.84 |
| | | | 07RDA D.2 | 23.98 | 67 | MCR | -5.23 | -5.33 | – | – |
| | | | 07RDA D.3 | 23.9 | 75 | MCR | -5.22 | -6.09 | – | – |
| | | | 07RDA D.4 | 23.9 | 75 | MCR | -4.80 | -3.33 | – | – |
| Aridisol | II | 119 | 07RDA E.1 | 24.86 | 277 | MCR | -4.93 | -3.49 | – | – |
| | | | 07RDA E.2 | 26.41 | 122 | MCR | -5.46 | -11.56 | – | – |
| | | | 07RDA E.3 | 26.41 | 122 | MCR | -5.94 | -10.96 | – | – |
| | | | 07RDA E.4 | 26.09 | 154 | MCR | – | – | – | – |
| | | | 07RDA E.5 | 27.03 | 60 | MCR | -5.12 | -8.46 | – | – |
| | | | 07RDA E.5a | 27.02 | 61 | MCR | -5.49 | -11.96 | – | – |
| Aridisol | II | 56 | 07RDA F.3 | 28.1 | 222 | MCR | -5.10 | -9.82 | – | – |
| | | | 07RDA F.4 | 28.1 | 222 | Spa | -5.72 | -11.94 | -7.07 | -6.02 |
| Aridisol | II | 70 | 07RDA G.1 | 29.58 | 74 | MCR | -6.05 | -11.68 | – | – |
| | | | 07RDA G.2 | 28.87 | 145 | MCR | -5.38 | -12.48 | – | – |
| | | | 07RDA G.3 | 28.87 | 145 | MCR | -5.05 | -12.12 | – | – |

| Classification | Calcrete stage | Depth to Bk horizon (cm) | Sample | Section height (m) | Paleosol depth (m) | Texture | microcrystalline areas ≤100µm | | Spar | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $\delta^{13}C$‰ VPDB | $\delta^{18}O$‰ VPDB | $\delta^{13}C$‰ VPDB | $\delta^{18}O$‰ VPDB |
| Aridisol | II | 32 | 07RDA H.1 | 32.8 | 91 | MCR | -5.82 | -11.44 | – | – |
| | | | 07RDA H.2 | 32.63 | 108 | MCR | -6.03 | -12.20 | – | – |
| | | | 07RDA H.3 | 32.63 | 108 | MCR | -6.24 | -11.25 | – | – |
| | | | 07RDA H.4 | 32.61 | 110 | MCR | -5.95 | -12.07 | – | – |
| Aridisol | II | | 07RDA I.3 | 32.93 | 78 | Spa | -5.83 | -11.59 | -7.01 | -10.79 |
| | | | 07RDA I.4 | 32.93 | 78 | MCR | -5.53 | -12.19 | – | – |
| | | | 07RDA I.5 | 32.87 | 84 | MCR | -5.26 | -11.47 | – | – |
| | | | 07RDA I.6 | 32.87 | 84 | MCR | -5.49 | -11.97 | – | – |