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Geochronology of salt-marsh sediments

Marshall, William Alderman

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Geochronology of salt-marsh sediments

by

William Alderman Marshall

A thesis submitted to the University of Plymouth in partial fulfilment for
the degree of

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Abstract

Salt-marsh sediments can provide important archives of past sea levels if they can be securely dated. This thesis investigates eight methods for dating salt-marsh sediments. These include traditional and established dating methods (^{14}C dating and the radionuclides ^{137}Cs and ^{210}Pb) and more novel approaches to dating the deposition of salt-marsh sediments (palaeomagnetic dating, the use of atmospheric stable lead deposition, tephra chronologies, pollen markers, SCP analysis and the use of atmospheric ^{14}C 'bomb spike' and high-precision AMS ^{14}C measurements). Sites were selected to provide contrasting sediment sequences that differed both in lithology and accumulation rates and included salt marshes from the Taf estuary (southwest Wales), the Arne Peninsula (southern England) and Viðarhólmi (western Iceland).

The investigations in the Taf estuary produced the first palaeomagnetic chronology from a salt marsh. From the Arne Peninsula this thesis reports the first successful use of bomb-spike calibrated ^{14}C analyses in a salt marsh as well as high-precision AMS ^{14}C ages for the 'problem' period AD 1700-1950. Stable Pb analysis at all three sites produced a number of chronological markers that signalled the timing of increases in industrial Pb emissions, and the later use of Pb petrol additives during the 20th century. In addition, a unique isotopic signal, attributed to the working of Pb metal during the height of the Roman Empire in Europe, was found in the Icelandic sediments.

The radionuclides ^{210}Pb and ^{137}Cs produced precise chronologies for the last 100 yr in the Taf estuary. However, post-depositional mobility of ^{137}Cs on the Arne Peninsula and low ^{210}Pb concentrations at Viðarhólmi prevents the construction of reliable ^{210}Pb and ^{137}Cs chronologies. In contrast, the use of tephra at Viðarhólmi, and pollen and spheroidal carbonaceous particle markers on the Arne Peninsula, showed great potential as independent unique-event dating tools that could be used to constrain conventional ^{14}C calibrations. Finally, the chronological information produced by all the individual methods was combined to construct an integrated chronology for each site. This approach significantly reduced age uncertainties and produced higher resolution, and more robust, salt-marsh sedimentation histories.

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Author's Declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award without the prior agreement of the Graduate Committee.

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This study has made significant contributions to papers published in scientific journals and the author has presented work at a number of relevant scientific seminars and conferences.

Journal papers contributed to:

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Gehrels, W. R., Szkornik, K., Bartholdy, J., Kirby, J. R., Bradley, S. L., **Marshall, W. A.**, Heinemeier, J., and Pedersen, J. B. T. 2006. Late Holocene sea-level changes and isostasy in western Denmark, *Quaternary Research*, 66, 288-302.

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Marshall, W., Gehrels, R. and Bryant, C. 2005. The use of the atmospheric bomb ^{14}C record as a dating tool in sea-level studies: an example from the Arne salt marshes, Poole Harbour (Dorset, England). *Late Quaternary Coastal Changes: Sea Level, Sediment*

Forcing and Anthropogenic Impacts. INQUA & IGCP-495 joint meeting. Dunkerque, France, 28th June - 2nd July 2005.

Marshall, W., Gehrels, R. and Bryant, C. 2005. The atmospheric ^{14}C 'bomb spike': an independent dating tool for recent salt-marsh sediments? In: Buscombe, D. (ed.), The Quaternary Research Association Fourth International Postgraduate Symposium Abstract Book, School of Geography, University of Plymouth, UK, August 31st to September 2nd (2005), p. 29.

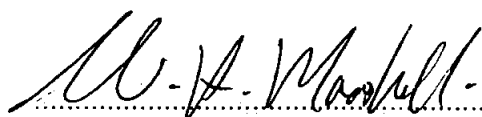
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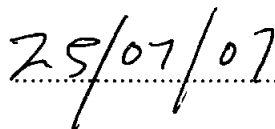
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Geochronology of salt-marsh sediments

Chapter 1

Introduction

This thesis reports an investigation into the use of a number of different chronological tools, or dating methods, applied to salt-marsh sediment sequences. The study of salt-marsh sediments has proved to be invaluable for Holocene sea-level studies. Beyond the range of tide-gauge records, salt-marsh sediment sequences represent one of the best high-resolution archives of palaeosea-level information available (Tooley, 1992; Allen, 2000; Adam 2002; Long, 2003).

It is known that long-term sea-level movement and climate change are coupled, but to investigate this linkage the sea-level change data must be supported by a precise, high resolution chronology (Gehrels *et al.*, 2006). Many sediment-based records lack the temporal resolution required to validate properly the new generation of fully coupled climate and oceanic response models (Maslin and Berger, 1997; Gregory *et al.*, 2001). In particular, there is a deficit of robust geo-records of past sea level which have good age control at the critical decadal-centennial scale. This project seeks to help resolve part of this problem by determining which dating methodologies can be best used to produce precise, high resolution, sea-level histories from salt-marsh sediments.

1.2. The dynamics of salt-marsh environments

Salt marshes are typically found in estuaries and sheltered embayments between intertidal mudflats and the extreme upper limit of marine influence (Allen, 2000). Their fine minerogenic and organic-rich sediments are reputed to hold unique evidence of the 'sedimentary and palaeoecological record of coastal and sea-level fluctuations during the recent geological past' (Tooley, 1992). Salt marshes are widely distributed from warm temperate to polar latitudes in low energy locations on accreting coasts, and preferentially form extensive developments on shores with a shallow landward gradient (Pethick 1992).

Salt marshes are maintained by regular tidal flooding. These periodic inundations act in two important ways. Firstly, each flooding event supplies vital nutrients,

suspended clays, silts and detrital organic material to the marsh surface. These sediments become incorporated with the decaying litter of the halophytic plants that colonise the marsh surface to form the emerging salt-marsh platform (Allen and Pye, 1992). Secondly, the height, duration and frequency of tidal flooding will control the submergence, and thus the environmental salinity gradient, of the marsh (Allen 2000). Different species have different ecological tolerances and requirements and, therefore, an altitude dependent sea-landward zonation of the flora and fauna that inhabit the surface of the salt marsh is produced. The zonation reflects the ability of each species to tolerate exposure to submergence and intertidal drying, and their preference for marine or terrestrial conditions (Figure 1.1).

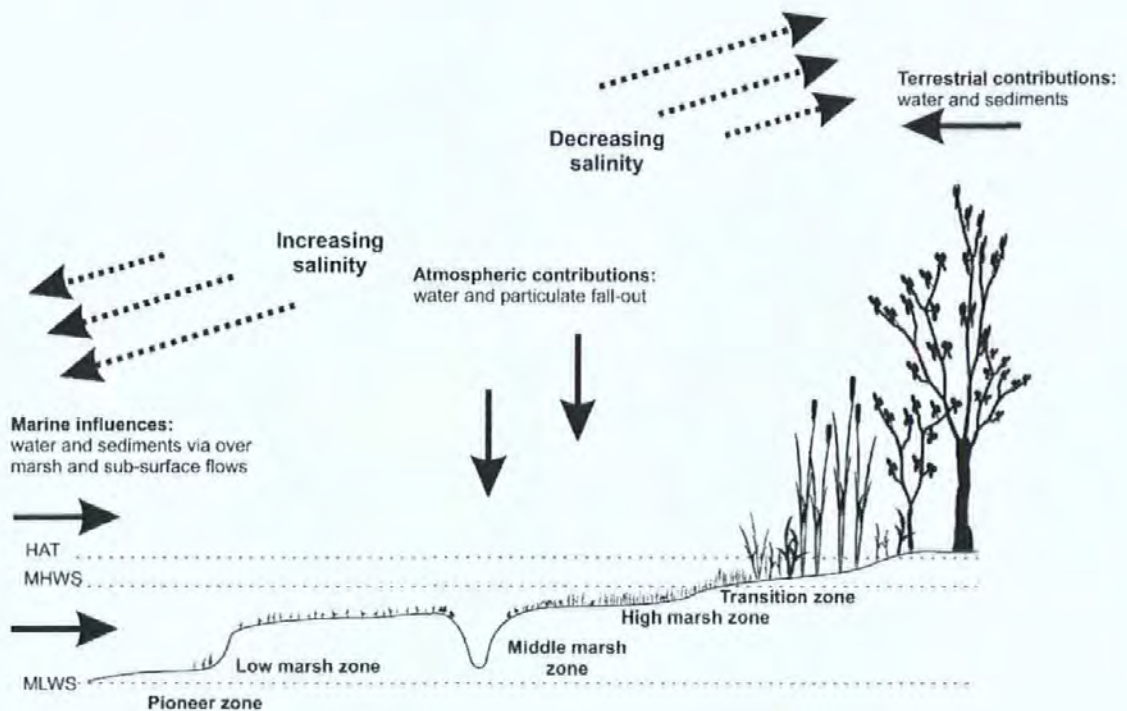


Figure 1.1. Salt-marsh plant succession, zones, sediment sources and tidal flooding. After Ranwell, (1972). HAT = Highest Astronomical Tide; MHWS = Mean High Water Springs; MLWS = Mean Low Water Springs.

A salt marsh is a dynamic environment controlled by a number of forcing factors (Allen 2000). It will evolve through time and will respond, to a lesser or greater extent, to changes in the rate and direction of sea-level movement, fluvial inputs, the size of the tidal prism, the rate of bioproduction and the available sediment budget. As a salt marsh matures, and its relative altitude to sea level increases, sedimentation will decrease as the number of over-surface tidal inundation events declines (Allen 2000). Slowly, as the marsh surface becomes elevated above the range of normal spring tides, sedimentation decreases and vertical growth may stop.

Gehrels *et al.* (2005) propose that the relative height of a salt-marsh surface is a function of sea-level movement and sediment accretion, balanced against sediment erosion and autocompaction. If sea level rises steadily, and all other factors remain in equilibrium, the marsh surface will maintain its relationship with sea level. If the available accommodation space increases, a transgressive overlap may form as the relative sea-level rise outpaces sedimentation. This typically happens after an acceleration in sea-level rise, or a reduction in the sediment budget, but may also result from a relative downward movement of the marsh surface through autocompaction or crustal down warping. In contrast, a regressive overlap is formed when the marsh surface is elevated relative to local sea level. This may occur because of an increase in the sediment budget, a fall in sea level or an increase in marsh bioproduction (van de Plassche, 1991; Jennings *et al.*, 1995; Allen, 2000).

1.3. Salt marshes as archives of palaeosea-level information

The close coupling of tidal inundation, sea level and the relative height of the ancient marsh surface means that palaeosea-level changes can be determined by the analysis of salt-marsh sediment sections. The lithostratigraphical analysis of salt-marsh sections can yield a considerable amount of data, but what makes these deposits so important for recent sea-level studies are the sub-fossil remains of micro organisms, like foraminifera and diatoms, that normally live on the marsh surface (Allen, 2000). These organisms exist in large numbers and many species have distinct species-specific ecological tolerances. They will respond to changes in tidal height by changing both the species present, and the proportion each species contributes to the total population. Each species will maintain its population maximum on a salt marsh where the environmental variables like salinity and pH, best meet its ecological requirements. The location of this population maximum, or optimum, can be conceptualised as a location along a gradient, the end members of which define the range of values found at a site for a particular environmental variable.

It is possible to analyse the fossil populations in a salt-marsh sequence, compare their characteristics to similar modern populations and establish where each fossil population would have existed along an environmental gradient of interest. In this way, the past relationship of the marsh surface to tidal flooding and salinity can be derived. This information can be used to track changes in palaeosea-level because

of the close interaction between tidal flooding, salinity and sea level (Allen 2000). Recent sea-level investigations that have applied this approach include the studies of Zong and Horton (1999) and Plater *et al.* (2000) who used diatoms, and Gehrels (2000), Haslett *et al.* (2001) and Gehrels *et al.* (2002) who used foraminifera.

1.4. Salt-marsh chronologies

The chronology of salt-marsh sediment sequences has been traditionally provided by ^{14}C dates. Increasingly this method is being combined with ^{210}Pb dating for the very recent record. However, it is now evident that both ^{14}C and ^{210}Pb dating suffer from a number of limitations, and several issues restrict the applicability of these methods for high resolution, late Holocene sea-level studies. These issues and limitations will be explored in more depth in Chapter 3 and Chapter 4, but in brief they are:

- Lack of suitable samples for ^{14}C dating. Radiometric carbon dating requires an uncontaminated organic carbon sample of sufficient mass. Ideally for sea-level reconstructions these samples should be individual and identifiable terrestrial plant macrofossils (See Gehrels, 1999; Edwards, 2001; Gehrels *et al.*, 2006). Unfortunately, many UK and Northern European salt-marsh sequences are very minerogenic and often do not contain sufficient material that is suitable for ^{14}C dating.
- The inherent uncertainties associated with the calibration of ^{14}C ages into calendar years. The ratio of ^{14}C to ^{12}C in the atmosphere is not constant through time (Suess, 1965; Stuiver and Braziunas, 1998). As a result the calibration curve for the Holocene has a number of plateaus and sections that can produce ambiguous dates and large uncertainties during certain time periods (Stuiver *et al.*, 1998; Telford *et al.*, 2004).
- The precise dating of samples less than 300 yr old. This is problematic and often viewed as impossible when using conventional radiocarbon methods (Turetsky *et al.*, 2004). There are three main reasons for this. (1) The best precision that is possible with ^{14}C dating of single recent samples is often inadequate. For example, the uncertainty factor may be ± 50 yrs on an calibrated age estimate of 200 yr BP. (2) Since the rise of industrial activities in the early-mid 1800s the burning of fossil fuels has released large volumes of old carbon into the atmosphere, thus reducing the ratio of ^{14}C to ^{12}C in the

atmosphere. (3) The fall-out from thermonuclear detonations since 1945 has achieved the opposite effect and has enriched the atmosphere with ^{14}C .

- The ^{210}Pb dating method only covers the last 100-150 yrs, and there are some concerns surrounding its independent use, particularly in marine sediments (Smith, 2001; Thomson *et al.*, 2002). Though it is possible to extrapolate dates back in time this is far from ideal. Beyond 1900 the chronology is based on modelled age estimates that rely on sedimentation rates remaining constant within that section of the sequence (Abril, 2004).

1.5. Thesis aims and objectives

The objective of this project is to develop novel, and improve existing, dating methods for salt-marsh sediments that, in the first instance, are suited to being used in high-resolution reconstructions of late Holocene sea-level change. One prime aim is to try and surmount some of the problems of dating young salt-marsh sediments, practically in the critical 25-500 yr BP period. Part of this work is an evaluation of the ^{14}C dating method for this period. A second crucial aim is to reduce the present reliance on the direct ^{14}C dating of the sediments of interest, and develop dating methods that are independent of the need for organic material. Concurrent with these primary aims it is intended that this work will help to provide more precise higher resolution salt-marsh chronologies, and reduce the need for excessive interpolation between isolated chronological markers.

Three categories of dating methodologies are to be investigated:

1. **Radioactive dating methods.** Three dating methods are investigated that use radioactive materials to produce deposition age estimates for sediments. These methods are the radiometric methods, ^{14}C dating, ^{210}Pb dating, and the fallout event method that use the history of the deposition of artificial radionuclides.
2. **Palaeomagnetic dating.** This unique-event method uses the record of past changes in the geomagnetic field, preserved in the sediments, to obtain the deposition timing of fine-grained minerogenic sediments.

3. **Stable particle chronologies.** These are also unique-event dating methods, and examined here as salt-marsh sediment dating tools are the history of regional atmospheric lead pollution, volcanic ash falls, pollen records, and the fall-out of industrial black carbon or spheroidal carbonaceous particles (SCPs).

In all some eight dating tools are examined that have not been (fully) applied in salt-marsh environments. Each of the dating techniques will be tested in two or more of the three sites selected for this study, and the chronologies obtained using the different techniques will be compared. The focus of this investigation is on sediments deposited during the last two millennia, but there is the potential for some methods to be used over longer time scales. In addition, although the focus of this study is the dating of salt-marsh sediments, the methodologies investigated here can be used in other sediments and other types of palaeoenvironmental investigation.

1.6. Thesis structure

This thesis is structured to present the different dating methodologies in individual chapters, each containing a review of the technique, a description of how it was applied and the results obtained. After the general introduction to the research topic the three study sites are described in terms of location, physical characteristics and lithology. To facilitate inter-site comparisons three standard sediment measurements, grain size, total carbon with loss-on-ignition and magnetic susceptibility were carried out and the results presented as part of the site descriptions in Chapter 2. Then the results of the use of the different dating methodologies are presented. Although not strictly one of the experimental methodologies, the use of radiocarbon dating is evaluated at each of the study sites in Chapter 3. This is followed by the sections on radionuclide dating, palaeomagnetic dating and the other experimental dating techniques. These sections report the use of each experimental dating method, apart from the use of tephra in Iceland, at two or more sites. In Chapter 8 the data are integrated to produce chronologies for each individual site, and finally the overall conclusions are presented in Chapter 9.

Chapter 2

The study sites

This chapter will describe the factors that must be considered in the selection of a salt-marsh site for a sea-level study, and why particular areas of an individual marsh will produce a better palaeosea-level record. It will then introduce the three salt-marsh sites used in this study. In these sections site descriptions, detailed sediment logs and other physical data will be presented for each site.

2.1 Salt-marsh sites and sea-level studies

2.1.1. The ideal site. Not all salt marshes are created equal, and not all salt-marsh sites are suitable for sea-level investigations. Therefore, the three sites used for this study (Figure 2.1) were selected after careful consideration of what constitutes an ideal salt-marsh site for reconstructing sea levels. A number of issues have to be considered in the selection of suitable site. For example, a marsh may be too young to provide the length of record required, or its stratigraphy may have been affected in the past by episodes of anthropogenic activity. Land surface disruption, like mining operations or deforestation, may dramatically increase the fluvial sediment flux. In some estuarine environments this has resulted in a rapid acceleration in local salt-marsh accretion rates (Berry and Plater, 1998; Pirrie *et al.*, 1999; Allen 2000). Major catchment disturbance can decouple the vertical growth of the marsh surface from the direct control of tidal inundation, therefore severely reducing the suitability of a site for palaeosea-level investigations.

In addition to human influences, some natural marsh-building dynamics can also disrupt the stratigraphy in a salt marsh. In a typical mature salt marsh the higher zones will contain abandoned creek systems and old salt pans. Once these drainage system become inactive they are filled in with material which is non-contemporaneous to the sediment matrix of the surrounding marsh. This local infill by younger sediments can severely disrupt the stratigraphy in the back-marsh zone. Other areas of disrupted stratigraphy can be found near the seaward margin of the marsh. In this forward zone, sections may be subjected to episodes of wave erosion during periods of increased storminess. Subsequently when the prevailing conditions once again allow the continued lateral expansion of the marsh platform

these sections may be rebuilt incorporating both new and re-worked older sediments (Allen, 2000).

2.1.2. Marsh zonation and sea-level studies. When a suitable salt-marsh is found, selecting the individual sampling sites needs careful consideration. Not all sections of a marsh are as good for palaeosea-level investigations as others. Within a typical salt-marsh the preferred area for reconstructing past sea level is the highest area of the marsh. This is because the most sensitive area of a salt marsh to changes in relative sea levels is the zone flooded only by uppermost extremity of the tidal inundation (Allen, 2000). In this transition zone (Figure 1.1) there is a progressive altitude-dependent shift from a full terrestrial, fresh water environment to one of increasing salinity and more marine conditions. Any small changes in sea-level height will result in a corresponding migration of this narrow transition zone up or down the coastal slope. This means that the transition zone is the most ecologically responsive to changes in sea level.

The flora and fauna that inhabit the transition zone have evolved to endure the stress of living in an environment subjected to brief periods of tidal flooding followed by prolonged periods of exposure. Some creatures have become adept at tolerating wide ranges in the values of the physical variables which are linked to tidal inundation, like salinity and pH. Other creatures are more sensitive and have become specialised. These species will seek out the vertical location that best allows them to flourish, and the more sensitive the organism the narrower the range of the conditions it can tolerate. So this means that some highly specialised species may flourish only in a narrow vertical range in the transition zone and this produces a distant 'staircases style' zonation in the species assemblages of some organisms. To be successful and flourish in the transition zone species assemblages have to migrate up, or down, the coastal slope in response to changes in local sea level to maintain their ideal environmental conditions.

One intertidal group of micro organisms that is now known to exhibit this vertical zonation of species is the benthic foraminifera. Pioneering investigations in North America marshes by Scott and Medioli (1978, 1986) identified a distinct vertical zonation of salt-marsh foraminifera which they related to marsh altitude and tidal flooding. They found the assemblages from the high marsh existed in some sites only in a narrow 10 cm zone at the top of the tidal range. A much wider altitude

range was found in the foraminiferal assemblages from the lower marsh zones. A similar system of zonation, controlled by altitude, tidal flooding and salinity, has been found in the populations of foraminifera in other coastal regions (Horton *et al.*, 1999; Haslett *et al.*, 2001; Ceareta *et al.*, 2002; Gehrels *et al.*, 2005; Gehrels *et al.*, 2006), and this altitude-specific zonation within a population is not confined to foraminifera. This phenomenon is evident in the distributions of salt-marsh dwelling diatoms (See Zong and Horton, 1999; Horton *et al.*, 2004; Caballero *et al.*, 2005; Szkornik *et al.*, 2006), and has also been demonstrated in testate amoebae (Gehrels *et al.*, 2001; Charman *et al.*, 2002).

In summary, altitude-specific flora and micro-faunal assemblages from the higher marsh zones are found to occupy a much narrower vertical range than assemblages found in lower marsh zones. This indicates that when using salt-marsh micro-faunal analysis to construct sea-level index points the best precision in altitude will be obtained by the analysis of sediments from the highest sections of the marsh. This equates to sites at, or near to, the upper limits of marine influence. Therefore, this zone is targeted by the present investigation.

2.1.3. The three study sites. After consideration of the factors outlined in Section 2.1.2 two salt-marsh sites in the UK and one in Iceland were selected (Figure 2.1). The sites selected were;

1. The Taf Estuary in Carmarthenshire, South Wales.
2. The Arne Peninsula, in Poole Harbour, Southern England.
3. Vðarhómi salt-marsh, Western Iceland.

The sites chosen provided a range of accumulation rates and sediment ages, and offered a range of lithologies and tidal ranges (Table 2.1). These sites also represent definitive examples of three different salt-marsh types as defined by Pye and French (1993); 1) estuarine fringing marsh, 2) restricted embayment marsh, 3) open embayment marsh, and the inclusion of the Icelandic site offered the opportunity to use tephra as a dating tool.

Site	Port	Spring range	Neap range
Taf Estuary, South Wales: 51° 46'N 004° 25'W	Ferryside, eastern Towy mouth (Milford Haven)	6.6 (6.3)	2.1 (2.7)
Arne Peninsular, Poole Harbour, Southern England: 50° 41'N 02° 02'W	Arne Peninsular (Poole Harbour)	1.2 (1.6)	0.4 (0.5)
Viðarhólmi, Western Iceland: 64° 47'N 22° 27'W	Borgarnes (Reykjavík)	3.8 (3.8)	1.6 (1.7)

Table 2.1. The tidal ranges at the sites. Data from Admiralty Tide Tables (2004) with secondary port corrections applied. Ranges in metres, with primary port names and data shown in parentheses.

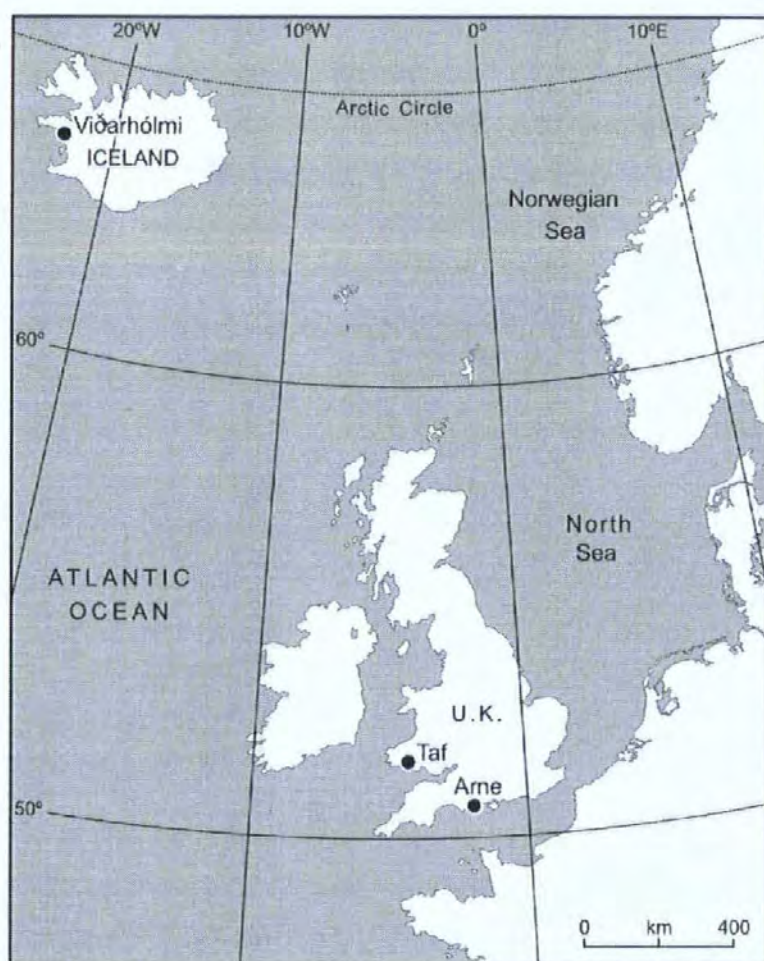


Figure 2.1. The regional location of the three salt-marsh study sites.

2.2. Field work and sediment sampling

To minimise sediment disturbance and maintain stratigraphic integrity it was decided to use sediment blocks, or monoliths, instead of cores. This meant that at the Taf and Arne sites pits had to be dug, but at Vðarhómi it was possible to sample an existing exposure in a creek bank. The salt-marsh surface at each sample site was surveyed to geodetic datum using a Zeiss total-station survey system with a closing error of less than ± 2 cm. At each site, once a clean and vertical exposure had been cut, stainless steel boxes, 60 X 6 X 12 cm, were arranged to give a minimum of 10 cm overlap (See Figure 2.3C), and driven into the sediments. During this process the boxes were kept vertical and aligned to azimuth. Once full penetration had been achieved the boxes were dug without disturbing the contents and, after cleaning, triple wrapped in plastic film. They were then transported in air-tight heavy duty PVC sleeves, and were subsequently kept in dark cold (-4°C) storage.

All steps to prevent air-borne and other contaminations during sampling were taken, and the sediment columns were resealed in plastic sleeves after each operation. The sediments were only sampled under clean-room conditions using plastic and non-magnetic surgical grade tools. The sediment columns were sequentially sampled from the surface to the base at 2 cm and 1 cm intervals as required for each of the different analysis. In addition, the Taf sequence was also sampled at 0.5 cm intervals from 0 cm to 15 cm specifically for geochemical analysis. Standard laboratory methods were used to measure grain size, total carbon content and low-field magnetic susceptibility values. These data can be found in Appendix 1. The details of any analytical work associated with the each dating method reported in this thesis are given in each specific chapter, and, where appropriate, any data not presented in these sections are tabulated in Appendix 2.

2.3. South Wales

2.3.1. The Taf Estuary site. This salt marsh is located near the confluence of the Towy and the Taf estuaries in south Wales across the valley from the village of Laugharne (Figure 2.2). It is protected from the direct influence of the open sea in Carmarthen Bay by an east-west trending glacial moraine, and can be categorised (Pye and French, 1993) as an estuarine fringing marsh. Extensive salt marshes, 200-400 m wide, fringe the left bank of the estuary for some 7 km north of the moraine. There is a significant fluvial influence in this estuary, and its proximity to the Bristol Channel ensures it experiences a macro tidal range (Table 2.1). The vegetation in the immediate vicinity of the sample site is a main cover of *Puccinellia maritima* with scattered tussocks of *Juncus maritimus* (See Figure 2.3A) and *Atriplex portulacoides* in the low creeks which changes abruptly to a broad stand of dense *Phragmites australis* inshore. The marsh is delimited on the landward side by a banked field boundary with agricultural pasture land beyond. The modern marsh is lightly free-grazed by sheep at the sample site (SN 315 109), but 1-2 km to the north of this location evidence of historic land claim, enclosure and extensive use of the salt marsh as pasture can be seen.

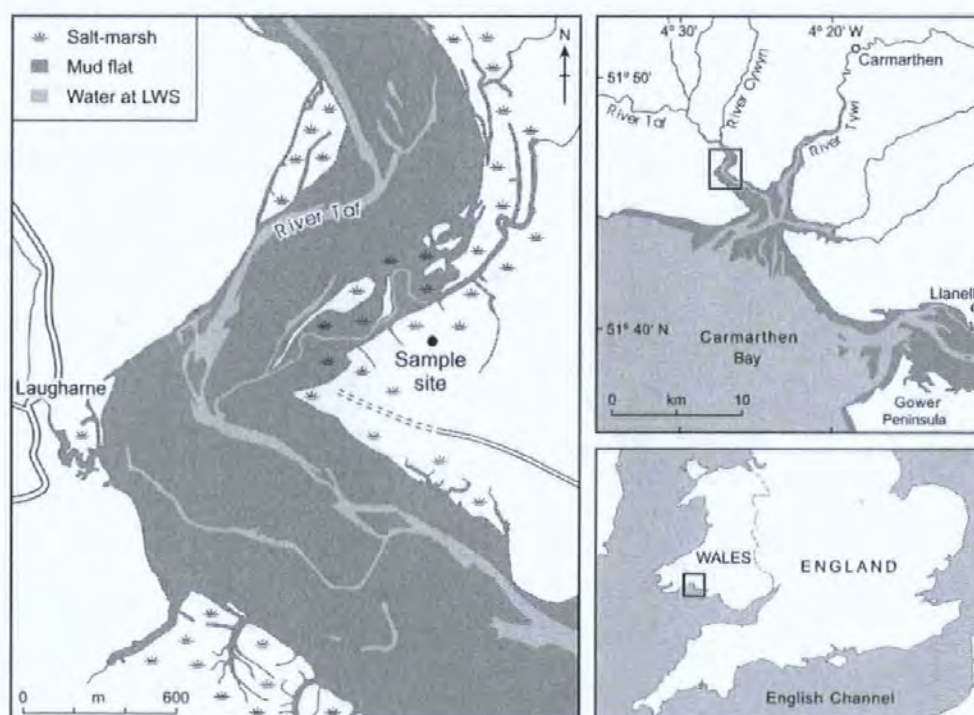
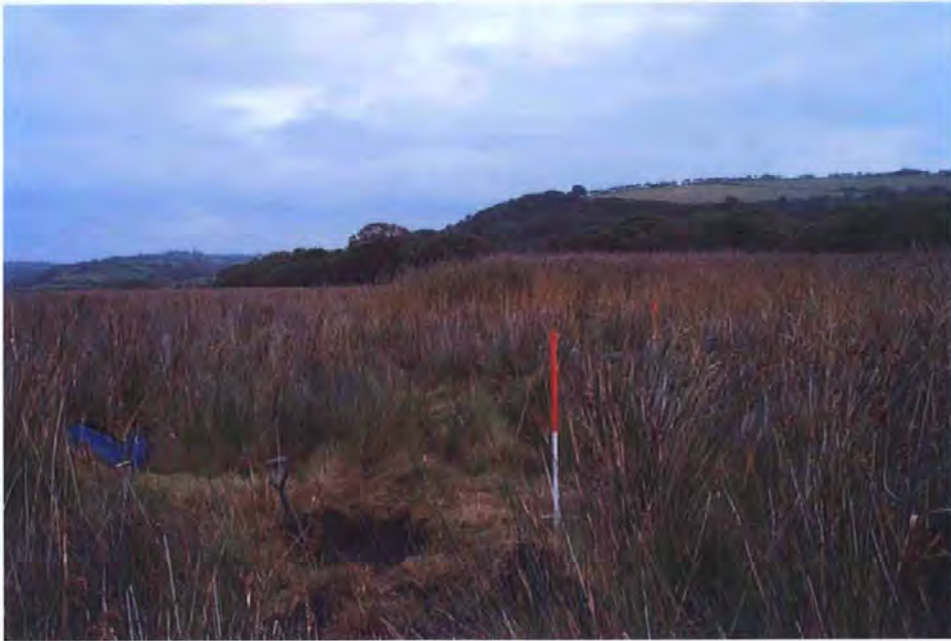


Figure 2.2. The location of the Taf site in South Wales.



A



B



C

Figure 2.3. Photographs of the 2002 and 2003 Taf sample pit site. Photograph A shows the view over the sample site looking northeast. Clumps of *Juncus maritimus* are present in the foreground and to the left in the photograph, and an extensive cover of *Phragmites australis* reeds starts immediately beyond the first red and white ranging pole. B shows the 2002 pit and the surface cover of *Puccinellia maritima* and C shows the stainless steel monolith boxes being positioned in the 2003 pit. White ruler is 1 m.

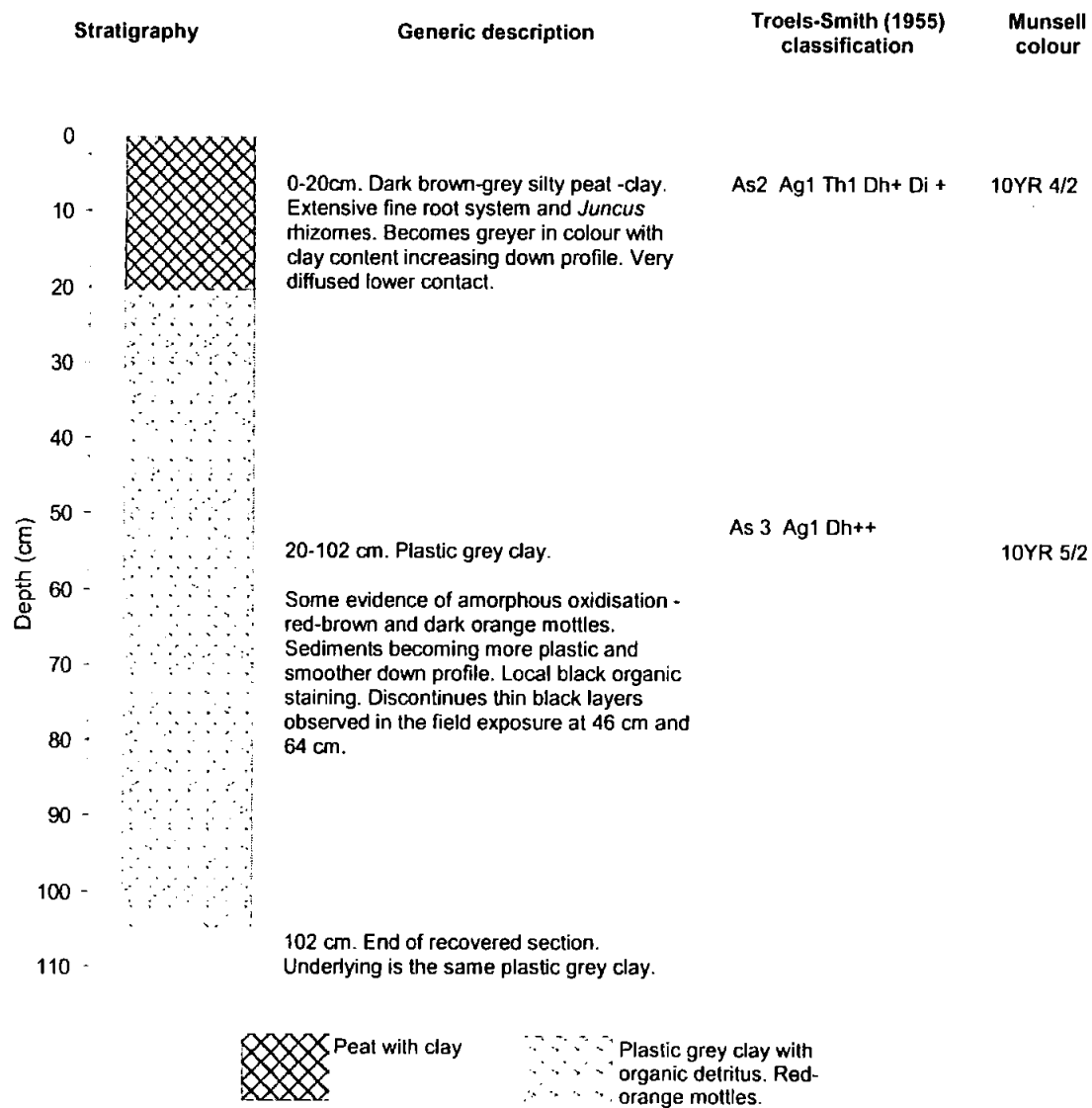
The bedrock geology is Millstone Grits and Old Red Sandstone (George 1970), with local coastal outcrops of red and grey carbonate-rich shales and mudstones observable near the mouth of the estuary. There are no metalliferous veins or ore bodies within the catchment, and all known prehistoric and historic Welsh metal-mining centres are to the north and east of this area (Dutton and Fasham 1994; Jenkins 1995; Timberlake 1990, 2001; Rosen and Dumayne-Peaty, 2001). This region was extensively glaciated in the Pleistocene and has a scattered cover of glacial and glacial-fluvial deposits of mixed lithologies. There is some local small-scale extraction of stone and aggregates in the catchment, but there is no history of metal-based industry or other pollution sources in the area. The dominant modern land use is agriculture, with some scattered plantations of conifers.

Shennan and Horton (2002) propose a mean sea-level rise of 0.5 mm yr^{-1} for the late Holocene in this region, but they emphasise that this figure is based on the limited number of sea-level index points for South Wales produced by Heyworth and Kidson (1982). Previous work by W. R. Gehrels (Unpublished data) has produced AMS ^{14}C and ^{210}Pb data from a core taken adjacent to the site of the 2002 pit. This work included a high resolution foraminifera analysis which found a fossil assemblage indicative of a high salt marsh environment throughout the upper 1 m of the sediments, and the associated ^{14}C dates indicated that the sediments at 108.5 cm depth had been deposited around 3.7 ka Cal yr BP. No significant vertical displacement existed between the surface of this core and the top of the sample pits, and so these data are presented in this thesis.

2.3.2 The Taf sediments. A 105 cm sediment monolith (Figure 2.4), Taf-02, was obtained from a pit dug in the high-marsh in November 2002. The surface of this monolith was surveyed in as 4.57 m OD. An independent replicate section, Taf-03, was obtained in 2003 from an adjacent pit located 5 m west, and was an identical section (Figure 2.3), with no vertical off-set in the surface or lithological boundaries. This second section was obtained primarily to test the reproducibility of the palaeomagnetic analysis (See Chapter 5). Concurrent to the digging of the 2002 field pit the marsh sediments were probed and logged along a shore-seaward transect using a narrow-bore gouge corer (Figure 2.5).

The sediments are low in organic carbon and are dominated by silt-sized grains (Figure 2.6). The dominant foraminifera species present in the sediments are indicative of a high salt-marsh e.g., *Jadammina macrescens* and *Miliammina fusca*

(W. R. Gehrels unpublished data). The section is homogenous minerogenic silty clay at depth with an increase in the organic fraction toward the surface above 30 cm. There is a corresponding fall in magnetic susceptibility values toward the surface (Figure 2.6).



Key to Troels-Smith (1955) sediment classifications used

Ag = <i>Argilla steatodes</i>	< 0.002 mm clay	Gg = <i>Grana glareosa</i>	2-20 mm gravel
As = <i>Argilla granosa</i>	0.002-0.06 mm silt	Th = <i>Turfa herbaceous</i>	Herbaceous peat
Dh = <i>Detritus herbosus</i>	Plant fragments > 2 mm	Tl = <i>Turfa lignosa</i>	Wood peat
Di = <i>Detritus lignosus</i>	Woody fragments > 2 mm	Sh = <i>Substantia humosa</i>	Humified organic matter
Ga = <i>Grana arenosa</i>	0.6-2 mm sand		

Figure 2.4. Stratigraphic log and description of the Taf-02 sediments. The Taf-03 monolith had the same stratigraphy.

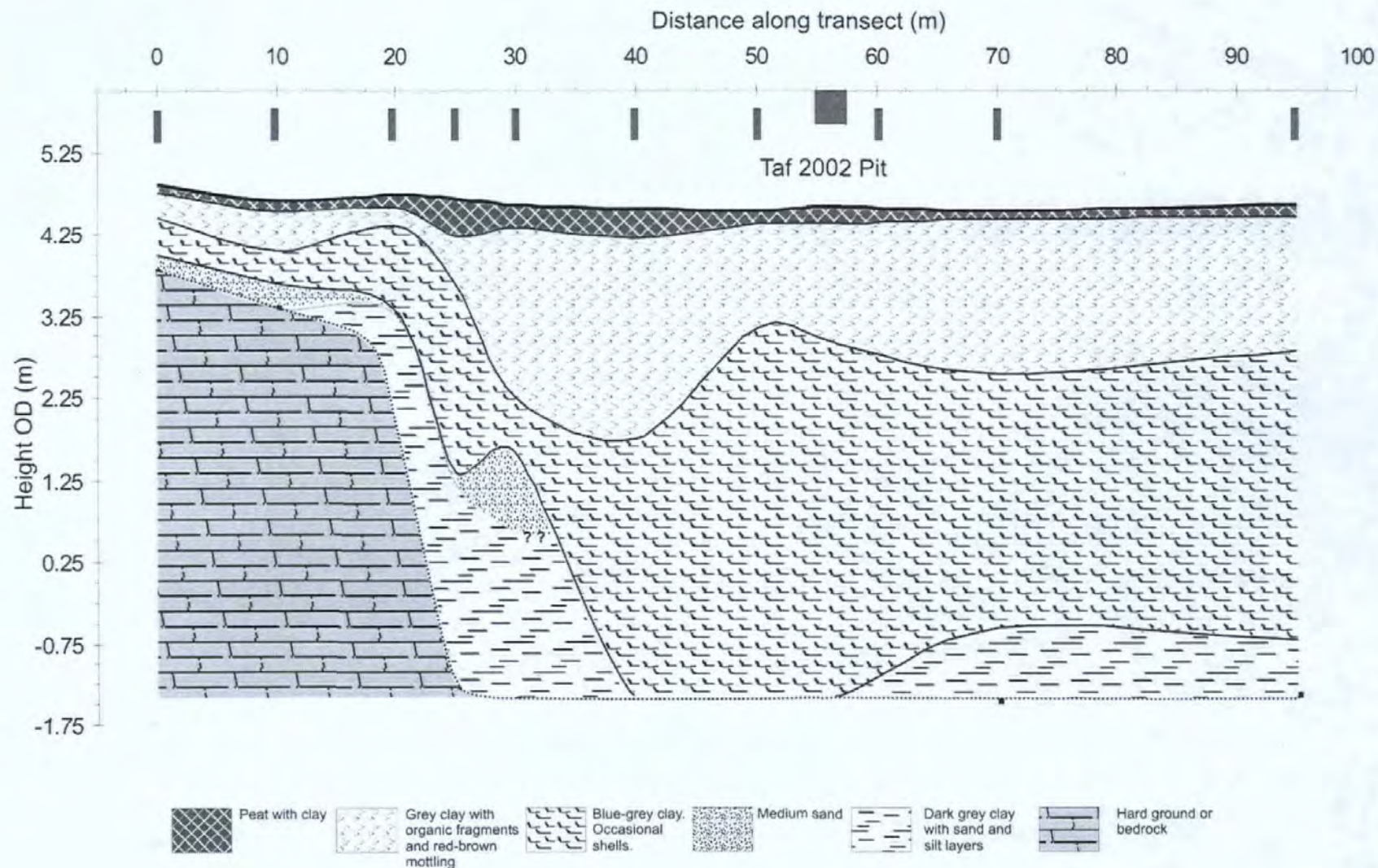


Figure 2.5. East-west transect of the Taf site. The 2002 pit location is shown.

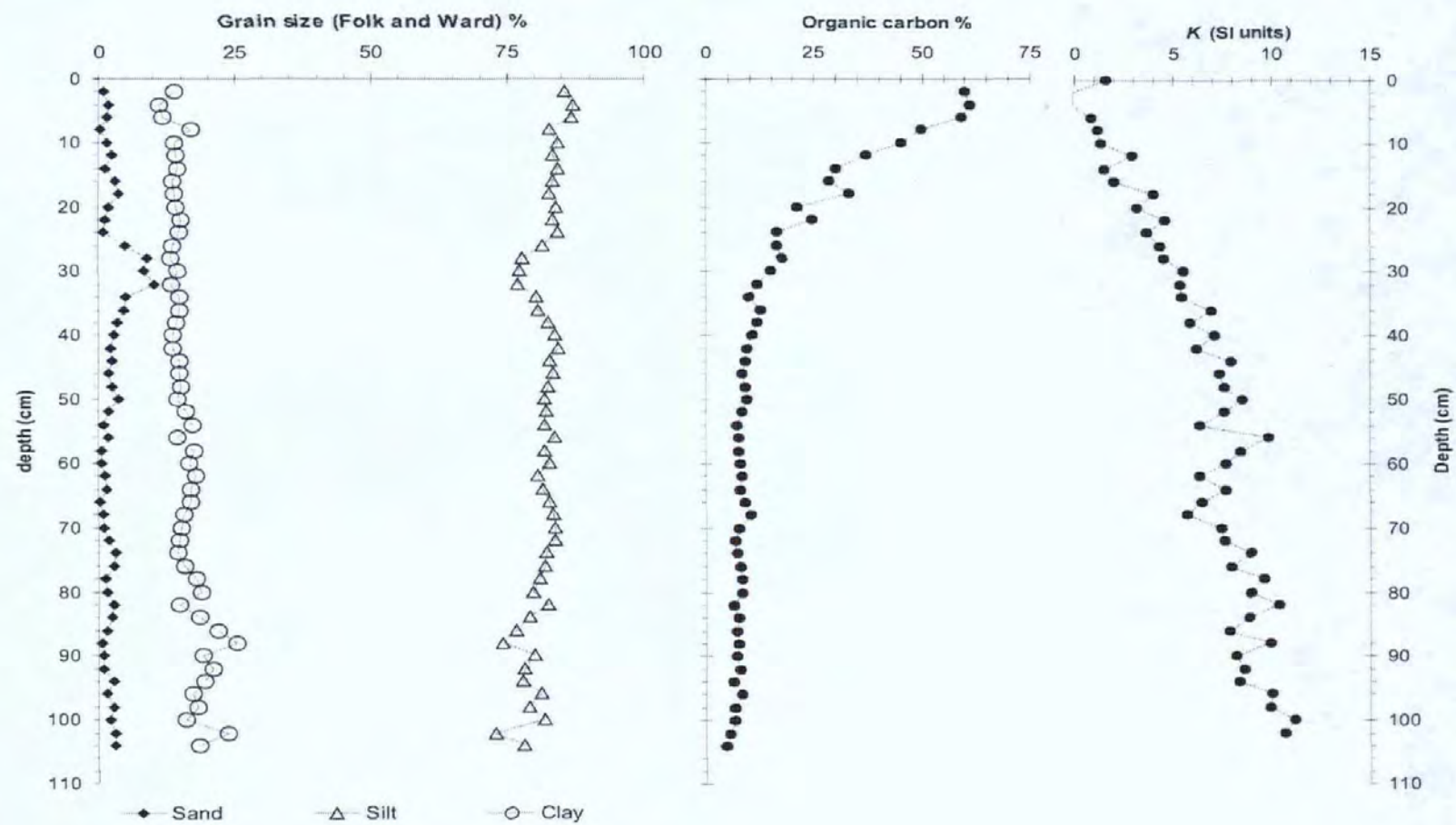


Figure 2.6. The Taf grain size %, organic carbon % and low-field magnetic susceptibility values (K).

2.4. Southern England

2.4.1. The Arne marsh site. The Arne Peninsula site is on the western shore of the enclosed embayment of Poole Harbour on the English Channel coast and forms part of a nature reserve controlled by the Royal Society for the Protection of Birds. The salt marsh at the site is approximately 130 m wide and is protected on the seaward side by number of small islands (Figure 2.7). The mid-marsh zone at this site has a fragmented vegetation cover dominated by *Spartina anglica*, and with *Atriplex portulacoides* on the creek edges. The high marsh is a mixed *Spartina anglica* - *Puccinellia maritima* sward with scattered clumps of *Juncus maritimus* and *Bolboschoenus maritimus* (Formerly *Scripus maritimus*) (Figure 2.8) and is heavily grazed by deer. In the wetter areas of the highest back-marsh *Phragmites communis* and *Iris pseudacorus* form dense stands. This vegetation zone changes abruptly landward into a mixed *Alnus glutinosa*, *Quercus robur* and *Salix alba* woodland with occasional *Ilex*, with a ground cover of *Sphagnum* and mixed fern species under the tree canopy. Inland, and to the north, occasional stunted *Pinus* can be found on the higher ground. The backshore open spaces contain *Corylus avellana* thickets surrounded by *Calluna vulgaris* heathland communities, and further west there are mature conifer plantations of *Pinus* sp. and more extensive open heathlands.

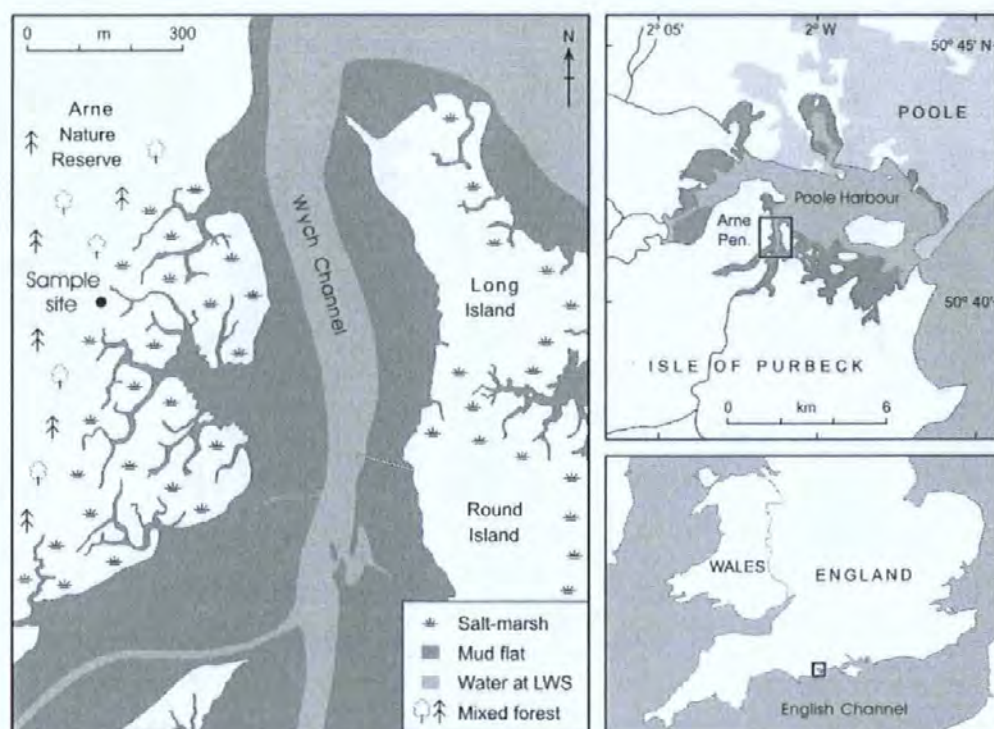


Figure 2.7. The location of the Arne Peninsula site in Poole Harbour, Southern England.



A



B



C

Figure 2.8. Photographs of the of the Arne sample site and sediment monoliths. Photograph A is looking at the sample site (Black arrow) from the south eastern edge of the marsh over *Spartina anglica* cover, and with *Atriplex portulacoides* in the middle of the foreground. Photograph B is looking over the sample pit toward Round Island with clumps of *Juncus maritimus* in view behind the pit, and photograph C is the upper 80 cm of the Arne-04 monolith. **Note:** The sediment surface is arrowed in red on the nearest box.

The tidal parts of Poole Harbour cover around 40 km² and in most areas are only 3-4 m deep at high water (Admiralty Chart Office 1998). The Harbour has a microtidal tidal range (Table 2.1) and a relatively high fluvial influence with around 2% of the low water volume being supplied by the four rivers that rise in the Cretaceous Chalk to the north and west (Edwards, 2001). The local geology is carbonate-rich, poorly consolidated, Tertiary sediment of the Bracklesham Group (Bristow *et al.*, 1991), with a scattered cover of Pleistocene fluvial gravels and sands.

This part of southern England was not overridden by ice during the Devensian, and mean sea-level rise on this section of the English south coast has been around 0.5 mm yr⁻¹ during the late Holocene (Shennan, 1989; Edwards, 2001; Shennan and Horton, 2002). Previous sea-level research at this site (Long *et al.* 1999; Edwards and Horton 2000; and Edwards 2001) indicates a relatively rapid accumulation rate in Poole Harbour in recent times, and that the majority of the sediments in the upper 100 cm were deposited during the last 1000 yr. This existing work confirmed the potential of this site as a testing ground for the experimental dating techniques under investigation in this present study e.g., ¹⁴C, ²¹⁰Pb and pollen.

2.4.2 The Arne sediments. A 98 cm sediment monolith (Figure 2.9), Arne-03, was obtained in the marsh transition zone during the summer 2003 from the pit shown in Figure 2.8B. The surveyed height of the ground surface here was 0.67 m OD. In the spring of 2004 a parallel replicate section, Arne-04, was obtained to provide a second set of magnetic samples, and to extend the radionuclide sequence range further back in time. In 2004 the original pit was reopened, and the new monolith (Arne-04) was taken from the same exposed face as the Arne-03 section. Correlations between these sequences confirmed that the second monolith was a reliable replicate, and that all the data could be considered as a single series. Concurrent with the collection of the 2003 monolith, a northwest southeast transect of six gouge cores was logged, and an additional 1 m reconnaissance pit dug at 37.5 m. The sediment logs of these sections were used to produce the cross section shown in Figure 2.10. A foraminifera analysis was carried out (Bugler, 2004) on the Arne-03 monolith indicates high salt-marsh conditions for the upper 60 cm of the section based on the presence of *Jadammina macrescens*, *Miliammina fusca* and *Trochammina inflata*.

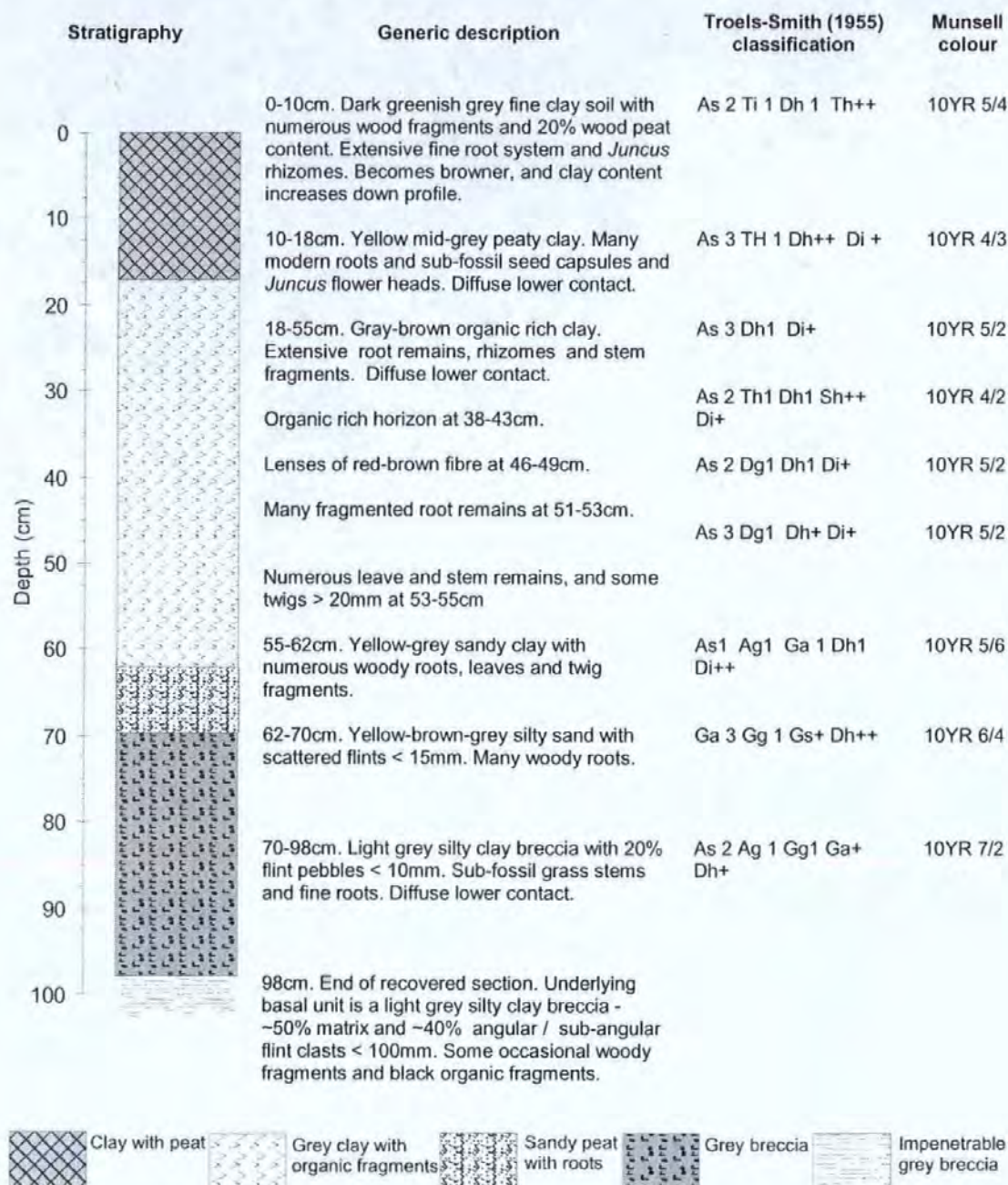


Figure 2.9. Stratigraphic log and description of the Arne-03 sediments. For Troels-Smith (1955) classification key see Figure 2.4.

The Arne sediment sequence is complex, and a number of changes are evident in both the analytical data and the observed lithology. There are two distinct changes in lithology separated by a band of sandy silt between 60 cm and 70 cm. This band contains numerous root fragments and is in marked contrast to the comparatively barren grey clay-silt of the underlying unit (Figure 2.8). The grain size data indicate a shift from a silt dominated environment to a sand dominated, environment between

70 and 60 cm, and it is in this zone the first salt-marsh foraminifera are found. Above the sand layer the presence of fine silt and clay coincides with an abrupt increase in organic carbon content. There are many plant fragments in some layers, with abundant recognisable salt-marsh grass stems being found above 35 cm. An abrupt excursion in the magnetic susceptibility is recorded between 48 cm and 38 cm. From 20 cm up to the surface the sediments are more organic. There is no change in the grain size %, but there is an increase in the number and size of plant macro fossils found in the sediments, i.e. *Juncus* flowers and rhizomes.

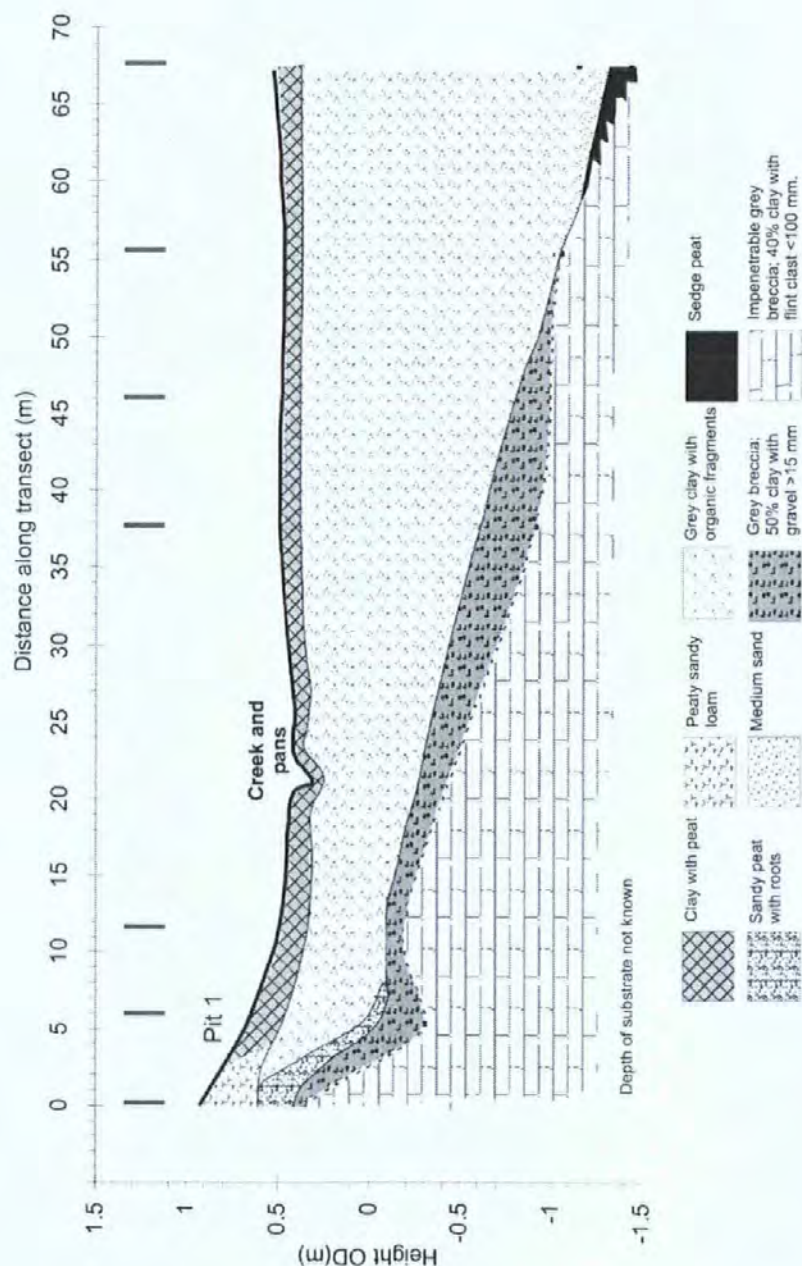


Figure 2.10. Cross section of the Arne site. The core sites, and the sample pit, are shown in grey. Pit 1 provided both the Arne-03 and Arne-04 monoliths.

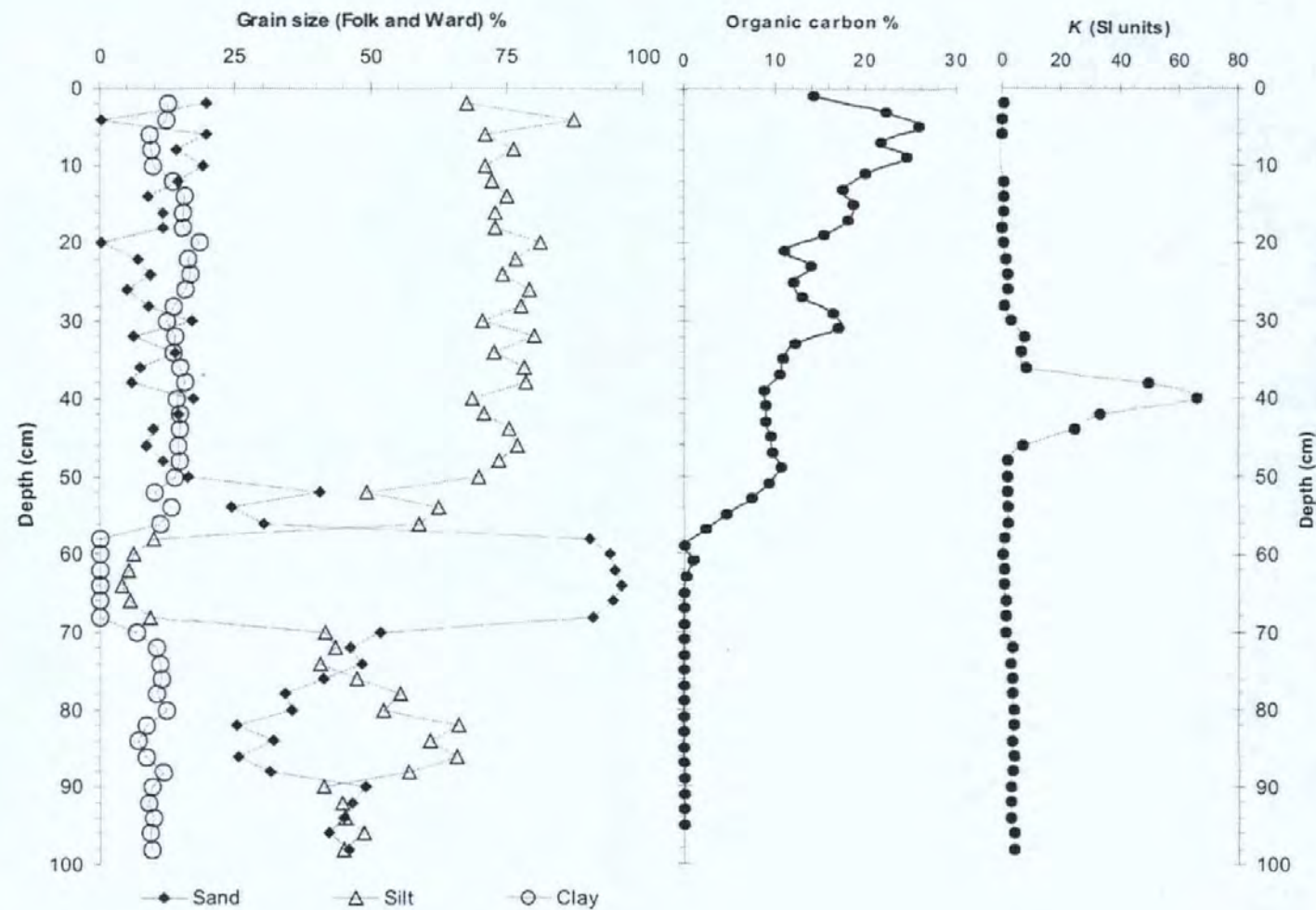


Figure 2.11. The Arne-03 grain size %, organic carbon % and the low-field magnetic susceptibility values (K).

2.4. Western Iceland

2.4.1 The Viðarhólmi site. Iceland was extensively glaciated during the late Pleistocene and still has a number of permanent ice domes. The land here is experiencing continuing glacio-isostatic recovery primarily centred on the Vatnajökull ice-dome (Hanson and Briggs 1991). Extant ice caps cover the higher land in the interior, and winter sea-ice is common on the more northerly sections of the coast (Doner, 2003). In contrast the south and west coasts are bathed by the northern arm of the North Atlantic Drift, the Irminger Current. This brings comparatively warm Atlantic waters, and a humid cold-temperate climate, to the southerly parts of the island, and produces a smaller seasonal variation in temperatures in Iceland than areas of similar latitudes (Doner, 2003).

Unlike the south of Iceland the area around Viðarhólmi is considered to be seismically inactive (Angelier *et al.*, 2004). Relative sea-level on this coast is estimated to have risen by 1.3 m since AD 100 (Gehrels *et al.*, 2006). The salt marsh at Viðarhólmi (Icelandic for 'wooded island') has developed on a Holocene basaltic lava flow from the Eldborg volcano (Thordarson and Höskuldsson, 2002), and is the largest area of salt-marsh in Iceland (Ingólfsson, 1994). The deposition of the sediments from 140 cm below the modern marsh surface is dated by Gehrels *et al.* (2006) to around 1 AD. The marsh has also been named in the literature as Melabakkar (Ingólfsson, 1994, Skirnisson *et al.*, 2004). The site is sheltered from the north by the Snæfellsnes peninsular, and to the west an off-shore bar and small islands protect the marsh from the direct influence of the open Atlantic (Figure 2.12). The local salt marshes are well developed, and exhibit a defined plant zonation with *Carex lyngbyei*, *Agrostis stolonifera*, *Festuca rubra* and *Puccinellia maritima* (Figure 2.13A) occupying the upper part of the intertidal zone (Ingólfsson, 1998). In common with much of modern Iceland, natural mature trees are not present in significant numbers in the catchment apart from the occasional solitary stunted birch.

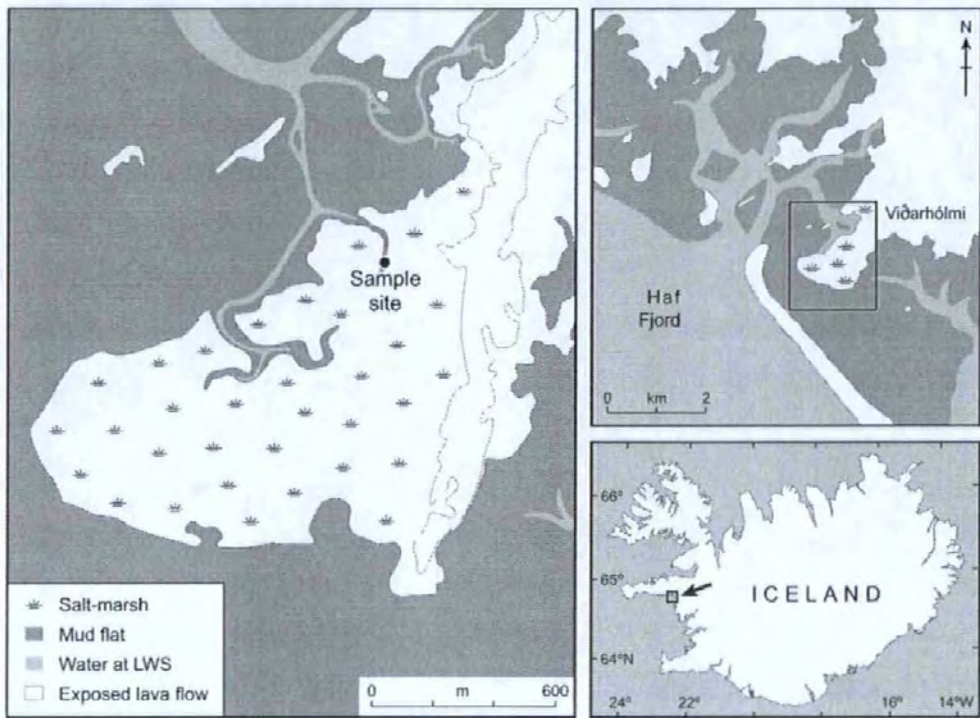


Figure 2.12. The location of Viðarhólmi salt-marsh in western Iceland.



A



B



C



D



E

Figure 2.13. Photographs of the Viðarhólmi salt-marsh site and sediments. A, looking north west over the marsh toward Snæfellsnes; B, The six sample boxes in position; C, the cleaned exposure showing the red pumice band around 60 cm; D, the boxes being aligned; E, the Viðarhólmi sediment column.

2.5.2 The Viðarhólmi sediments. Two 140 cm sediment monoliths (Figure 2.13C and Figure 2.14), Vid-03 and Vid-03-B, were obtained from a natural creek bank in September 2003. Vid-03 was used for this study and Vid-03-B was archived. These 2003 monoliths were precisely cut from the exact same location on the exposure as a monolith obtained in 2001 by members of the School of Geography (University of Plymouth, UK). This is reported in Gehrels *et al.* (2006) as section 3A, and the Vid-03 monolith replicated this original stratigraphy with no vertical off-set. As part of the 2001 visit the site was surveyed into geodetic and tidal datum, and other nearby sediment sections and cores. These data are reported, with a detailed foraminifera analysis, site cross-section and high resolution sea-level reconstruction for this coast, in Gehrels *et al.* (2006).

The sediments of the Vid-03 section can be broadly described as a minerogenic salt-marsh peat sequence with discrete sand-rich laminations divided around 60 cm by a band of red-brown granulated pumice (Figure 2.13D and Figure 2.14). The overall sediment lithology is ~45 % silt-sized minerogenic material of mainly volcanic origin. Some quartz, and other exotic mineral grains, were noted in the sediments when viewed under a microscope, but these are scarce and, in the main, sand sized.

The total minerogenic fraction in most of the Vid-03 samples is 65% - 75%, and the ratio between the different grain sizes and organic carbon changes little throughout the section apart from an abrupt fluctuation between 94 cm and 90 cm (Figure 2.15). The sediments at 92 cm contain less silt and have a relatively high organic carbon %. No grain size data are available for the pumice layer. The magnetic susceptibility values are all significantly positive and relatively stable from 140 cm up to around 50 – 40 cm. Above this level the *K* values rapidly increased to > 100 SI, and this increase was concurrent with a decrease in the organic carbon %.

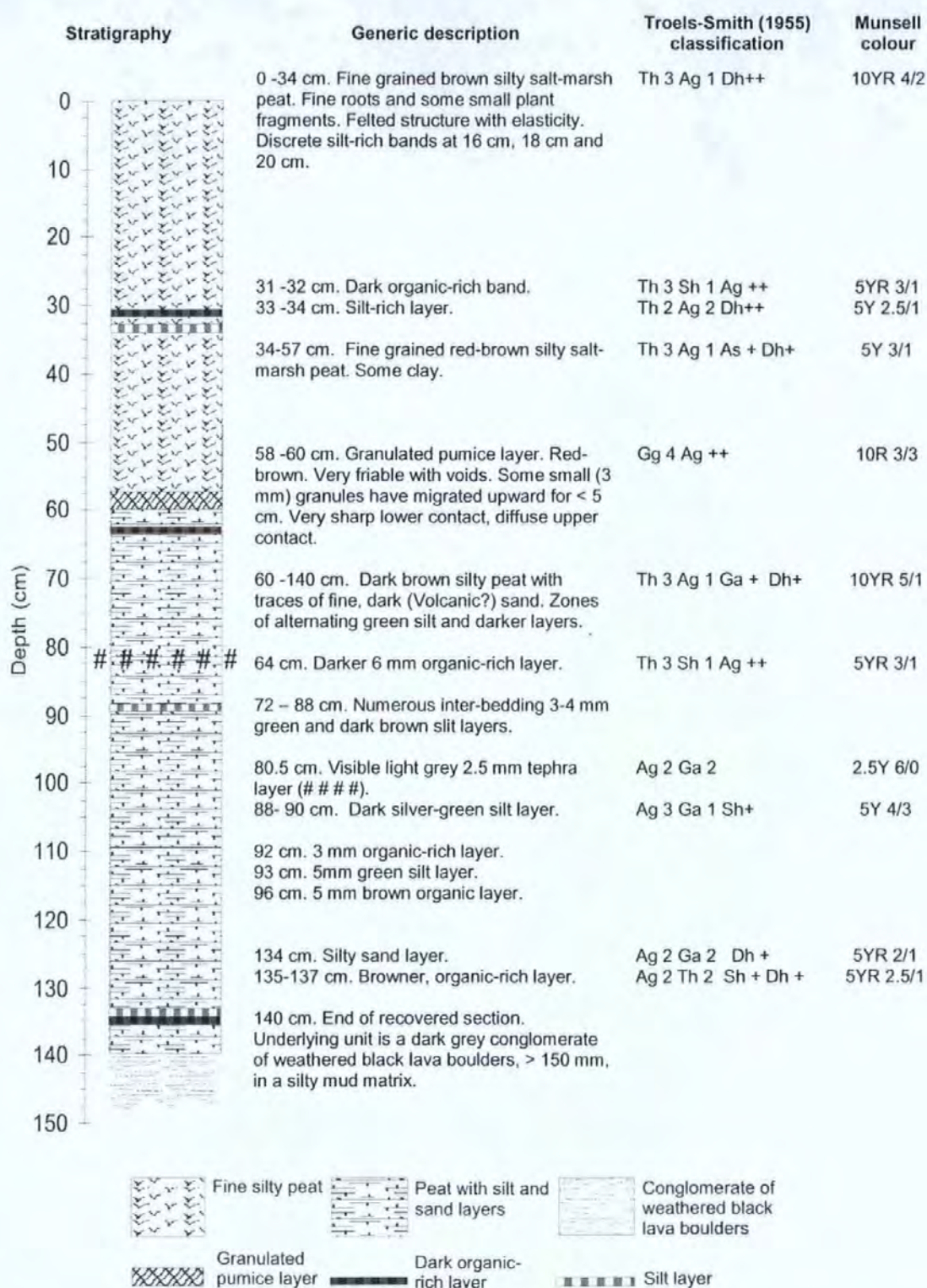


Figure 2.14. Stratigraphic log and description of the Viðarhólmi (Vid-03) sediments. For Troels-Smith (1955) classification key see Figure 2.4.

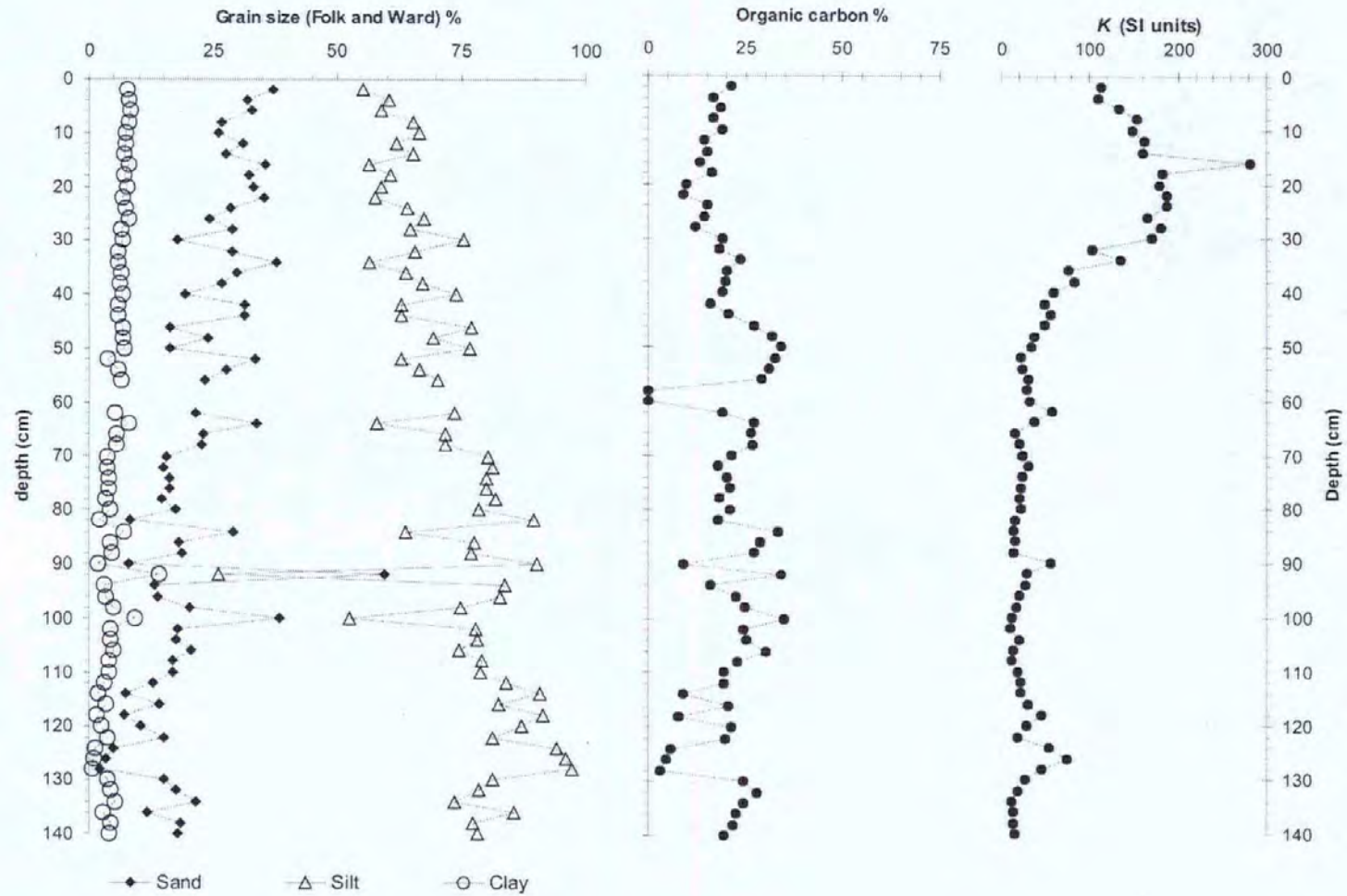


Figure 2.15. The Viðarhólmí grain size %, organic carbon % and low-field magnetic susceptibility values (K).

2.5. Synopsis

The descriptions of the three sites, and the associated physical data, presented in this chapter highlight both the similarities and the differences between the sites. In the first instance the sites are near pristine examples of temperate salt marshes. There has undoubtedly been some impact on the sites from human activities in the catchment especial at the Arne, but any direct anthropogenic influence is considered minimal. All three sample sites are located in the highest area of a salt marsh, and the minerogenic fraction of the sediments in each of the sequences sampled was predominately silt sized. There is microfaunal evidence present in all the sediments that confirms that a salt-marsh environment has been extant at each of the sites for all, or, in the case of the Arne, for a significant portion of the time spanned by the monoliths. The lithology of the Arne section has a number of marked changes in its lithology, whereas the Taf, and to a lesser extent the Viðarhólmi, sediments do not change as dramatically from base to surface. In addition, there are some very significant differences in the physical sediment descriptors. For example, the Viðarhólmi samples have a much higher magnetic susceptibility than those from the Taf and the Arne. The organic carbon % is higher in the Icelandic sediments than in those from Poole Harbour. Finally, and of great importance for a study on dating methods, the sediment deposition rates and ages of each of the marshes are very different. Existing information and previous studies at the sites (e.g., Gehrels, unpublished data (Taf); Long *et al.*, 1999 (Arne) and Gehrels *et al.*, 2006 (Viðarhólmi) indicates that the time needed to accumulate a 1 m sediment section would be around 3500-4000 yr in the Taf Estuary, 800-1000 yr on the Arne Peninsula and 1400- 1600 yr at the Viðarhólmi salt-marsh site.

Chapter 3

Radioisotopic dating part 1: Introduction to radionuclides and ^{14}C dating

Chapter 3 and Chapter 4 of this thesis will examine the radiometric dating of salt-marsh sediments. This present chapter will introduce radiometric dating, and outline the concepts on which methodologies depend. This chapter will then focus on the use of ^{14}C as a dating tool at the Arne site, and compare the Arne result with previously obtained ^{14}C chronologies at the Welsh and Icelandic sites. The chapter closes with an evaluation of the usefulness of the ^{14}C method with salt-marsh sediments, and how effective this radionuclide has been in dating sediments from the three sites examined in this thesis.

Comprehensive introductions to radioactivity and the development of radiometric dating are to be found in Smart and Frances (1991) and Lowe and Walker (1997). More technical descriptions, covering the use of different radionuclides and methods are presented in Rutter and Catto (1996), Dickin (1997) and Carroll and Lerche (2003). Carbon-14 dating, its development and application, are covered in depth on a number of dedicated World Wide Web sites and the reader is specifically directed to those resources maintained by the Oxford Radiocarbon Accelerator Unit at <http://c14.arch.ox.ac.uk/index.php>, and the Radiocarbon Laboratory, University of Waikato at <http://www.c14dating.com/>.

3.1. Radionuclides: production, decay and radiometric dating

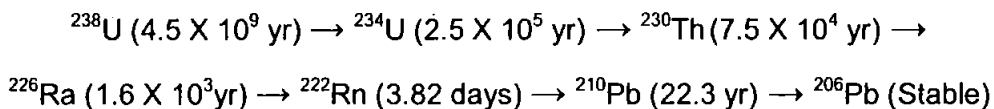
3.1.1. Radionuclides and isotopes. A nuclide is a species of atomic nucleus that is characterized by the number of protons and the number of neutrons, and is therefore defined by both the mass number and the atomic number. Nuclides with the same proton numbers, but differing neutron numbers, are called isotopes. Although strictly speaking the terms 'nuclide' and 'isotope' are not synonymous it is common to find the distinction not made clear, even in specialist texts, and radionuclides are often referred to as radioactive isotopes or radioisotopes. A radionuclide is an atom with an unstable nucleus that undergoes radioactive decay, or transmutation, by emitting or receiving sub-atomic particles by α or β decay. This decay is random and it cannot be changed by normal environmental conditions (Lowe and Walker, 1997; Carroll and Lerche, 2003).

In nature radionuclides are formed in two ways:

1. They originate from the nuclear transmutation of unstable materials in the primeval lithosphere.
2. They are produced by the interaction of cosmic rays with atoms in the atmosphere, and with atoms in sediments and rocks at, or near, the Earth's surface.

The original unstable atoms in the primeval lithosphere have continually decayed through time and form decay chains, or decay series, of radionuclides. These primeval nuclides initially became unstable parents with high atomic numbers. These subsequently decayed to create unstable daughter radionuclides with lower atomic numbers. The daughters then became unstable parents, and produced their own radioactive progeny who continue the transmutation sequence. This parent-daughter-parent-daughter decay continues until a stable isotope is formed.

There are three main radioactive decay chains in the lithosphere: (1) the thorium series, (2) the radium series, and (3) the actinium series. All three of these decay chains end in a stable lead isotope, but the most important one for dating recent sediments, and of primary interest to this thesis, is the radium series chain. This name is a legacy from the early investigations into radioactivity when they were unaware of the existence of the preceding isotopes in the chain (e.g., Curie, 1902; Rutherford, 1904). This series is now known to start with ^{238}U and eventually ends in the decay of ^{210}Pb , via some short-lived daughters, to stable ^{206}Pb . Lead-210 is commonly used to date recent sediments, and its application is examined in Chapter 4. The main nuclides (Half-lives in parentheses) in the radium series chain are:



In addition to ^{210}Pb , other radionuclides originating in the lithosphere can be used for dating sediments. The use of 'decay series dating' using the changes in the ratios between parents and progeny has been established for suitable ancient sediments (Carroll and Lerche, 2003), but until recently the inherent analytical uncertainty in this method constrained its use to relatively long time-scales (Henderson and O'Nions 1995). This situation has now improved, but the typical error is still large. However, it should be noted that work in Ireland by McDermott *et al.* (2001) using

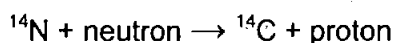
the $^{230}\text{Th}/^{234}\text{U}$ analysis of speleothem calcite gives errors for Holocene dates that compare with typical ^{14}C dating errors for compatible ages; e.i. $\pm 20\text{-}60$ yr for ages of 1000-8000 yr. Radium-226, with half-life of 1620 yr, may also offer possibilities for dating minerogenic marine sediments of Late Holocene age. Kim and Burnett (1985) experimented with ^{226}Ra using offshore marine materials, and earlier work by Koide *et al.* (1976) attempted to use ^{226}Ra to determine accumulation rates in the San Clemente Basin, Southern California, but this method is not applicable to salt-marsh sediments.

Cosmic ray bombardment of the earth produces a number of cosmogenic radionuclides, e.g. ^{26}Al , ^{10}Be , ^{14}C and ^{41}Ca (See Gosse and Phillips, 2001). The most well known, and widely used, cosmogenic radionuclide is ^{14}C and the use of this carbon isotope as a dating tool is examined later in this chapter. Other 'terrestrial' cosmogenic radionuclides can be used as tools for dating the exposure by erosion of land surfaces, and there may be some application for these methods in low-resolution sea-level studies, i.e. for dating the exposure of an ancient shoreline. However, as yet, these dating methods are still experimental, and only useful over time scales from 10^2 to 10^7 years (Gosse and Phillips, 2001).

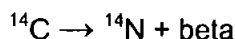
To be regarded as unique a nuclide, must be extant for more than 10^{10} second. Many short-lived radionuclides have been artificially created in laboratories, but some natural ones have half-lives of less than one second; e.g. ^{214}Po , the grandparent of ^{210}Pb , has a half-life of only 0.1643 ms. Since 1945 artificial radionuclides have been produced by nuclear activities associated with both weapons development and energy production (e.g., ^{90}Sr , ^{134}Cs and ^{137}Cs , ^{239}Pu and ^{240}Pu , ^{241}Np , ^{241}Pu and ^{241}Am , and $^{14}\text{C}_{\text{bomb}}$). Quantities of these products have subsequently been introduced into the environment by accidental discharges, fallout from thermonuclear weapons detonations and deliberate releases from nuclear facilities. This radiogenic contamination can be detected in sedimentary sequences, and because the production history of specific radionuclides is well known in some situations this information can be used to date very young sediments (See Chapter 4).

3.1.3. Carbon-14 production. Carbon has 13 known isotopes, of which ^{12}C and ^{13}C make up over 99.999% of all the elemental carbon on Earth. Carbon-14 is the third most abundant carbon species but it is only present some 1^{-10} % of the time. Natural ^{14}C is produced when free neutrons, produced by cosmic rays interaction with the

upper atmosphere, occasionally collide with a $^{14}\text{N}_2$ molecule and displace a proton from one of the atoms:



The resulting unstable carbon nucleus contains 8 neutrons and six protons and has a half-life of 5,730 yr. Carbon-14 subsequently reverts back to ^{14}N is by beta decay:



The residence time of carbon as CO_2 in the atmosphere is estimated as being between 5 yr and 17 yr (Levin and Hesshaimer, 2000), and so once produced there is a relatively rapid dispersal of ^{14}C between the atmosphere, the hydrosphere and terrestrial systems (McGee *et al.*, 2004). Although cosmogenic ^{14}C production was originally assumed to have remained relatively constant through time recent research has shown that there are periods in the past when the production of ^{14}C has varied significantly (Bard *et al.*, 1997; Stuiver *et al.* 1998; Mauquoy *et al.*, 2002). The occurrence of these ^{14}C plateaus appear to be linked with major climatic shifts and past fluctuations in the geomagnetic field modulation of the number of cosmic ray strikes in the stratosphere (Goslar *et al.* 1995; Dergachev and Chistyakov 1995; Kromer *et al.* 2001; Snowball and Sandgren 2002).

In addition to the natural fluctuations in atmospheric carbon isotope ratios recent anthropogenic activity has both reduced and increased ^{14}C concentrations. The increase in the burning of fossil fuels and other industrial emissions, over the last 200 years has changed the natural atmospheric carbon isotope ratios by releasing 'old carbon' into the atmosphere. This ancient carbon is highly depleted in ^{14}C and it distorts the ^{14}C , ^{13}C and ^{12}C ratios measured in organic carbon formed during the 19th and 20th centuries (Suess, 1970; McCormac *et al.*, 1998). Therefore, ^{14}C dates produced for that epoch using the conventional radiometric approach are apparently older than the biological death of the sample. This is known as the 'Suess effect'.

In the latter half of the twentieth century the situation reversed. Following the dawn of the nuclear age, and subsequent releases of artificial radionuclides associated with above-ground thermonuclear weapons tests since 1950, the atmospheric concentration of ^{14}C has increased (Hua and Barbetti, 2004; McGee *et al.*, 2004). This production peaked in the early 1960s (Figure 3.1), and levels of over 180% of the 1950 ^{14}C atmospheric concentration were measured in 1963 at a number of Northern Hemisphere locations (Hua and Barbetti, 2004; Turetsky *et al.*, 2004).

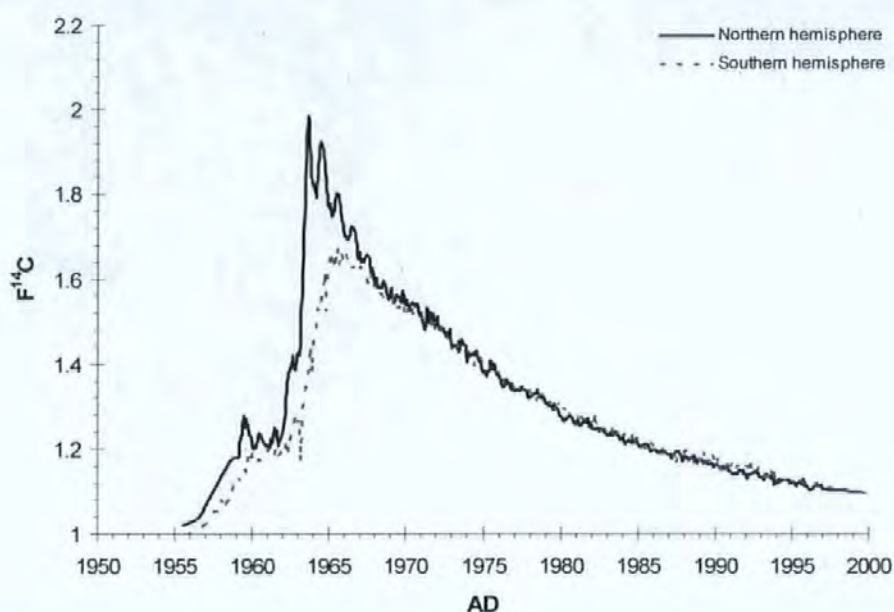


Figure 3.1. Global atmospheric ^{14}C levels since 1955. Shown here as $F^{14}C$ after the conventions proposed by Reimer *et al.* (2004) (See Section 3.2). Data from Hua and Barbetti (2004).

3.1.2. Radiometric dating. The basic theory of radiometric dating states that for a particular radionuclide, for which the decay rate is known, it will take a certain time for a specified number of atomic transmutations to take place. These basic principles of radioactive decay are pivotal to radiometric dating (Lowe and Walker, 1997; Carroll and Lerche, 2003). Therefore, if the decay rate of the parent is known, and the number of atomic transmutations that have taken place can be determined (e.g., by measuring the amount of activity of the daughter nuclide present), it is possible to calculate the time required for this transmutation.

The time it takes for a given number of atoms of a particular nuclide to decay to 50% of their original number is termed one half-life (Figure 3.2). Radiometric dating uses the number of the parent nuclide atoms remaining, compared to the number of daughter atoms present, to find the number of half lives that have passed since the decay started (e.g., if there are equal amounts of parent and daughter nuclide present, then one half-life has passed and if there is three times as much of the daughter nuclide present compared to the parent nuclide then two half-lives have passed; Figure 3.2).

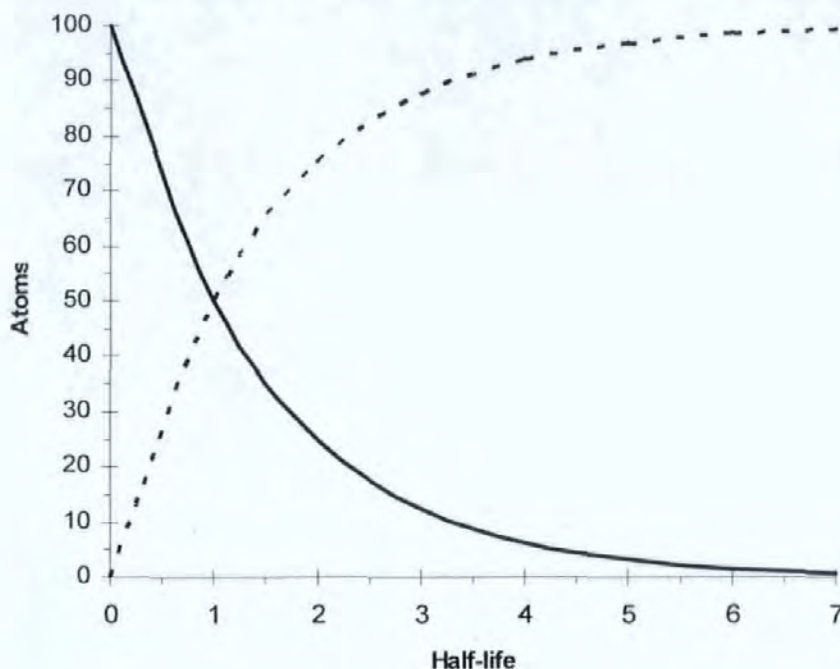


Figure 3.2. Radiometric exponential decay. The number remaining of the original parent atoms per half life of time passed (Solid line) for a given number of daughter atoms (Broken line) present.

The rate of transmutation from the parent to the daughter is described by the decay constant. This is simply the proportion of a number of atoms of a radionuclide that decay in a unit of time. It is inversely proportional to the radioactive half life and is commonly expressed as:

$$\lambda = \frac{\ln (2)}{t_{1/2}} \quad (3.1)$$

Where $t_{1/2}$ = radioactive half life in years, λ = decay constant and $\ln$ = natural logarithm.

For example, if the Libby ^{14}C half-life (See section 3.2) is used in Equation 3.1 then:

$$\lambda = \frac{0.693}{5568} = 1.245 \times 10^{-4} \quad (3.2)$$

The numbers of parent and daughter atoms are established by analysis. Therefore by using the decay constant the radiometric age relationship can be expressed by:

$$t = \frac{1}{\lambda} \times \ln \left(1 + \frac{D}{P} \right) \quad (3.3)$$

Where t = age, D = number of daughter atoms, P = number of parent atoms, λ = decay constant and $\ln$ = natural logarithm.

The simple radiometric dating principle is only perfectly applicable when radioactive equilibrium exists; i.e. in a closed system where the daughter radionuclide activity in the sample is the product only of the atomic transmutations of the parent. If there has been any movement of unsupported progeny into or out of the system this addition or loss must be factored into the calculation (See Chapter 4). Likewise, if episodic erosion has preferentially removed numbers of one of the nuclides, or introduced exotic material depleted in one of the nuclides and effectively diluting its representation, then radiometric dating methods become more difficult to apply (Carroll and Lerche, 2003).

3.2. Carbon-14 dating

3.2.1 Conventions. In reporting any ^{14}C data this thesis follows, where appropriate, the conventions of Stuiver and Polach (1977) and those proposed by Reimer *et al.* (2004). These conventions have been established by the ^{14}C community to facilitate comparisons between dates. The internationally accepted half-life of ^{14}C used for calculating a conventional radiocarbon age is the original half-life measured by W. F. Libby of 5568 ± 30 yr, even though it is now known that the true ^{14}C half life, sometimes referred to as the 'Cambridge half life', is 5730 ± 40 yr (Stuiver and Polach, 1977). The year AD 1950 has also been established by the ^{14}C community as 'present' or 'year zero', and all ^{14}C ages are referenced to this year.

Conventional radiocarbon ages are always reported in terms of years 'before present', and the standard deviation uncertainty, when known, stated (e.g. 590 ± 50 ^{14}C yr BP). This is the figure derived from the proportion of ^{14}C measured in the sample using the Libby half life and is calculated on the assumption that the atmospheric radiocarbon concentration has always been the same as it was in 1950. If the ^{14}C concentration is close to, or exceeds, the 1950 value the data is reported as 'F ^{14}C ' after the conventions proposed by Reimer *et al.* (2004) (e.g., F ^{14}C = % $^{14}\text{C}_{\text{modern}}$ / 100 when 100% $^{14}\text{C}_{\text{modern}}$ is taken to be atmospheric ^{14}C levels in 1950).

3.2.2. Carbon-14 age measurement. Carbon-14 becomes incorporated into the atmospheric CO₂ pool and thus becomes part of the global carbon budget. Carbon is assimilated by living plants and animals into their structure. The ¹⁴C fraction is constantly decaying in the tissue, and this transmutation continues when the organism dies. This means that because new carbon is no longer being assimilated, the ¹⁴C / ¹³C ratio in dead tissue declines over time, and so the older the material the smaller the fraction of ¹⁴C present. Therefore, as a general principle, because the decay rate is known, by measuring the amount of ¹⁴C present in ancient organic material an estimate of the time-of-death, in terms of '¹⁴C decay years', can be made (Lowe and Walker, 1997). This is the ¹⁴C age and is reported in ¹⁴C yr BP.

The lower age limit of the method has been effectively limited by the analytical difficulties involved in measuring the very small % of ¹⁴C remaining in a carbon sample after five, six or more half-lives of decay (See Figure 3.1). The first ¹⁴C date, published by Libby *et al.* (1949), was produced using a solid carbon analysis method, but now there are three principal analytical methods of measuring ¹⁴C activity: Gas Proportional Counting (GPC), Liquid Scintillation Counting (LSC) and Accelerator Mass Spectrometry (AMS).

The AMS method is the most modern development, and although expensive to operate, it has rapidly become the method of choice for most dating applications when sample size is restricted (Wohlfarth *et al.*, 1998). This is because a mass spectrometer continually counts all the carbon atoms presented to the Faraday Cups, or collectors, produced from a sample, and not just those produced by the decay during the active counting time. This allows for the option of an absolute 'on-line' ratio of ¹⁴C / ¹³C to be determined, and therefore removes the need for a separate ¹³C determination to be made if the sample size is small. The use of AMS analysis has improved analytical sensitivity and enabled the ¹⁴C dating of samples containing only a few milligrams of carbon.

As laboratories have improved the methodology many technical and analytical issues have been surmounted and the lower age limit for ¹⁴C dating has slowly been extended back in time. The main analytical problem is that in samples older than seven to eight half-lives the $\delta^{14}\text{C}$ is so low it sometimes can not be reliably distinguished from laboratory background count-rates. In this instance, a minimum

age would be calculated, e. g. >50,000 yr BP (Gupta and Polach, 1985). At present, under the best conditions available, the analytical limit is around 10 half-lives. Plastino *et al.* (2001) used synthetic samples with extended counting times to achieve a theoretical lower limit approaching 62000 yr BP. However, financial and practical considerations ensure that this extended range is not achievable during the 'normal' ^{14}C dating of environmental samples.

3.2.3. Carbon-14 age calibration. When the first ^{14}C dates obtained by Libby and later workers in the 1950s were compared with ages derived from archaeological information and documented historic records they were found to be underestimating the true age of a carbon sample. It subsequently became apparent that there was some 'non-systematic divergence' between the absolute chronological ages and the calculated ^{14}C ages. This divergence was subsequently attributed to:

1. The difference between the true half life of radiocarbon of 5730 years and the original Libby half-life of 5568 years.
2. The natural and, in the recent epoch, the anthropogenic induced changes in atmospheric ^{14}C (See Section 3.1.3).

The Libby half-life issue is easily addressed by a simple calculation, but the past changes in atmospheric ^{14}C concentrations necessitate the use of a non-systematic calibration to transform ^{14}C ages into chronological dates. This procedure has been facilitated by the development of a number of ^{14}C calibration programs, including OxCal and CALIB. The natural changes in ^{14}C production have produced extended periods in the past (e.g., the Younger Dryas) when the ^{14}C time scale has effectively become decoupled from the 'real' chronological time scale. Comparisons of ^{14}C dates with incremental dating methods, like dendrochronology and varve sequences, have confirmed the variability in ^{14}C production. This produces the first order fluctuations, or 'wiggles' (Figure 3.3), that are found in modern ^{14}C calibration curves (McCormac *et al.* 1993; Stuiver *et al.* 1998; Ramsey *et al.* 2001; McCormac *et al.* 2002; Blaauw *et al.* 2004).

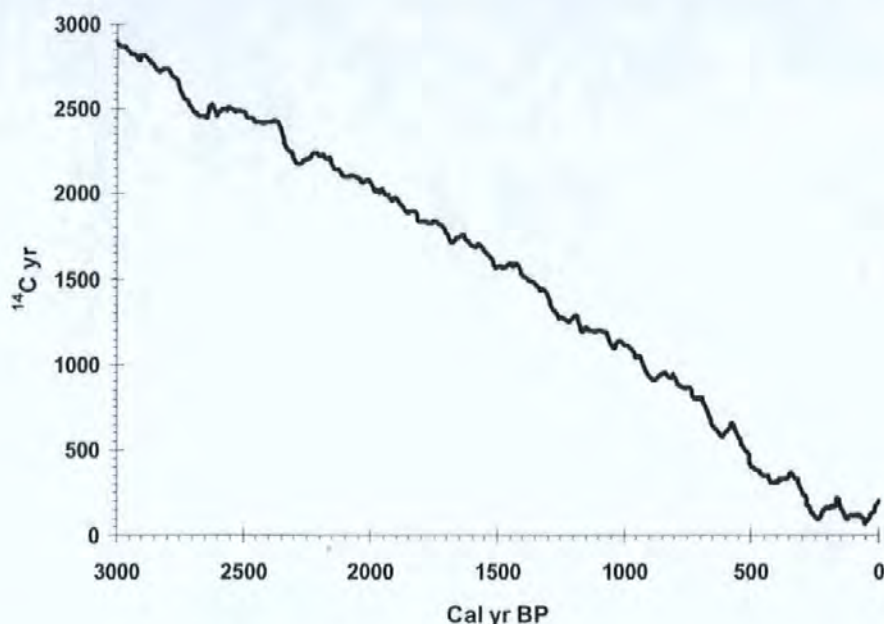


Figure 3.3. IntCal04 ^{14}C calibration curve for the last 3000 yr (Reimer *et al.*, 2004).

3.2.2. Carbon-14 and the important issues for sea-level studies. Carbon-14 dating is the most common method used to date Holocene and late Pleistocene sediments and archaeological artefacts. This dating method works well for suitable organic carbon samples from terrestrial environments. However, there are some inherent problems and restrictions in its use with salt-marsh sediments. Even if suitable organic carbon is present (See Chapter 1), complications can arise if the exchange between the contemporary atmospheric carbon store and the organic sample is not a simple photosynthetic pathway from atmospheric carbon pool. In aquatic environments problems may be encountered with ^{14}C dating if biogenic carbonate or aquatic plant tissue is used for dating. Shell-building organisms and submerged plants obtain carbon from dissolved carbonates in the host water. This dissolved carbon may be depleted in ^{14}C resulting in a 'hardwater effect', and result in the production of ^{14}C dates significantly older than the true age of the samples (e.g., Hall and Henderson, 2001; Clotts *et al.*, 2005). In a lake this can be simply the result of the catchment geology (e.g., limestone). If the underlying bedrock contains carbonate it can be easily dissolved and will contribute to the lake water chemistry. However, with large water bodies, such as oceans and very large lakes, an additional age off-set can be found because of the inherent time-lag between the exchange of atmospheric carbon, as CO_2 , at the surface and its dispersion, particularly to the benthos, in the water body. This age-offset effect is commonly found when dating marine carbonates (e.g., when ^{14}C ages are obtained using gastropod shells or foraminiferal tests).

The average marine reservoir age off set of surface ocean waters is approximately 400 ^{14}C yr., but, because of the influences of climate and the oceanic circulation systems there are substantial spatial variations in some regions (Reimer *et al.*, 2002; Angulo *et al.*, 2005; Ascough *et al.*, 2006). The polar regions have ^{14}C reservoir off-sets of between 400 yr. to 800 yr., but near the equator the oceanic-atmospheric exchange CO_2 is more direct and the age offset in some places is less than 14 yr. (Ascough *et al.*, 2005). Reservoir age offsets can be corrected by comparing the ^{14}C ages of samples with dates obtained for the same samples using independent chronological tools (e.g., uranium-thorium dating (Hall and Henderson, 2001), tephra chronology (Andrews *et al.*, 2002) or electron spin dating (Radtke *et al.*, 2003)).

In a salt-marsh environment the marine reservoir effect can be avoided by using organic carbon that has been produced only by terrestrial plants. If identifiable plant remains are present that are clearly associated with the palaeo marsh surface, i.e. 'detrital macrofossils' (Gehrels, 1999), these will be free from any marine reservoir effects and 'ageing effects' from minerogenic carbonate (Edwards, 2004). In addition, if only fragile plant macrofossils, such as grass stems or parts from herbaceous plants, are used they are unlikely to have been reworked. This type of carbon sample offers the best potential for providing ^{14}C chronologies that can be confidently used for high resolution-high precision sea-level reconstructions (Törnqvist *et al.*, 1998; Edwards, 2001; Gehrels *et al.*, 2005).

3.3. Carbon-14 dating of the Arne sediments

The conventional use of ^{14}C to date the lower section of the Arne sequence was investigated using both standard and high precision AMS analysis. A comparison and evaluation of the two precision levels is presented at the end of this section. The upper section of the Arne sequence was calibrated using the history of the enrichment of the atmospheric ^{14}C from nuclear weapons tests. This 'bomb spike' or 'bomb carbon pulse' approach has been applied successfully in recent peat sections in Denmark and Greenland (Shotyk *et al.*, 2003), Ireland (McGee *et al.*, 2004) and northern England (Garnett and Stevenson, 2004). These studies have all been in organic-rich terrestrial sites. As yet there have been no reports published of the use of this method in a salt marsh.

3.3.1. Sampling and analysis. The top 76 cm of the Arne sequence was sampled for ^{14}C dating. Below this level the sediments comprised of silts and clay and did not contain any organic material suitable for ^{14}C dating. When sampling for the ^{14}C analysis the detrital remains of stems, and other above-ground parts, of salt-marsh grasses were targeted, and of this material, only those fragments lying horizontal in the sediment matrix were picked to minimise the chance of younger root material being selected. The frailty of these grass fragments ensured that the possibility of transportation and re-deposition was minimal. In addition, to avoid any possible down-profile contamination from the digging out of the monolith in the field, or removing the samples in the laboratory, only the samples that were totally contained in the central section of the monolith were used.

The selected fragments of grass stem were manually isolated from the sediments, carefully washed in deionised water and checked for visible contamination of fine roots or other contamination under a binocular microscope. A suitable grass stem sample could not be found between 16 cm and 25 cm and a small fragment of a fibrous woody plant stem, Arne-03-20 (SUERC-5234), was used instead. The samples were individually oven-dried at 50°C and then placed in sterile screw-top plastic tubes for storage. At the NERC Radiocarbon Laboratory in East Kilbride the samples were subjected to an acid wash (2 M HCl), combusted in sealed quartz tubes, and the sample CO_2 cryogenically recovered and converted to graphite. The ^{14}C content was measured at the Scottish Universities Environmental Research Centre (SUERC) AMS Facility. As part of the SUERC ongoing research and development program, five of the deeper samples were prepared as multiple

graphite targets and ran at 2‰ precision instead of the 3‰ normally used for ^{14}C samples at this laboratory. The samples were subdivided after the conversion of the organic carbon to CO_2 into two, or more replicates, and individual graphite targets produced from these splits. This process requires a larger sample, and costs proportionally more to produce one age estimate than the lower precision analysis, but it was hoped it would result in a smaller uncertainty in the data.

3.3.2. Results. The transition from pre-bomb atmospheric ^{14}C values (e.g., less than 1.0 $F^{14}\text{C}$) to post-bomb values occurred in 1955 (See Figure 3.1). On inspecting the Arne AMS results it was decided that this transition was likely to lie between 26.5 cm and 34 cm because these values (Tables 3.1 and 3.2) were above and below 1.0 $F^{14}\text{C}$. The standard precision AMS results are shown in Table 3.1. The analysis of the seven samples above 31 cm all produced values more than 1.0 $F^{14}\text{C}$ suggesting a post-bomb age for this material (See Section 3.2.1), and consequently no ^{14}C age is tabulated for these samples. The maximum $F^{14}\text{C}$ values were found at 25 cm (1.4609) and 26.5 cm (1.4637).

Publication no.	Sample identifier	Depth (cm)	$F^{14}\text{C} \pm 1\sigma$	$\delta^{13}\text{C}_{\text{V-PDB}} \text{‰}$	^{14}C yr BP $\pm 1\sigma$
SUERC-6330	Arne-03-04	4	1.1262 ± 0.0035	-29.6	N/A
SUERC-5232	Arne-03-08	8	1.1825 ± 0.0038	-28.8	N/A
SUERC-6331	Arne-03-11	11	1.2390 ± 0.0039	-27.5	N/A
SUERC-5233	Arne-03-16	16	1.3363 ± 0.0043	-27.5	N/A
SUERC-5234	Arne-03-20	20	1.0418 ± 0.0035	-27.9	N/A
SUERC-5235	Arne-03-25	25	1.4609 ± 0.0049	-26.0	N/A
SUERC-5237	Arne-03-26.5	26.5	1.4637 ± 0.0049	-24.7	N/A
SUERC-5238	Arne-03-31	31	0.9798 ± 0.0031	-27.0	164 ± 25
SUERC-5239	Arne-03-56	56	0.9817 ± 0.0031	-28.8	148 ± 26
SUERC-6333	Arne-03-76	76	0.9712 ± 0.0024	-27.7	234 ± 20

Table 3.1. The standard precision AMS results for the Arne samples. Radiocarbon content is reported as 'fraction modern' ^{14}C ($F^{14}\text{C}$) after Reimer *et al.*, (2004a).

The five high-precision samples all had a $F^{14}\text{C}$ one-sigma analytical uncertainty of 0.0018 (Table 3.2). There was little variation between these multiple targets so the replicates are treated here as if the AMS ^{14}C data came from one cathode. Calib 5.0 (Stuiver *et al.*, 2005) was used to combine the multiple ^{14}C ages (Table 3.2).

Publication no.	Sample identifier	Depth (cm)	F ¹⁴ C ± 1σ	δ ¹³ C _{V-PDB} ‰	¹⁴ C yr BP ± 1σ	Combined ¹⁴ C yr BP ± 1σ
SUERC-6364	Arne -03-34 X	34	0.9809 ± 0.0018	-29.5	155 ± 15	
SUERC-6365	Arne -03-34 Y	34	0.9819 ± 0.0018	-29.5	146 ± 15	146 ± 9
SUERC-6366	Arne -03-34 Z	34	0.9831 ± 0.0018	-29.5	137 ± 15	
SUERC-6369	Arne -03-42 X	42	0.9851 ± 0.0018	-28.2	120 ± 15	
SUERC-6370	Arne -03-42 Y	42	0.9843 ± 0.0018	-28.2	127 ± 15	131 ± 9
SUERC-6371	Arne -03-42 Z	42	0.989 ± 0.0018	-28.2	147 ± 15	
SUERC-6374	Arne -03-47.5 X	47.5	0.9785 ± 0.0018	-29.0	174 ± 15	
SUERC-6375	Arne -03-47.5 Y	47.5	0.9785 ± 0.0018	-29.0	175 ± 15	175 ± 11
SUERC-6376	Arne -03-55 X	55	0.9898 ± 0.0018	-28.7	83 ± 15	
SUERC-6377	Arne -03-55 Y	55	0.9864 ± 0.0018	-28.7	110 ± 15	92 ± 9
SUERC-6380	Arne -03-55 Z	55	0.9898 ± 0.0018	-28.7	82 ± 15	
SUERC-6381	Arne -03-62 X	62	0.9768 ± 0.0018	-28.8	188 ± 15	
SUERC-6382	Arne -03-62 Y	62	0.9742 ± 0.0018	-28.8	210 ± 15	199 ± 9

Table 3.2. The results for the five high precision AMS Arne samples. Replicated graphite target results differentiated as X, Y and Z. Radiocarbon content is reported as 'fraction modern' ¹⁴C (F¹⁴C) after Reimer *et al.*, (2004a).

3.3.3. Calibration of radiocarbon results

The pre-bomb samples, Arne-03-31 and below, were first calibrated using Calib 5.0 (Stuiver *et al.*, 2005) using the Intcal04 calibration curve (Reimer *et al.*, 2004b) (Table 3.3). The seven post-bomb F¹⁴C results were selected for calibration to the bomb carbon record using Calibomb (Reimer *et al.*, 2004a) (Table 3.5). The ¹⁴C analysis of the sample from Arne-03-31 was considered to be transitional between pre- and post-bomb so it was calibrated using Calib 5.0 and Calibomb.

Pre-bomb samples. Calib 5.0 produced a number of age ranges for each pre-bomb ¹⁴C age, because of the problems with calibration in some periods (See Section 3.2). In some instances the spread of the age ranges for each sample meant that a single range needed to be selected to make the results useful. The exception was from the deepest sample, Arne-03-76, which calibrated to AD 1650-1665 or AD 1785 -1793, but these two estimates still spanned around 150 years. One way of selecting the most likely age-range is to use the one associated with the best calibration peak relative value (CPRV), or if a single date must be quoted then the median age given by the calibration program is widely accepted as a valid option (Telford *et al.*, 2004). However, if these simple approaches are used with the Arne samples they produce questionable results.

Sample identifier	Depth (cm)	No. of graphite targets	^{14}C yr BP $\pm 1\sigma$	Calibrated 2σ age ranges AD	Calibration peak relative area value	Median age from Calib 5.0
Arne -03-31	31	1	164 $\pm$ 25	1665 to 1697	0.18	1768
				1725 to 1786	0.43	
				1792 to 1815	0.11	
				1835 to 1878	0.08	
				1917 to 1952	0.20	
Arne -03-34	34	3	146 $\pm$ 9	1677 to 1694	0.17	1761
				1726 to 1767	0.37	
				1772 to 1777	0.01	
				1799 to 1813	0.15	
				1838 to 1842	0.01	
				1853 to 1858	0.01	
				1862 to 1867	0.01	
Arne -03-42	42	3	131 $\pm$ 9	1918 to 1940	0.26	1841
				1950 to 1952	0.01	
				1682 to 1699	0.18	
				1721 to 1737	0.12	
				1758 to 1761	0.00	
Arne -03-47.5	47.5	2	175 $\pm$ 11	1803 to 1818	0.11	1765
				1833 to 1880	0.39	
				1667 to 1683	0.20	
				1735 to 1782	0.54	
Arne -03-55	55	3	92 $\pm$ 9	1797 to 1805	0.09	1830
				1932 to 1952	0.17	
				1697 to 1726	0.33	
				1814 to 1836	0.23	
Arne -03-56	56	1	148 $\pm$ 26	1844 to 1851	0.24	1796
				1877 to 1917	0.42	
				1668 to 1707	0.17	
				1719 to 1782	0.33	
Arne -03-62	62	2	199 $\pm$ 9	1797 to 1826	0.12	1785
				1832 to 1886	0.19	
				1912 to 1953	0.19	
				1662 to 1677	0.25	
Arne -03-76	76	1	234 $\pm$ 20	1766 to 1772	0.03	1662
				1777 to 1800	0.48	
				1940 to 1951	0.24	
				1643 to 1669	0.63	
				1780 to 1798	0.34	
				1945 to 1951	0.03	

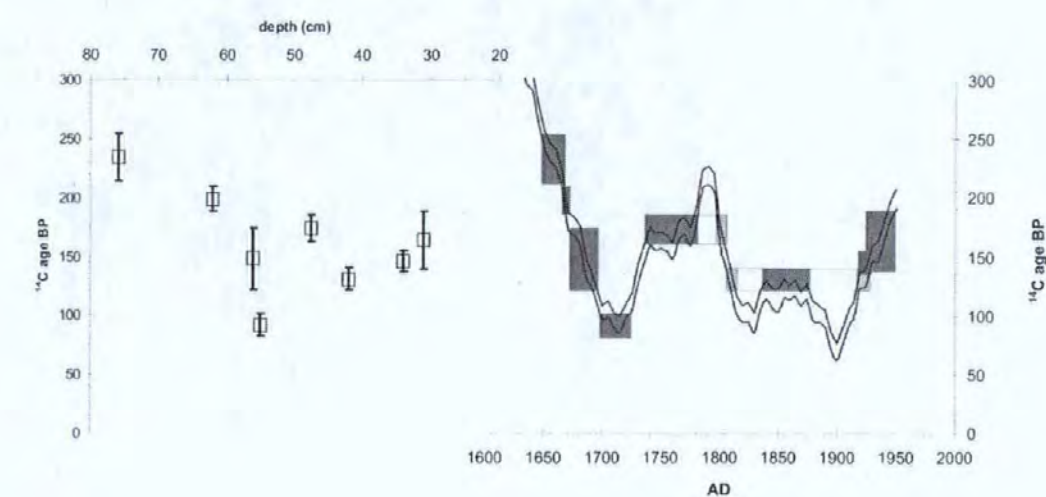
Table 3.3. Calib 5.0 (Stuiver *et al.*, 2005) calibrations of the pre-bomb Arne samples.

The most likely calibration of the pre-bomb sample nearest the surface, Arne-03-31, was suggested by a CPRV of 0.43 to be AD 1725-1786 (Table 3.3). This age appeared too old, as did the median age of AD 1768. This date was not in chronological agreement with the age ranges selected for some of the lower samples using the CPRV method, or the median ages produced by Calib 5.0. As an alternative to using an abstract numerical method it was decided to try a slightly more intuitive approach, and therefore a simple wiggle matching exercise was used to fit the pre-bomb ^{14}C dates on to the Intcal04 calibration curve (Reimer *et al.*, 2004b). This fit of the data was constrained using the location of each sample in the stratigraphy, i.e. the concept of 'prior chronological knowledge' (Figure 3.4). The

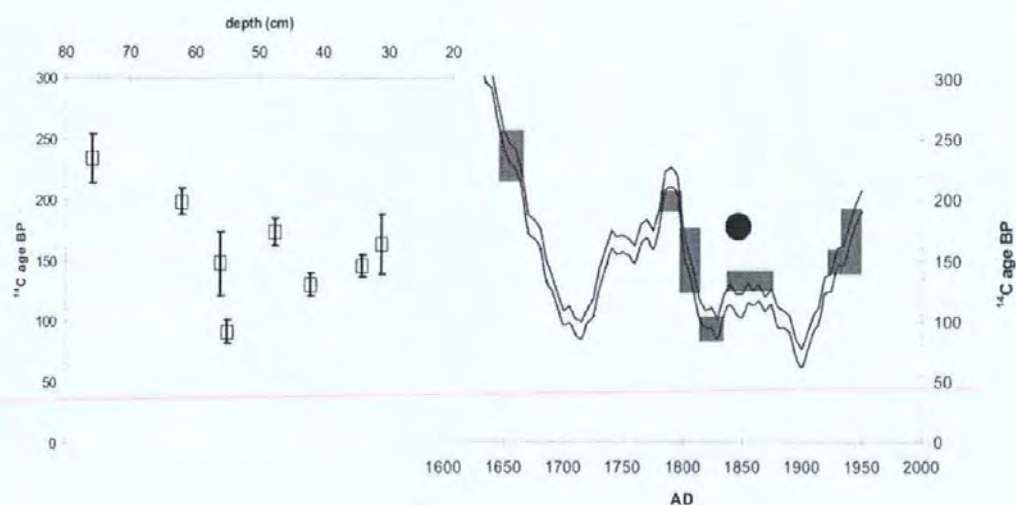
calendar date indicated by the X axis of the calibration curve was then used to select the closest match of the age ranges suggested by Calib 5.0.

The principle of wiggle matching to calibrate ^{14}C dates is recognised as a robust method for dating of terrestrial sequences (Hogg *et al.*, 2003; Wille *et al.*, 2003; Mauquoy *et al.*, 2004), and the potential of this ^{14}C calibration method for sea-level studies has been successfully demonstrated by one salt-marsh study (van de Plassche *et al.*, 2001). Ideally a larger data set is used than was available here, and it is often matched to the calibration curve using dedicated software, but it was felt it a simple manual approach could be legitimately used to improve the initial Calib 5.0 (Stuiver *et al.*, 2005) results. By maintaining the inter-sample stratigraphic relationship the most likely solutions from the results of the initial Calib 5.0 (Stuiver *et al.*, 2005) calibrations could be selected. The data were fitted to the calibration curve by overlaying the plotted array of ^{14}C ages in Figure 3.4 onto the Intcal04 calibration curve using CorelDraw while maintaining the alignment of the ^{14}C age scales of the Y axis. Then the Arne data were 'walked' along the X axis, representing depth, until a good fit of the data to the calibration curve was archived with the minimum of inter-sample movement and while maintaining the stratigraphic relationship of each sample. The AD date was then read off the X axis of the calibration curve. The results are shown in Table 3.5 with the closest date ranges produced by the Calib 5.0 (Stuiver *et al.*, 2005) calibration.

Two plausible solutions were produced. In solution 1, the sample from 56 cm had two possible age solutions from Calib 5.0 that fitted in the wiggle matching exercise; 1668 to 1707 (CPRV 0.17) and 1719 to 1782 (CPRV 0.33). The next sample toward the surface, Arne-03-55, had calibrated to 1697 to 1726, and the one above that, Arne-03-47.5, calibrated to 1735 to 1782. This information indicated that it was unlikely that Arne-03-56 was younger than 1735, so the 1668 to 1707 solution was selected. Solution 2 had less inter-sample movement and reduced the uncertainty of the fit of Arne-03-42, but to maintain the stratigraphic relationship the sample from 47.5 cm had to be discarded. In so much as it uses all the data solution 1 may be more accurate, but with only the ^{14}C data an informed judgment can not be reliably made and so both solutions are presented here. This issue is examined further in Chapter 8 where all the chronological information available for each site are used. The Calib 5.0 age ranges selected by the wiggle matching are shown in Figure 3.5 as simple age-depth models.



A

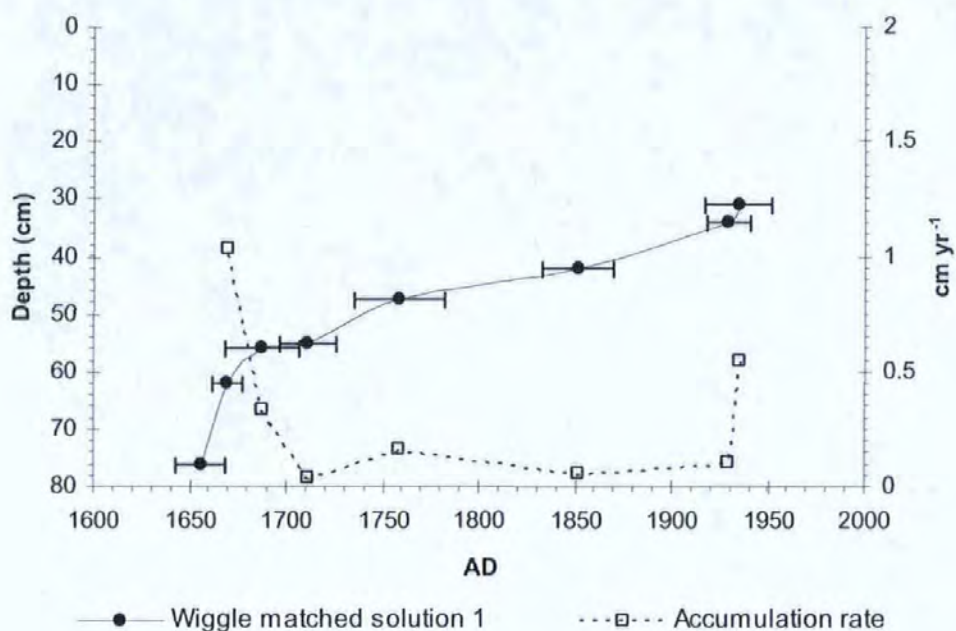


B

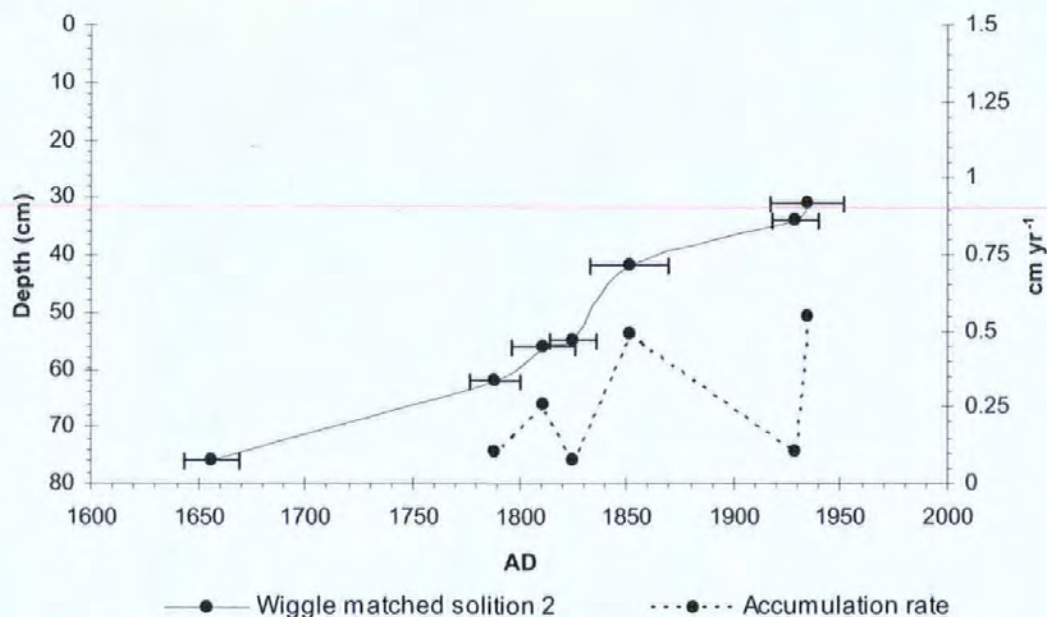
Figure 3.4. The pre-bomb (2 sigma) ^{14}C ages plotted against depth and the manual fitting of these data to the Intcal04 calibration curve (Reimer *et al.*, 2004b). Dark fill shows best-fit, light and open boxes shows possible but unlikely fit. Panel A is solution 1, panel B is solution 2. Black circle in B is where the discarded sample from 47.5 cm would plot. See text for further explanation.

Depth (cm)	Wiggle matched solution AD	Nearest Calib 5.0 range AD	Calibration peak relative value
Solution 1			
31	1923 - 1950	1917 - 1952	0.20
34	1917 - 1924	1918 - 1940	0.26
42	1835 - 1875	1833 - 1880	0.39
47.5	1735 - 1785	1735 - 1782	0.54
55	1695 - 1725	1697 - 1726	0.33
56	1670 - 1695	1668 - 1607	0.17
62	1662 - 1670	1662 - 1677	0.25
76	1645 - 1665	1643 - 1669	0.63
Solution 2			
31	1923 - 1950	1917-1952	0.20
34	1917 - 1924	1918-1940	0.26
42	1835 - 1875	1833-1870	0.39
55	1810-1830	1814-1836	0.23
56	1790-1810	1797-1826	0.12
62	1775-1795	1777-1800	0.48
76	1645 - 1665	1643-1669	0.63

Table 3.5. The age ranges suggested by manually fitting the pre-bomb Arne data to the Intcal04 calibration curve (Reimer *et al.*, 2004b) and the closest 2 sigma age ranges derived by Calib 5.0 (Stuiver *et al.*, 2005) from the ^{14}C ages.



A



B

Figure 3.5. The age-depth models and accumulation rates suggested by manually fitting the Arne pre-bomb ¹⁴C dates to the Intcal04 calibration curve (Reimer *et al.*, 2004b). Panel A is solution 1 and B is solution 2.

Post-bomb samples. The eight data with post-bomb $F^{14}C$ values were fitted to the post-bomb Northern Hemisphere atmospheric ^{14}C calibration curve (Figure 3.6) published by Hua and Barbetti (2004) using CALIBomb (Reimer *et al.*, 2004a). For the youngest sample, Arne-03-04, CALIBomb produced four possible age solutions that spanned 2.37 yrs (1994.3 ± 1.19 AD). To estimate the most likely single solution, and having no other chronological information for this sample, the relative area value of the calibration probability distribution produced by CALIBomb was considered. This was highest (at 0.86) for 1993.58 to 1994.99 (Table 3.6), so this was used as the age range in Figure 3.6. The CALIBomb (Reimer *et al.*, 2004a) calibration for most of the samples produced two or more possible fits, but using the stratigraphic order of the samples and the $F^{14}C$ values of the adjacent samples it was possible in most cases to fit confidently the data to the calibration curve using a single solution.

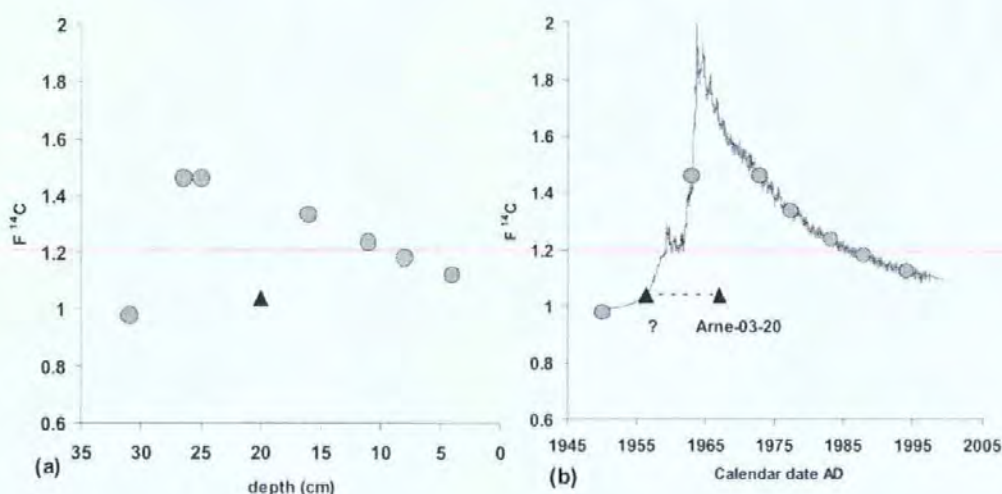


Figure 3.6. The Arne ^{14}C post bomb data: plotted against sediment depth (a) and fitted to the atmospheric ^{14}C curve of Hua and Barbetti (2004) (b). The black triangle shows where the displaced 'woody' sample, Arne-03-20, plots. Analytical $F^{14}C$ 1 sigma uncertainty is smaller than the symbols.

Sample identifier	Depth (cm)	No. of graphite targets	^{14}C yr BP $\pm 1\sigma$	Calibrated 2σ age ranges AD	Calibration peak relative area value
Arne -03-04	4	1	N/A	1957.50 (Jul) to 1958.01 (Jan)	0.07
				1992.06 (Jan) to 1992.37 (May)	0.04
				1992.77 (Oct) to 1995.76 (Oct)	0.89
Arne -03-08	8	1	N/A	1958.50 (Jul) to 1959.12 (Feb)	0.14
				1985.82 (Oct) to 1989.12 (Feb)	0.85
Arne -03-11	11	1	N/A	1959.25 (Apr) to 1959.39 (May)	0.04
				1959.72 (Sep) to 1959.95 (Dec)	0.07
				1960.35 (May) to 1960.70 (Sep)	0.11
				1961.16 (Feb) to 1961.97 (Dec)	0.16
				1982.20 (Mar) to 1984.12 (Feb)	0.60
				1984.34 (May) to 1984.39 (May)	0.002
				1984.90 (Nov) to 1984.99 (Dec)	0.12
Arne -03-16	16	1	N/A	1962.22 (Mar) to 1962.31 (Apr)	0.02
				1976.16 (Feb) to 1976.33 (May)	0.04
				1976.72 (Sep) to 1978.69 (Sep)	0.93
Arne -03-20	20	1	N/A	1956.60 (Jul) to 1956.76 (Oct)	1.00
Arne -03-25	25	1	N/A	1963.07 (Jan) to 1963.18 (Mar)	0.01
				1971.17 (Mar) to 1971.20 (Mar)	0.001
				1971.50 (Jul) to 1971.55 (Jul)	0.005
				1972.10 (Feb) to 1973.87 (Nov)	0.87
Arne -03-26.5	26.5	1	N/A	1963.07 (Jan) to 1963.20 (Mar)	0.11
				1971.16 (Feb) to 1971.23 (Mar)	0.01
				1971.50 (Jul) to 1971.56 (Jul)	0.008
				1971.85 (Nov) to 1971.97 (Nov)	0.000
				1972.10 (Feb) to 1973.77 (Oct)	0.87
Arne -03-31	31	1	164 $\pm$ 25	1664 to 1697	0.18
				1724 to 1788	0.43
				1790 to 1815	0.11
				1834 to 1878	0.08
				1916.00 (Jan) to 1951.10 (Feb)	0.20

Table 3.6 CALIBomb (Reimer *et al.*, 2004a) calibrations of the post-bomb samples. Age-ranges plotted in Figure 3.6 and used in Figure 3.7 are underlined in **bold**.

A satisfactory fit to the calibration curve for all but one sample (Arne-03-20, SUERC-5234) was obtained. The AMS result for this sample was 1.0418 F¹⁴C which had a single CALIBomb calibration solution of 1956.5-1956.7. This result was considered to be out of sequence when compared to the adjacent samples, so this sample was assumed to be displaced in the stratigraphy, and is ignored for the purposes of the ¹⁴C chronology shown in Figure 3.7. Arne-03-26.5 (1.4637 F¹⁴C) could have been fitted to either the rising or the falling limb of the bomb carbon peak, calibrating as 1963.07-1963.2 or 1971.6 - 1973.7 respectively. The older calibration is shown in Figure 3.7 and this issue is discussed further in section 3.3.4.

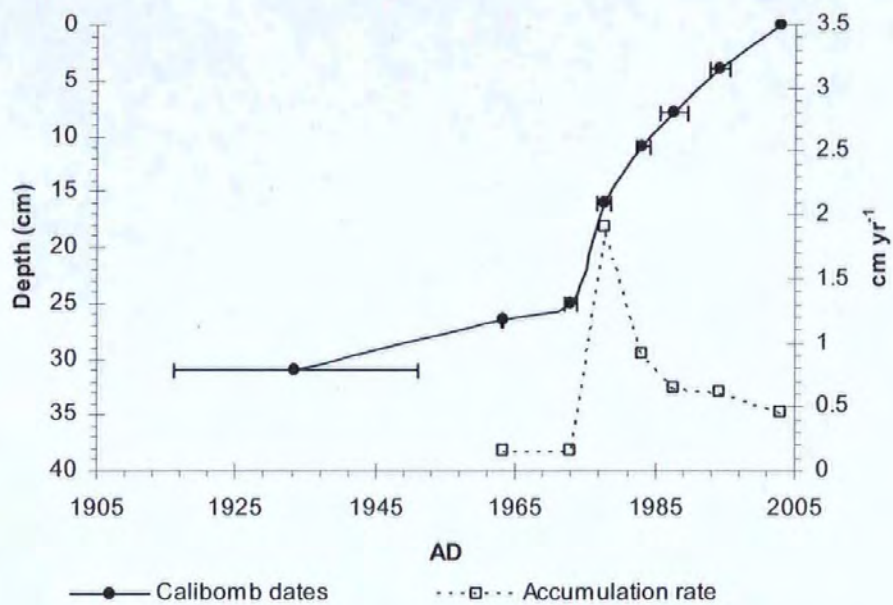


Figure 3.7. Age-depth model and accumulation rates derived from the Arne bomb carbon calibration results. Chronological uncertainty shown is the CALIBomb range (2 sigma).

3.3.4. Chronological issues. A number of discrepancies and disagreements arose out of the Arne ^{14}C calibration. Firstly, there was the apparent chronological displacement of sample Arne-03-47.5 in the sequence if solution 2 is accepted. The Calib 5.0 calibration (2 sigma) for this sample produced four possible solutions which spanned the time period of 1667 to 1952 (Table 3.3), but given the stratigraphic location of this sample, i.e. below the sample from 42.0 cm which was calibrated as older than AD 1880, we could reject the youngest solution from Calib 5.0 (1932 to 1952). However, as illustrated by Figure 3.4, to accept the next youngest remaining solution (1797 to 1805) and still maintain a chronological sequence would necessitate moving this sample physically down sequence to a level below the samples from 55 cm and 56 cm to maintain chronological order. A possible explanation of the uncertainty surrounding this data is contamination with older carbon during sampling or preparation, but it is most likely that this sample has been eroded and re-worked after its initial deposition. This issue is resolved in Chapter 8 where the chronological information obtained by all the dating methods is combined.

Secondly, the sample from 20 cm, Arne-03-20, calibrated somewhat off the bomb curve in Figure 3.6, and was also disregarded in the construction of the chronology. It is noted that this was the only sample in the set not to have been a grass stem fragment. It was described during sampling as a 'woody stem or wood fragment' and it is concluded that the ^{14}C in this sample was 'in the system' for some years before it was finally deposited on the marsh surface and entombed in 1966-1967. Although the ^{14}C analysis does not provide accurately the date of deposition, it is highly likely that the date of AD 1956, obtained from the $1.0418 \text{ F}^{14}\text{C}$ value, precisely dates the assimilation of atmospheric carbon in this material. As in the case of the Arne-03-47.5 the ^{14}C analysis seems faultless, and the lack of chronological fit is due to the sample being displaced in the stratigraphy.

The simple stratigraphic rule was also used to choose between the two solutions that appear possible for fitting of the sample from 26.5 cm (Arne-03-26.5) to the bomb spike curve. The sample had a result of $1.4637 \text{ F}^{14}\text{C}$, and it could have been fitted to either the rising or the falling limb of the bomb carbon peak, calibrating as 1963.07-1963.2 or 1971.6 - 1973.7 respectively. However, the sample above it, Arne-03-25, calibrates to 1972.7-1973.6. If it is accepted that Arne-03-25 is the younger sample, and if the younger age for 26.5 cm is used, it means that 15 mm of sediment deposition would have occurred between February 1972 and October 1973. This is not impossible (Allen, 2003; Cundy *et al.*, 2005) but it is a rapid

accumulation rate for a high salt-marsh environment, and is excessive when compared to the rest of the Arne sequence. The calibration result shown in Figure 3.6 gives accumulation rates (Figure 3.7) that agree with the expected rate of accretion expected in a temperate high marsh environment (e.g., Stevenson *et al.*, 1986; Wood *et al.*, 1989; Allen and Duffy, 1998; Bartholdy *et al.*, 2004; Price *et al.*, 2005).

Finally, there was a small difference in the two alternative calibration results obtained for the sample from 31 cm, Arne-03-31. The most likely age estimate from Calib 5.01 for this sample was 1917-1952, but the CALIBomb calibration was 1916.00-1951.10. After consideration of the adjacent samples it was felt that the most likely solution was the CALIBomb result.

3.3.5. Evaluation of low and high precision results. In addition to the use of both conventional and unconventional ^{14}C calibration methods, a combination of normal precision 3 ‰ and high precision 2 ‰ AMS analysis has been used on the Arne samples. To justify the extra commitment of laboratory resources there must be an apparent benefit from the use of higher precision analysis. This advanced type of ^{14}C AMS analysis demands an organic carbon sample of sufficient size for the production of multiple graphite targets, and requires proportionally more preparation time to produce these replicates. Then the extended analytical time on the AMS, and the cost of running the instrument at 2 ‰, must be considered. An inspection of the Arne AMS results shows that the use of high precision analysis had reduced the analytical one sigma uncertainty from approximately 0.0030 F^{14}C to 0.0018 F^{14}C (Table 3.1 and Table 3.2). This translated to a one sigma ^{14}C yr uncertainty of ± 15 yr for the 2 ‰ data (Table 3.2) instead of the ± 20 to 26 yr (Table 3.1) associated with the 3 ‰ data. By combining the replicate data for each ^{14}C sample in Calib 5.0 this uncertainty was further reduced to ± 9 ^{14}C yr (Table 3.2).

Telford *et al.* (2004) state that when ^{14}C data are considered 'a low standard deviation will give a tight calibrated probability distribution'. Therefore it is assumed the reduction in analytical and ^{14}C yr uncertainty to be gained by using a high-precision analysis would result in a corresponding reduction in the spread of the Cal yr age ranges of each of the calibration solutions. This did seem to be the case, but to evaluate this more formally the results obtained from the 2 ‰ analysis of the Arne samples were compared with the same ^{14}C yr data using an arbitrary ± 25 ^{14}C yr uncertainty to simulate a 3 ‰ analysis (Table 3.7).

¹⁴ C data	Publication no.	¹⁴ C yr BP uncertainty $\pm 1\sigma$	Age-ranges of the Calib 5.0 calibration solutions (Cal yr)	Mean and [1 σ] of each of the Calib 5.0 age-ranges
ARN-03-34 2 ‰ AMS data: X	SUERC-6364	155 $\pm$ 15	8, 34, 3, 8, 13, 0	11.0 [12.13]
Y	SUERC-6365	146 $\pm$ 15	12, 35, 10, 19, 11	15.4 [12.70]
Z	SUERC-6366	137 $\pm$ 15	14, 11, 3, 11, 7, 18, 4, 19, 1	9.8 [6.45]
Combined ARN-03-34 2 ‰ data	na	146 $\pm$ 9	10, 6, 7, 8, 14, 0	8 [4.60]
Simulated 3 ‰ data using $\pm$ 25 yr uncertainty: X _s	na	155 $\pm$ 25	16, 38, 3, 13, 2, 4, 4, 22, 1	20.6 [18.31]
Y _s	na	146 $\pm$ 25	18, 41, 6, 13, 4, 14, 1, 22	14.9 [12.74]
Z _s	na	137 $\pm$ 25	17, 15, 19, 13, 44, 22, 1	18.7 [13.00]
Combined simulated 3 ‰ : X _s , Y _s and Z _s	na	146 $\pm$ 14	12, 35, 10, 18, 1	15.2 [12.64]
ARN-03-42 2 ‰ AMS data: X	SUERC-6369	120 $\pm$ 15	12, 2, 10, 10, 47, 11, 0	13.1 [15.65]
Y	SUERC-6370	127 $\pm$ 15	14, 8, 8, 44, 12, 0	14.4 [15.31]
Z	SUERC-6371	147 $\pm$ 15	12, 35, 10, 19, 1	15.4 [12.70]
Combined ARN-03-42 2 ‰ data	na	131 $\pm$ 9	11, 7, 6, 5, 16, 3, 10	8.3 [4.39]
Simulated 3 ‰ data using $\pm$ 25 yr uncertainty: X _s	na	120 $\pm$ 25	21, 12, 18, 54, 15, 0	20.0 [18.17]
Y _s	na	127 $\pm$ 25	58, 19, 95, 36, 2	42.0 [36.16]
Z _s	na	147 $\pm$ 25	19, 50, 14, 3, 14, 0, 23, 1	15.2 [16.34]
Combined simulated 3 ‰ : X _s , Y _s and Z _s	na	131 $\pm$ 14	12, 9, 8, 12, 27, 12, 0	11.5 [8.08]
ARN-03-47.5 2 ‰ AMS data: X	SUERC-6374	174 $\pm$ 15	12, 17, 18, 4, 8	11.8 [5.93]
Y	SUERC-6375	175 $\pm$ 15	12, 16, 18, 4, 8	11.6 [5.73]
Combined ARN-03-47.5 2 ‰ data	na	175 $\pm$ 11	12, 12, 18, 4, 7	10.6 [5.24]
Simulated 3 ‰ data using $\pm$ 25 yr uncertainty: X _s	na	174 $\pm$ 25	15, 45, 8, 13, 0	16.2 [17.11]
Y _s	na	175 $\pm$ 25	14, 46, 7, 16	20.8 [17.27]
Combined simulated 3 ‰ : X _s and Y _s	na	174 $\pm$ 18	12, 18, 19, 5, 8	12.4 [6.11]
ARN-03-55 2 ‰ AMS data: X	SUERC-6376	83 $\pm$ 15	13, 12, 31, 2	14.5 [12.07]
Y	SUERC-6377	110 $\pm$ 15	14, 9, 14, 22, 4, 22, 8	13.3 [6.90]
Z	SUERC-6380	82 $\pm$ 15	13, 12, 30, 2	14.3 [11.62]
Combined ARN-03-55 2 ‰ data	na	92 $\pm$ 9	1, 14, 13, 12, 10	10.0 [5.24]
Simulated 3 ‰ data using $\pm$ 25 yr uncertainty: X _s	na	3 $\pm$ 25	25, 18, 38, 2	20.8 [15.00]
Y _s	na	110 $\pm$ 25	17, 10, 78, 10, 0	23.0 [31.34]
Z _s	na	82 $\pm$ 25	25, 18, 38, 2	20.8 [15.00]
Combined simulated 3 ‰ : X _s , Y _s and Z _s	na	92 $\pm$ 14	22, 15, 16, 12	16.3 [4.20]
ARN-03-62 2 ‰ AMS data: X	SUERC-6381	188 $\pm$ 15	14, 20, 4, 12	12.5 [6.61]
Y	SUERC-6382	210 $\pm$ 15	6, 16, 3	8.3 [6.81]
Combined ARN-03-2-62 2 ‰ data	na	199 $\pm$ 9	5, 6, 6, 8	6.3 [1.29]
Simulated 3 ‰ data using $\pm$ 25 yr uncertainty: X _s	na	188 $\pm$ 25	16, 16, 23, 8, 14	15.4 [5.37]
Y _s	na	210 $\pm$ 25	22, 21, 10	17.7 [6.66]
Combined simulated 3 ‰ : X _s and Y _s	na	199 $\pm$ 18	13, 1, 22, 10	11.5 [8.67]

Table 3.7. The mean ranges and one standard deviations of the age-solutions derived by Calib 5.0 from the high-precision 2 ‰ Arne AMS data and simulated 3 ‰ data.

The mean and standard deviation was calculated for each of the age ranges produced by Calib 5.0 for both the real and simulated ^{14}C yr data (Table 3.7). Then the X, Y and Z replicates were combined in Calib 5.0 and those data evaluated in the same way. The data showed that using a ^{14}C yr uncertainty consistent with a 2 ‰ analytical precision there was a reduction of >45% in most cases of the spread of the age ranges for individual or single-point data. A further reduction in the means and standard deviations of the age ranges was apparent when the X, Y, and Z replicates were combined. However, this exercise also showed that if two or more normal 3 ‰ precision replicates were analysed, and then combined using Calib 5.0, a real improvement in the age range spread of the calibration results could be achieved over individual or single-point data.

3.4. Inter-site comparisons and evaluation

Two contrasting ^{14}C dating results obtained by previous work at the Taf (W. R. Gehrels, unpublished data) and Viðarhólmi salt-marsh (Gehrels *et al.*, 2006) sites will now be examined and then compared to ^{14}C analysis and dating results presented here from the Arne site.

3.4.1. The Taf analysis. As part of ongoing work in the Taf Estuary (e.g. Gehrels *et al.*, 2001; Charman *et al.*, 2001; W. R. Gehrels, unpublished data) a number of ^{14}C dates were obtained for a sediment core collected in 1998 (Table 3.7). The Taf sediments are extremely minerogenic (See Chapter 2), especially in the lower horizons, and the ^{14}C 'samples of choice', discrete identifiable detrital macrofossils of the above-ground parts of terrestrial plants, are not present in this section. Therefore two alternative approaches were tried to obtain a robust ^{14}C chronology for this site. The ^{14}C analysis was carried out by the Utrecht AMS facility in the Netherlands.

In the first instance a number of samples were obtained of sub-fossil root material, identified as belonging to *Juncus maritimus* (salt-marsh reeds). Normally this material would be avoided because dates from sub-surface root material reflect the age of the plant growing at the surface, not the time of deposition of the sediments surrounding the sample, but the original idea was to correct the sample depth by establishing the root penetration of modern plants. Unfortunately this proved to be not feasible. Due to differences in the depth of root penetration of the fossil *Juncus* plants at the site or the misidentification of subsurface roots, the dates obtained

were too young, and some of the samples from below 70 cm produced modern ^{14}C ages. The second attempt to date the sediment was more successful. Amorphous black carbon was separated from bulk sediment samples and concentrated by selective sieving. The residue was then manually screened under a low power microscope, and any visible root fragments were picked out and discarded. The residues were then submitted to Utrecht for ^{14}C AMS using their normal laboratory processes, and the ^{14}C results (Table 3.7) subsequently calibrated using Calib 4.0 and the INTCAL98 curve (Stuiver *et al.*, 1998).

Publication code	Depth (cm)	¹⁴ C age		Calibration peak relative area value	median age	AD - BC	
		¹⁴ C yr BP	± 1σ			lower	upper
Bulk sediment ages							
UIC-11036	30.5	509	33	0.937	1419	1395	1445
UIC-11037	34.5	746	37	0.998	1268	1218	1299
UIC-11038	39.5	692	39	0.637	1300	1261	1327
UIC-11039	44.5	842	41	0.85	1200	1155	1278
UIC-11040	49.5	982	36	0.527	1063	993	1073
UIC-11041	54.5	1237	43	1	786	684	890
UIC-11042	59.5	1028	28	0.966	1005	975	1036
UIC-11043	64.5	1637	28	0.751	415	377	472
UIC-11044	69.5	1416	36	0.919	632	596	674
UIC-11045	74.5	1524	42	0.998	540	431	620
UIC-11046	79.5	2070	39	0.973	-86	-177	4
UIC-11047	84.5	2061	42	0.989	-76	-174	26
UIC-11048	89.5	2044	41	0.976	-51	-167	29
UIC-11049	94.5	4800	45	0.947	-3572	-3660	-3508
UIC-11050	99.5	3047	33	0.897	-1314	-1407	-1255
UIC-10587	106.5	3099	37	0.944	-1366	-1435	-1287
UIC-10588	107.5	3047	36	0.883	-1313	-1407	-1247
UIC-10589	108.5	3456	36	0.76	-1770	-1830	-1686
Root fragment ages							
UIC-10286	55.5	-793	32	na	Modern	na	na
UIC-11033	59.5	-812	39	na	Modern	na	na
UIC-10194	65.5	-752	30	na	Modern	na	na
UIC-10195	75.5	-502	31	na	Modern	na	na
UIC-11034	79.5	-62	42	na	Modern	na	na
UIC-10196	85.5	441	33	0.985	1450	1412	1494
UIC-10197	95.5	489	39	0.971	1426	1397	1473
UIC-11035	99.5	236	33	0.524	1665	1632	1680
UIC-10198	105.5	189	32	0.592	1770	1726	1813
UIC-10287	115.5	477	30	0.975	1431	1405	1455
UIC-10199	125.5	716	33	0.887	1285	1239	1305
UIC-10200	135.5	567	35	0.573	1356	1303	1368
UIC-10356	145.5	468	38	1	1436	1402	1485
UIC-10201	155.5	862	42	0.677	1176	1150	1263
UIC-10202	165.5	660	37	0.548	1349	1342	1396
UIC-10203	175.5	906	40	1	1118	1031	1213
UIC-10204	185.5	1080	43	1	960	884	1025
UIC-10205	195.5	950	50	0.984	1096	1001	1192

Table 3.8. The ^{14}C dates obtained on bulk sediment black carbon detritus and the root fragments. Calibration (2 sigma) by Calib 4.0 using the INTCAL98 curve (Stuiver *et al.*, 1998).

The sample from 94.4 cm produced a ^{14}C age of 4800 ± 45 yr BP which appeared anomalous when compared to the other ^{14}C ages so it is disregarded as an unexplained outlier. The age ranges indicated by the best CPRV are shown in Figure 3.8 plotted on the Intcal04 calibration curve (Reimer *et al.*, 2004b). The insert shows how some data elegantly fit onto a number of steep sections of the Intcal04 calibration curve. The resulting lack of ambiguity does confirm the robustness of the chronology, and the 2nd order polynomial fit shown in Figure 3.9 offers a plausible simple age-depth model. The Taf age-depth plot shown in Figure 3.9 does not change significantly if the age-ranges indicated by the calibration peak values, or the median age probability of each sample (Table 3.8), are used to produce it. A mean accumulation rate of 0.3 cm yr^{-1} can be calculated for the time spanned by the model, and this compares well with the 0.5 cm yr^{-1} calculated for the section above the youngest sample at 30.5 cm to the surface.

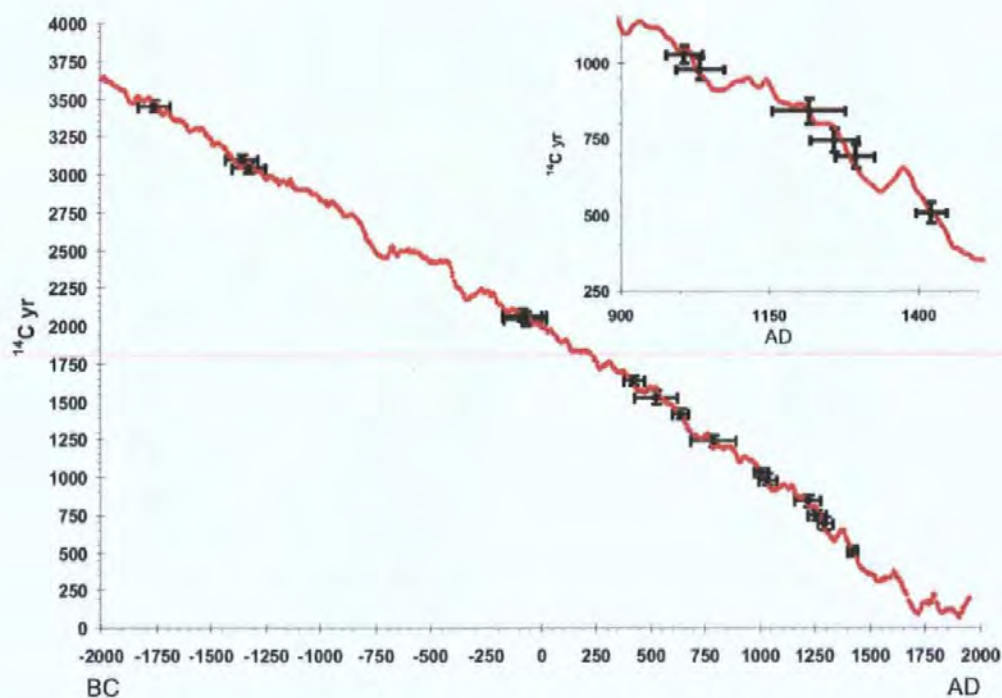


Figure 3.8. The Taf ^{14}C age-ranges (1 sigma) associated with the best CPRV plotted on the Intcal04 calibration curve (Reimer *et al.*, 2004b). Insert is the detail of AD 1000 to AD 1500.

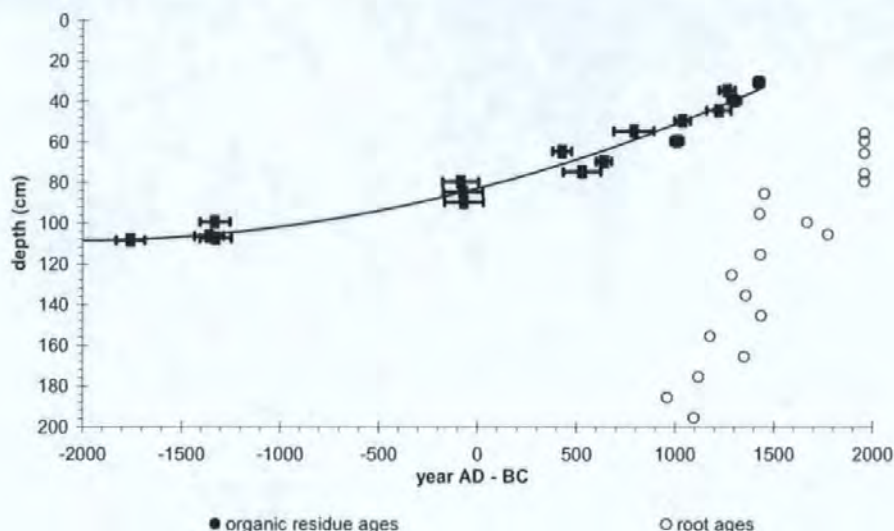


Figure 3.9. The Taf ^{14}C dates (2 sigma) with a 2nd order polynomial fit. The 'root ages' are shown only for comparison, and the uncertainty for these data is omitted for clarity.

However, the bulk sediment approach can not give the chronological resolution that is possible using individual organic carbon samples taken from identified macro fossils. It has a higher vertical uncertainty attached to it because of the size of the samples required. It can be seen that in some zones there are a number of dates that, even though the samples are separated in the stratigraphy by several centimetres, the calibrated ages are statistically similar and form clusters around a mean date. This is most likely a reflection of some vertical diffusion of the black carbon residue in the sediments blurring the division of the ^{14}C values for the individual samples in these areas. This may have been caused by diagenesis, vertical ground water flows, or it may be an artefact of the coring or sampling processes. Consequently, there are some gaps in the series of dates used to construct the Taf chronology, and in these zones the only option is to assume a linear trend in accumulation rates. However, what this method has effectively produced is a number of replicates for the sediments in the sections 34.5-44.5 cm, 79.5-89.5 cm and 99.5-107.5 cm, thus increasing the robustness of the overall age-estimate for those sections.

3.4.2. The Viðarhólmi ^{14}C analysis. As part of the contribution by the University of Plymouth to the HOLSMEER Project (See Scourse *et al.*, 2006 for project details) a series of ^{14}C dates were obtained by Gehrels *et al.* (2006) for the Viðarhólmi site in northwest Iceland (Table 3.8). The ^{14}C analysis was carried out at the AMS Dating Centre, Department of Physics and Astronomy, University of Aarhus, using a tandem AMS. As with the Arne sequence, only fragile, horizontally embedded, detrital plant fragments were selected for the ^{14}C analysis in an attempt to ensure that the dated carbon samples were contemporaneous with the ancient marsh surface. The Viðarhólmi radiocarbon ages presented here (Table 3.9) were calibrated using Calib 5.0 (Stuiver *et al.*, 2005) and the Intcal04 calibration curve (Reimer *et al.*, 2004b).

Publication code	Depth (cm)	^{14}C age		Calibration peak relative area value	AD - BC		
		^{14}C yr BP	$\pm 1\sigma$		median age	lower	upper
AAR-8031	36	105	47	0.583	1830	1810	1895
AAR-8032	39	168	43	0.434	1779	1727	1785
AAR-8033	51	314	36	0.767	1562	1517	1594
AAR-8034	63	735	35	1.0	1270	1257	1289
AAR-8036	83	1081	42	0.636	957	945	997
AAR-8037	86	1090	47	0.648	947	935	994
AAR-8038	88	1312	38	0.732	702	661	710
AAR-8039	99	1553	41	0.601	497	434	494
AAR-8040	113	1696	44	0.802	345	323	406
AAR-8041	129	1887	44	0.758	119	66	140
AAR-8042	145	1920	43	0.901	82	49	129
AAR-8043	162	2052	41	0.814	-70	-112	-17

Table 3.9. The Viðarhólmi ^{14}C results and the 1 sigma calibration from Calib 5.0 (Stuiver *et al.*, 2005).

The calibration of the Viðarhólmi ^{14}C results indicates that the sample from 162 cm was just over 2 ka yr in age, which meant that the means accumulation rate for the complete sequence was approximately 0.08 cm yr^{-1} . The best CPRV is used to select age ranges, and these are fitted to the Intcal04 calibration curve (Reimer *et al.*, 2004b) to evaluate the security of the chronology. It is evident that the older ^{14}C ages fit the calibration curve (Figure 3.10) with a reasonable lack of ambiguity, but this is not the case with the samples above 63 cm (Figure 3.10 insert). The three youngest samples all have multiple intersects on the calibration curve. This means that the use of the age ranges indicated by the best CPRV, or the median probability method, are not capable of producing a high resolution chronology for these sections of the calibration curve.

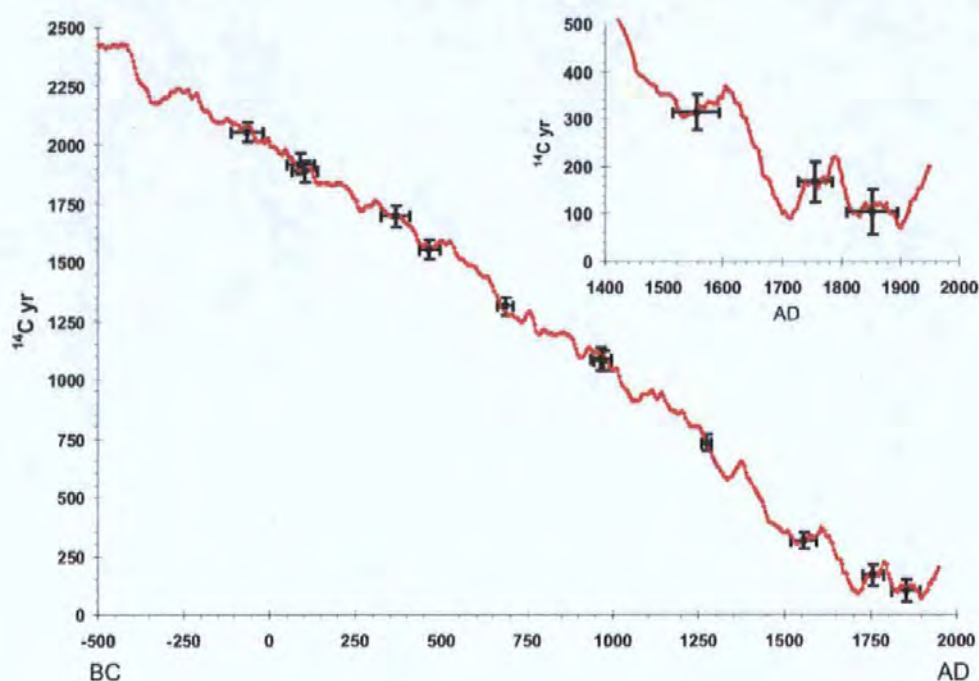


Figure 3.10. The Viðarhólmi ^{14}C age-ranges (1 sigma) associated with the best CPRV plotted on the Intcal04 (Reimer *et al.*, 2004b) calibration curve (Red line). Insert is the detail of AD 1400 to AD 1950. Filled shapes highlight the multiple intersects and the zone of the overlap of the calibration of the samples from 36 cm and 39 cm.

An examination of the probability distribution curves of the youngest four samples (Figure 3.11) illustrates how the use of the CPRV range, or the median age, can not be used to resolve reliably multiple intersects. This information can not describe the total uncertainty. It can be seen how the normal Calib 5.0 calibration for each of the upper two samples is not statistically unique, and, despite having a vertical separation of 3 cm in the sequence, these samples can be interpreted as having the same age if the total uncertainty is considered. In fact if the 2 sigma calibration results are considered there is an overlap, and thus no secure chronological separation, between the samples from 39 cm and 51 cm (Figure 3.11). It is not possible to refine reliably a solution for the Viðarhólmi ^{14}C ages further without more chronological information. In Chapter 8 all the available dating information, e.g. dated tephra layers, is used to construct the 'definitive' chronology for each site, but when only the ^{14}C data tabulated in Table 3.9 are considered the model shown in Figure 3.12 is considered a valid and plausible solution.

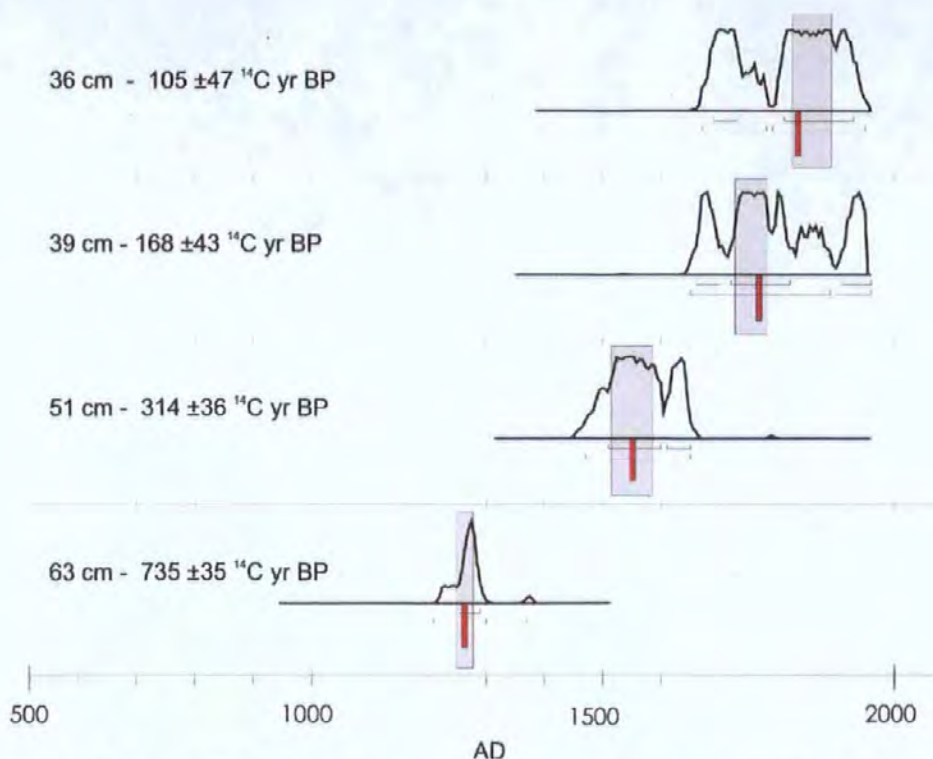


Figure 3.11. The probability distribution curves for the upper four Viðarhólmi ^{14}C ages produced by Oxcal (Bronk Ramsey, 1995, 2001) using the Intcal04 calibration curve (Reimer *et al.*, 2004b). Arbitrary Y axis scale. Thin horizontal bars show 1 sigma (Upper) and 2 sigma (Lower) Cal ranges. Grey rectangles show age range associated with the best CPRV, red bars show the median age probability produced by Calib 5.0 (Stuiver *et al.*, 2005).

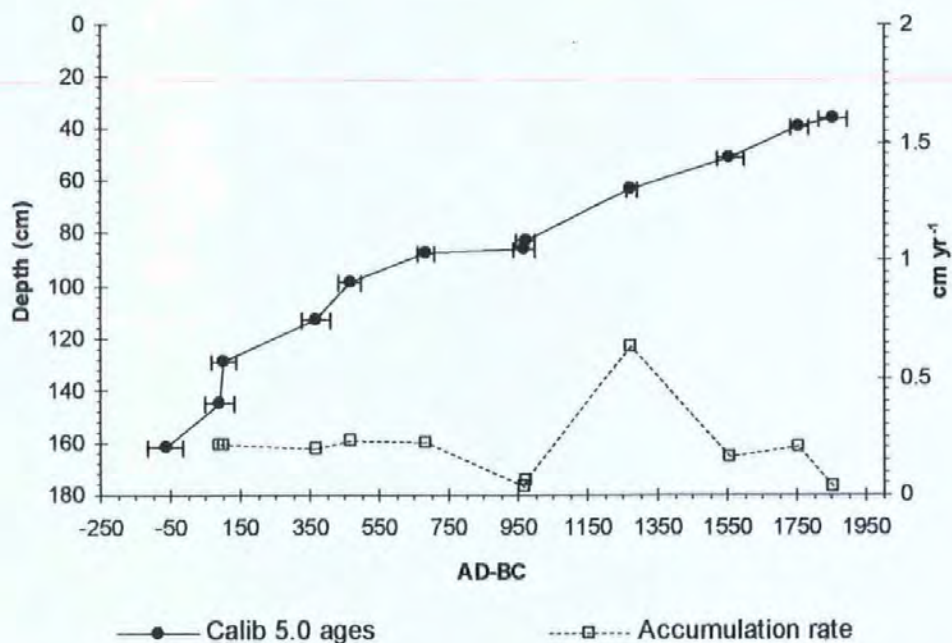


Figure 3.12. The Viðarhólmi age-depth model and accumulation rates derived from the age-ranges associated with the best CPRV produced by the Calib 5.0 ^{14}C calibration.

3.5. Discussion and synopsis

3.5.1. Resolution and sample density. If the objective is to create a high resolution chronology, it follows that sufficient samples must be available to create the ^{14}C ages at the resolution required. Therefore, some consideration of likely past accumulation rates must be entered into when a sampling strategy is being designed. Further to this, the investigation reported here has shown that a high-resolution chronology can best be created using ^{14}C dating when there is sufficient sample density to allow adjacent samples to act as analytical checks for their neighbours. In addition, a high sample density will help to flag up inconsistencies in the chronology after calibration, as in the case of the Arne post-bomb samples. If the intention is to date the deposition of sediments using contemporary macro fossils then the time lag between the assimilation of atmospheric CO_2 by the plant, and the subsequent deposition of the carbon sample must be as short as possible.

In the Arne analysis, sample Arne-03-20 appeared to be displaced in the chronology defined by the other samples in the set. When the adjacent data were considered it was decided that this material had most likely been deposited in the sediments some time after the last integration of atmospheric ^{14}C into the organic carbon sample. The sample description of Arne-03-20 suggested that it was most likely a fragment of a woody perennial, possibly a bush or tree. In contrast to grasses and reeds, a woody perennial can have a life span of several years, and, in the case of a tree many decades. Trees build up incremental annual rings that faithfully record the ^{14}C concentration of each individual growth year, and this characteristic is utilised to construct ^{14}C calibration curves using dendrochronology (See section 3.1). In addition, it is possible for a tree to die and fall, but not become fragmented and entombed in sediments for many years. Given the diversity of pathways that a single fragment of wood could take from a growing tree that would eventually lead to it being incorporated in the Arne salt-marsh it is remarkable that the woody sample, Arne-03-20, was less than 10 years out of chronological sequence.

The calibration of Arne-03-20 using CALIBomb dated the assimilation of the carbon in the sample to the period of January 1956 to August of the same year. When the timing of the growing season in Southern England is considered this calibration translates to a likely range of less than four months, i.e. the late spring and summer. This is excellent chronological precision but, unfortunately it is not the date the sample was deposited. No matter what type of AMS analysis, or what form

of calibration is used for the ^{14}C data subsequently produced, if the carbon sample has been displaced within the context of the stratigraphy any deposition age that is obtained from it will be wrong. In addressing this issue the chances of post-deposition reworking or vertical migration with the sub-surface sediments can be minimised by adopting the approach used in the Arne and Viðarhólmi ^{14}C analysis; i.e. the preferential selection of identifiable macro-fossils that are too frail to remain intact if subjected to erosion and transportation, but are also too large to be dispersed by pore-water movement.

The movement of detritus suspended in pore-water is viewed as a potential mechanism for the blurring of the definition of a ^{14}C analysis of bulk sediments, as in the case of the Taf sequence. In addition, this type of sample may consist of a complex mixture of organic carbons from a number of sources, and may therefore be subject to unknown 'reservoir' effects. For example, it would be logical to assume that some proportion of the black organic detritus present in the Taf sediments was the residue of above-ground plant fragments that had fallen on the marsh surface in the past. However, there will most likely have been some contribution from decayed sub-surface root material which would have had a younging effect on the data. There was no way of determining if this was an issue with the Taf data, and it is possible that there was a systematic offset to all the dates obtained by that analysis. Without some form of independent confirmation of the chronology this possibility cannot be excluded.

If the option exists to improve the analytical precision it should be exploited. Simply by ensuring the carbon sample is as large as possible can allow the multiple target approach to be used. The simple combining of the results of a number of replicates has been shown in 3.3.5 to reduce significantly the one sigma uncertainty in the ^{14}C data. The improvement of the analytical precision of the initial AMS ^{14}C analysis has also been shown by the evaluation of the 2 ‰ and 3 ‰ results in 3.3.5 to offer a further reduction in the final chronological uncertainty attached to the calibrated dates. In addition, newer and more advanced facilities can be expected to perform at a higher precision than older AMS laboratories, and so a ^{14}C analysis performed some years ago may have been produced to a significantly lower standard than current work. There was some evidence for this when the Arne and Viðarhólmi data were compared. The Arne 3 ‰ normal precision data, produced by a newly installed AMS instrument at SUERC in East Kilbride, had consistently smaller uncertainties attached to the ^{14}C ages than the results from the Viðarhólmi analysis that were

obtained using the less advanced AMS facility that had been operating for some years at the University of Aarhus.

3.5.2. Calibration issues. The calibration of the ^{14}C ages into calendar dates was not a simple task, and the robustness of the results was very dependent on the part of the calibration curve that the ^{14}C data intercepted. A number of calibration 'complications' were highlighted and discussed in the Arne report, but there were issues with the other two calibrations. For example, the Viðarhólmi analysis produced a chronology that was apparently robust for the pre-medieval period, but in the more recent part of the record the uncertainty of the calibration using the normal approach was disproportionately high. This highlighted the short-comings in the normal calibration of ^{14}C ages that fall on the problematic sections of the calibration curve, and specifically any that have multiple intersects on the reversals and peaks during the last 500 yr. The data showed that individual ^{14}C ages calibrated on this section of the curve can produce a total uncertainty of <150 yr.

There is the need for more chronological information to help interpret ^{14}C ages that cannot be calibrated using the standard approaches. One approach would be the use of a denser sampling interval in the higher sections of a sequence. This would offer the chance to use wiggle matching as a calibration method, but this ideally needs sufficient samples to span a number of unique sections of the calibration curve. However, as the fit of the Arne data to the calibration curve showed, if a set of ^{14}C ages are considered as a group, and the simple rule of stratigraphic position maintained, the number of possible solutions can be confidently reduced. Alternatively, ^{14}C calibrations can be constrained using the simple concept of 'prior knowledge' offered by independent age markers. Independent chronological information can also be integrated into more complex statistical age models based on calibrated ^{14}C ages as used by Gehrels *et al.*, (2005). This issue is explored further in Chapter 8 when the results from the different dating methods are amalgamated to produce combined chronologies for each site using all the information available.

3.5.3. Synopsis. The use of ^{14}C dating has been examined in some detail at the Arne site. This section of this study has successfully used the 'bomb spike' calibration method, a somewhat novel approach, to date very recent sediments using ^{14}C . This method was shown to be capable of creating robust chronology spanning the post-bomb era from suitable organic carbon samples, and it appeared to work well in the sequence investigated. An uncertainty of >3 months was shown to be theoretically obtainable during some periods. The Arne investigation also used a form of wiggle-matching to refine the normal calibration of pre-bomb ^{14}C data. This approach reduced the size of the uncertainty attached to the calibrated Arne dates for the period spanned by a section of the ^{14}C calibration curve that often produces ambiguous dates. This method did appear to offer a plausible solution for the problematic period of the last three centuries, and allowed data to be used in the chronology that would, using the conventional calibration approach, have been inconclusive. Finally this section of the thesis has tested and evaluated the effects of two different AMS analytical precision levels on the potential size of ^{14}C age uncertainties and the size of the calendar age-range after calibration.

The pre-existing ^{14}C data from the Taf and the Viðarhólmi salt-marsh were presented and calibrated using Calib 5.0. In the case of the Taf it was demonstrated that a good quality low-precision chronology spanning the last 4000 yr BP could be constructed from the ^{14}C analysis of black organic carbon detritus. In contrast, carefully selected individual organic carbon samples were used for the Viðarhólmi analysis. The stratigraphic control of these data appeared to be better than in the Taf salt marsh, but this was not conclusive. In addition, the analytical uncertainty of the results was not significantly better with the Viðarhólmi individual carbon samples when they were compared to the data obtained from the Taf bulk sediment carbon residue. However, the normal precision Arne analysis did have lower uncertainties for similar ^{14}C ages (e.g., Arne-03-31, 164 ± 25 ^{14}C yr BP, Viðarhólmi 39 cm, 168 ± 43 ^{14}C yr BP).

Chapter 4

Radioisotopic dating methods part 2: Lead-210 and nuclear fallout radionuclides

This chapter will continue with the theme of dating of salt-marsh sediments using radioactive isotopes and will present an investigation into the use of three non-carbon radionuclides, ^{210}Pb , ^{137}Cs and ^{241}Am . By way of introduction to this section the occurrence, transport and deposition of ^{210}Pb , ^{137}Cs and ^{241}Am will be reviewed, and then the use of these radionuclides as dating tools will be described. The application of these dating tools in a salt-marsh environment is introduced in 4.2.3, and section 4.3 reports the results obtained by this study in using radionuclides to date the Arne sediments. These results are compared with those obtained at the Taf and Viðarhólmi sites and finally the methods are evaluated in section 4.5.

4.1. Lead-210

4.1.1. Lead-210 production. Lead-210 is commonly used to date sediments deposited during the last 150 years in both terrestrial and marine environments. The original proposal of ^{210}Pb as a dating tool is attributed to Goldberg (1963), but it was not widely used until after it was first applied to lake sediments by Krishnaswami *et al.* (1971). Lead-210 has a half-life of 22.26 years and is produced in the lithosphere by the transmutation of primeval ^{238}U (See 3.1.1). Radioactive equilibrium is assumed to have been maintained at each successive step until ^{226}Ra decays to gaseous ^{222}Rn which has a half-life of 3.82 days. This gas diffuses through the pores and voids in the fabric of rocks and sediments. At this stage some is released into the atmosphere (Figure 4.1) and is effectively lost from the radionuclide inventory in the sediments. The remaining ^{222}Rn will decay below ground to form ^{210}Pb producing what is termed the 'supported' ^{210}Pb fraction in the sediments, i.e. the ^{210}Pb activity of the total inventory produced only by the ambient sub-surface ^{226}Ra and ^{222}Rn activity in the sediments (Appleby, 2001; Carroll and Lerche, 2003).

The loss of gaseous ^{222}Rn to the atmosphere means the remaining ^{226}Ra , ^{222}Rn and ^{210}Pb activity in the sediments is no longer in radioactive equilibrium. The ^{222}Rn that escapes from the ground into the atmosphere quickly decays to particulate ^{210}Pb . Once formed, this lead has a residence time of around ten days in the atmosphere where it can be transported large distances by air-mass movement before being scavenged by precipitation and deposited onto the Earth's surface. It is incorporated into accumulating sediments and becomes the 'unsupported' or 'excess' fraction of

the total ^{210}Pb inventory at a site. In other words, it is the amount of measurable ^{210}Pb activity in a sample that can not be attributed to the local ambient ^{222}Rn activity in the host sediments (Appleby, 2001; Carroll and Lerche, 2003).

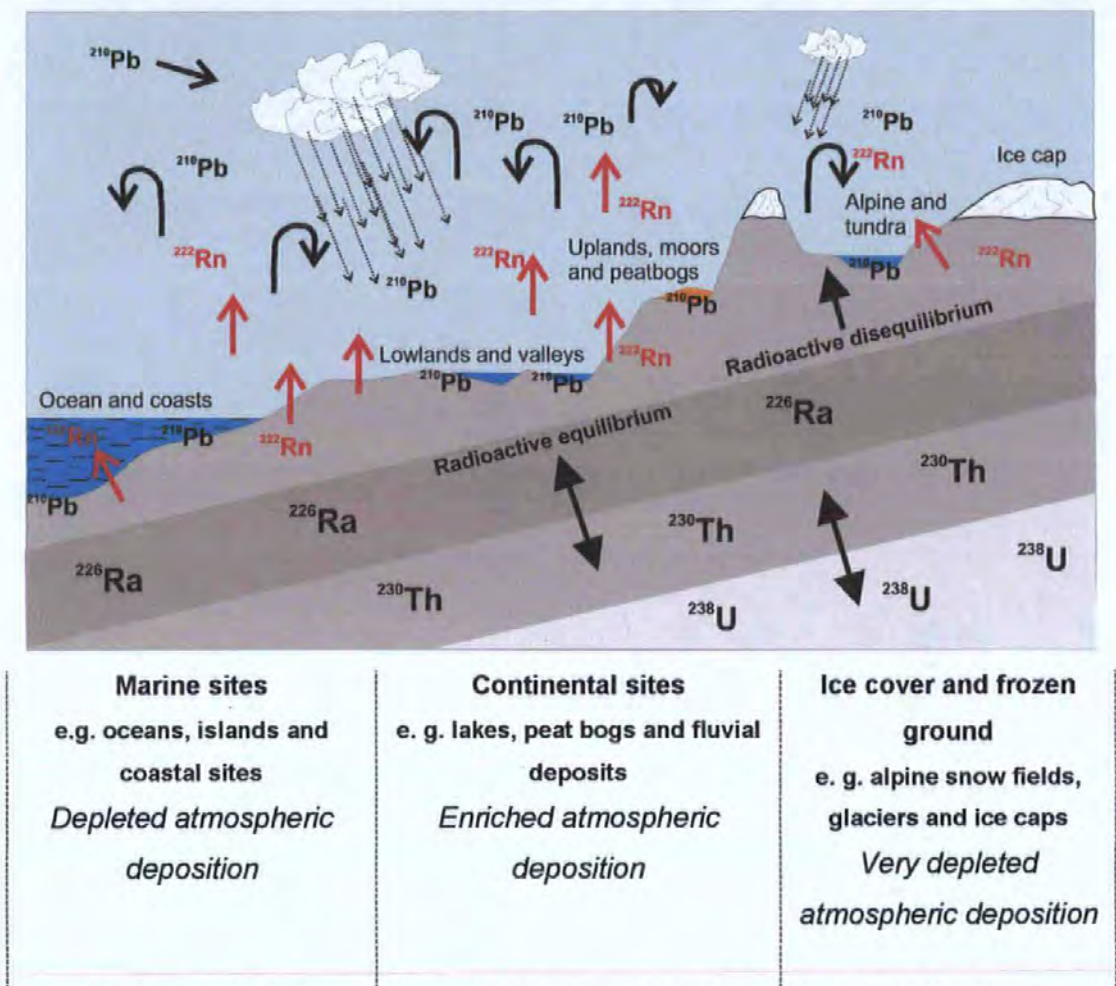


Figure 4.1. Lead-210 production and relative atmospheric deposition levels. (After Preiss *et al.*, 1996).

The ambient sub-surface ^{222}Rn activity is dependent upon the local and regional geology. Bedrock containing high levels of ^{238}U will contain proportionally high levels of the daughter radionuclides resulting from the decay of this uranium radioisotope. For example, in Western Europe close association is found between high ^{226}Ra , ^{222}Rn and ^{210}Pb activity in sediments and the uranium-rich granites emplaced during the Variscan Orogen in the southwest of Ireland and western England, central France and the Iberian Peninsula (Plant *et al.*, 2003). Other geologies, including volcanic terrains (e.g., D'Alessandro and Vita, 2003), can produce ^{226}Ra , ^{222}Rn and ^{210}Pb activity, but at reduced levels when compared to the activity found in soils and sediments formed over crystalline granites (Plant *et al.*, 2003).

Radon-222 distribution in surface air, and hence atmospheric ^{210}Pb production, is not spatially uniform across the surface of the Earth (Table 4.1). If produced under a lake or ocean, a significant fraction of the gaseous ^{222}Rn will defuse into the overlying water body and be contained there. Therefore, surface air concentrations of ^{222}Rn tend to be higher at sites near to the middle of continental land masses (Chevallard *et al.*, 2002; Conen and Robertson, 2002). As shown in Figure 4.1, if the atmospheric pathway of ^{222}Rn is obstructed by water or ice cover the local atmospheric ^{210}Pb production is much reduced. Permanently frozen ground restricts ground-atmosphere gas exchange, and oceans emit approximately two orders of magnitude less ^{222}Rn to atmosphere than ice-free continental land surfaces (Lambert *et al.*, 1982). As a general rule, atmospheric ^{210}Pb levels tend to be depleted in rain-shadow zones on the 'wrong side' of mountain ranges, and a trend exists for decreasing ^{210}Pb deposition when moving westward across continents (Appleby, 2001).

Location	^{210}Pb concentration (mBq.m ²)	Location	^{210}Pb concentration (mBq m ²)	Location	^{210}Pb concentration (mBq m ²)
Anchorage (Alaska)	310	Dye 3 (Greenland)	180	Calcutta (India)	945
Salt Lake City (Utah)	707	Tromsø (Norway)	167	Chiba (Japan)	370
Los Angeles	540	Moscow	310	Pretoria (S. Africa)	750
Washington (W.D.C.)	465	Chilton (UK)	230	Reunion Island (Indian Ocean)	110
New York City	580	Dublin	135	Honolulu (Hawaii)	178
Winchester (Mass.)	635	Galway	130	Brisbane (Aust.)	260
New Orleans	770	Rosslare	205	Melbourne (Aust.)	190
Miami	283	Brunswick	370	Lower Hutt (S. NZ)	75
Panama City	116	Warsaw	320	Falkland Islands	50
Lima (Peru)	247	Paris	480	Antarctica	14
Santiago (Chile)	332	Bordeaux	590	Peninsula South Pole research station	32

Table 4.1. Variations of annual mean ^{210}Pb concentration in surface air at different geographic locations. Selected from Preiss *et al.* (1998).

Radon-222 emissions and atmospheric ^{210}Pb production are controlled in the main by the dominant bedrock geology of an area. This factor will be the primary control on the ^{226}Ra content of the local soils (Schery and Wasiolek, 1998), but atmospheric ^{210}Pb will also be strongly influenced by regional weather patterns, air mass trajectories and precipitation (Appleby, 2001; Ferry *et al.*, 2001). Other, more local, factors controlling ^{222}Rn emissions, and subsequent atmospheric ^{210}Pb production, are erosion and weathering rates (Xu *et al.*, 1993), soil moisture levels (Nazaroff, 1992), water table depth (Conen and Robertson, 2002) and soil texture (Dörr and Münnich, 1990). In addition, some increases in ^{222}Rn emissions to atmosphere often

occur preceding, and during, volcanic and seismic events (Segovia *et al.*, 1999; Gauthier *et al.*, 2000; Segovia *et al.*, 2001).

4.1.2. Dating with ^{210}Pb . Lead-210 dating produces age estimates for a sediment sequence by measuring the activity level of unsupported, or excess, ^{210}Pb activity in a sequential set of sediment samples, and then comparing this information with the measured activity for the modern surface activity at that site (Appleby, 2001; Carroll and Lerche, 2003). Assuming a closed system, the unsupported ^{210}Pb activity in a sample will depend on:

- The initial ^{210}Pb activity when the sediment was deposited.
- The decay time period, in half lives, that has elapsed since this deposition.

The unsupported fraction of the ^{210}Pb activity cannot be measured directly from the sediments. It must be derived by subtracting the activity of supported ^{210}Pb from the measured of total ^{210}Pb activity. The total ^{210}Pb activity can be determined directly by gamma spectrometry, or indirectly by measuring ^{210}Po activity, assuming radioactive equilibrium exists between the ^{210}Pb and its progeny. Likewise, the activity of supported ^{210}Pb can be determined indirectly by measuring the activity of ^{226}Ra using either alpha or gamma spectrometry. For a detailed description of the analytical methods involved in ^{210}Pb analysis the reader is directed to Appleby (2001) and references therein.

To obtain deposition ages from sequential ^{210}Pb data they are processed using an appropriate model of radioactive decay through time. A number of subtle models have been developed of varying degrees of sophistication and complexity (Carroll and Lerche, 2003), but only the most common three will be examined here.

The CFCS Model. The original model of ^{210}Pb dating (Krishnaswami *et al.*, 1971; Robbins, 1978) was developed by Appleby and Oldfield (1978) as their Constant Flux - Constant Sedimentation (CFCS) model. This model is a simple development of the basic radiometric dating principal shown in Chapter 3 (3.3). It makes these assumptions:

1. There has been a constant rate of ^{210}Pb deposition from the atmosphere.
2. The unsupported, or excess, ^{210}Pb fraction in the sediments is only due to atmospheric deposition.

3. There has been no post-deposition disturbance, or redistribution, of the accumulated sediment.
4. There has been steady-state dry-mass sedimentation rate.

Under these conditions the depth that the sediments, defined by cumulative mass m , were deposited at age t will simply be a function of the sedimentation rate r , thus

$$t = \frac{m}{r} \quad (4.1)$$

where t = time elapsed since deposition, m = cumulative dry-mass and r = dry-mass sedimentation rate.

Therefore, if the above conditions are met then the unsupported ^{210}Pb activity in the sub-surface sediments will be governed by the exponential law and the relationship can be written as

$$A(x) = A(0) \exp\left(-\frac{\lambda m}{r}\right) \quad (4.2)$$

where A = unsupported ^{210}Pb activity, 0 = surface and λ = ^{210}Pb decay constant (0.03114 yr^{-1}).

A logarithmic plot of $A(m)$ vs. depth should result in a linear relationship and the sedimentation rate, r , can be determined from the slope of this line.

The numbers of environments that satisfy all the prerequisites needed for the CFCS model to perform satisfactorily are limited (Carroll and Lerche, 2003). Short-term fluctuations superimposed on longer-term changes in sedimentation rates are a common feature of many dynamic sedimentary environments like salt marshes. Changes in sediment supply, sea level, and anthropogenic disturbance have resulted in many sites experiencing significant changes in sedimentation rates during the past 150 years. Often unsupported ^{210}Pb records from salt marshes will be complex and, when plotted on a logarithmic scale, will be non-linear in profile (Appleby, 2001).

The CRS Model. To facilitate the use of ^{210}Pb dating at sites where the sedimentation rate has not been constant a more sophisticated model was devised that could compensate for changes in the dry sediment supply. This development became known as the Constant Flux (CF) (Robbins, 1978) model or the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 1978; Appleby *et al.*, 1979). In this model it is assumed that the ^{210}Pb flux has remained constant through time, but the sediment supply is allowed to change. When the unsupported ^{210}Pb record is integrated to a depth x , or dry mass m , it will equal the ^{210}Pb flux integrated over the time elapsed since the deposition in years of those sediments. To find the elapsed time (t) when the unsupported ^{210}Pb is integrated to depth the CRS model can be written as

$$t = \frac{1}{\lambda} \ln \left(\frac{A(0)}{A(x)} \right) \quad (4.3)$$

where A = unsupported ^{210}Pb activity, (0) = surface, (x) = depth of interest, λ = ^{210}Pb decay constant and $\ln$ = natural logarithm.

The CRS model is the most common approach to ^{210}Pb dating used today. It is known to produce reasonable results in most environments that have received a steady flux of unsupported ^{210}Pb directly from atmosphere (Appleby, 2001). This condition applies particularly to salt marshes where the organic content changes with depth.

The CIC model. An alternative to the CRS model is the Constant Initial Concentration (CIC) model (Appleby, 2001). Sometimes termed the Constant Initial Activity (CIA) (Appleby and Oldfield, 1978) or the Constant Specific Activity (CSA) model (Robbins, 1978), this model was developed for environments where the unsupported ^{210}Pb flux is not supplied directly by local atmospheric fall-out. It is designed to work when the local ^{210}Pb flux is responding to remote changes in larger sedimentary systems (e.g., abyssal environments in deep ocean basins or large lakes). In these situations variations in the sedimentary system are damped and muted, and conditions are very different to that usually found in near-shore or terrestrial environments. This model allows the sedimentation rate to change through time, but unlike the CRS model, the CIC model assumes that initial unsupported ^{210}Pb activity has remained in proportion to the sediment supply (Appleby, 2001). A typical situation where this model can produce a more reliable result than the CRS model is where autochthonous sediments have scavenged

^{210}Pb from the water column, and therefore any changes in grain production will be reflected in changes in ^{210}Pb activity.

When using the CIC model the time elapsed since the deposition of sediment at depth x can be derived from the equation

$$A(x) = A(0) \exp(-\lambda t) \quad (4.4)$$

where A = unsupported ^{210}Pb activity, 0 = surface, (x) = depth of interest, t = time elapsed since deposition and λ = ^{210}Pb decay constant (0.03114 yr^{-1}).

The sedimentation rate can be obtained by dividing the decay constant by the slope of the line described by the right-hand side of the above equation.

Model selection and validation. The dating model used will depend on the sedimentary characteristics of each site, and the quality of the ^{210}Pb record. The 'perfect site' that allows the use of the simple CFCS model is a rarity, but this model can still be used as an initial trial to test the quality of the data before a more sophisticated conceptual model (e.g., the CRS model) is used.

In essence the CRS model will be applicable at most sites where a steady-state ^{210}Pb flux has prevailed from the atmosphere. However, a hiatus in the sequence or abrupt changes in the sediment supply will prevent the reliable use of the CRS model (Carroll and Lerche, 2003). The use of the CRS model will also be precluded if an excessively high, or low, level of unsupported ^{210}Pb activity is apparent when the expected local flux from atmosphere is considered. Under these circumstances, as long as there have been no changes in the initial concentration of ^{210}Pb , the CIC model may offer a satisfactory solution. There are more complex alternatives to these common models. Some preliminary work has been done using inductive modelling, and in some situations this approach may offer a workable alternative to conceptual modelling (e.g., Sediment Isotope Tomography (SIT); Carroll *et al.* (1999); Carroll and Lerche (2003)). However, in most situations where the basic requirements are met either the CRS model or the CIC model will produce reasonable results (Appleby, 2001).

It is desirable to validate ^{210}Pb chronologies using some form of independent age marker (Smith, 2001; Abril, 2004). If one or more sediment horizons can be independently dated by chronological markers a composite approach can be used to

model deposition rates for separate sections of a sediment sequence (Appleby, 2001). For example, it is now becoming common practice to use the documented history of the releases of anthropogenic radionuclides associated with nuclear activity into the environment (Cundy and Croudace 1996; Cundy *et al.* 1997; Appleby, 2001; Carroll and Lerche, 2003). Other possible calibration tools are pollen chrono-markers, tephra falls and documented pollution events (See Chapters 6 and 8). If available, this information can be used to confirm the reliability of a ^{210}Pb chronology, and in some situations it is not feasible to model reliably ^{210}Pb dates at all without some supplementary chronological information (Appleby, 2001).

4.2. Nuclear fall-out radionuclides: ^{137}Cs and ^{241}Am

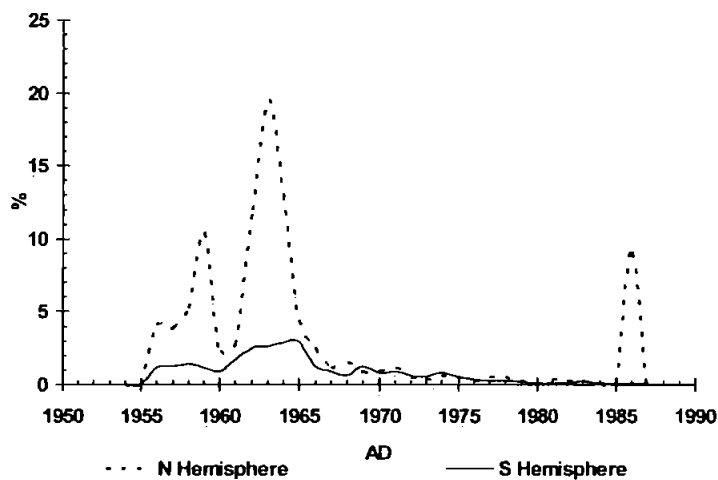
4.2.1. Thermonuclear by-products. Since the middle of the 20th century radionuclides have been produced by nuclear weapons tests and accidental discharges into the environment. This contamination has left a detectable signal of radioactivity in the sedimentary record (Wright *et al.*, 1999; Smol, 2002), and thermonuclear by-products have become recognised as potential dating tools for recent sediments (Appleby, 2001). They are examined here as supplements, or alternatives, to the use of ^{210}Pb for dating salt-marsh sediments.

Caesium-137, with a half-life of 30.3 years, did not exist in the environment before anthropogenic nuclear activity, and was first introduced into the global stratosphere in November 1952 following the start of high-yield atmospheric nuclear tests. Caesium-137 activity became detectable at significant levels in the northern hemisphere atmosphere in 1954 (Smol, 2002), and reached maximum activity levels in 1963 (Figure 4.2). In the southern hemisphere the nuclear fallout activity record has been lower, and has consistently slightly lagged when compared to that found in the north. Cambray *et al.*, (1989) estimated total global ^{137}Cs deposition from the weapons test fallout to be some 4.3×10^{17} Bq when decay corrected to 1986.

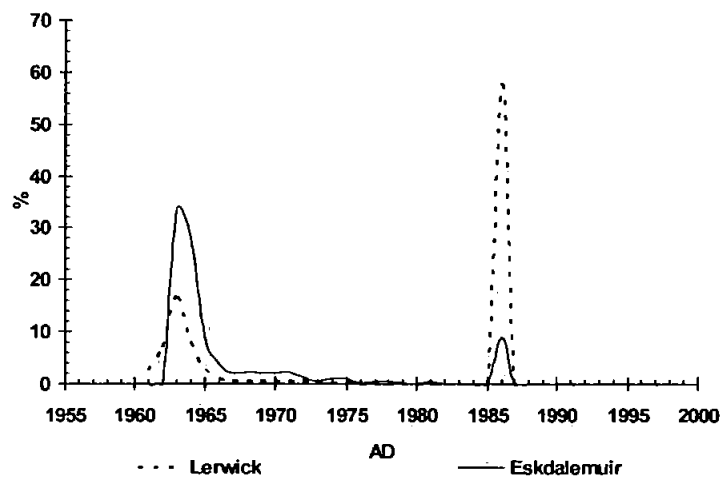
After the 1963 Nuclear Test Ban Treaty all fallout levels rapidly declined steadily over the next two decades until the catastrophic reactor failure of Reactor Four at Chernobyl in the Ukraine on the 26th April, 1986 (Appleby, 2001). The resulting explosion and fire initially released approximately 2×10^{18} Bq of radioactive materials into the lower atmosphere (Smol, 2002; Kashparova *et al.*, 2003). The gases and particulate debris derived from the destruction of the reactor containment vessel and active fuel rods contained significant quantities of ^{90}Sr , ^{106}Ru , ^{134}Cs , ^{137}Cs and ^{241}Pu plus lesser amounts of ^{131}I , ^{239}Pu , ^{240}Pu and ^{241}Am (Table 4.2).

Radionuclide	Half-life	Activity (Bq X 10 ⁹)	Radionuclide	Half-life	Activity (Bq X 10 ⁹)
⁹⁰ Sr	29.1 yr	5837.84	¹⁴⁴ Ce	284.6 days	65675.68
¹⁰⁶ Ru	1.02 yr	25621.62	²³⁸ Pu	87.7 yr	18.92
^{110m} Ag	249.8 days	1094.59	²³⁹ &	24100.0 &	40.00
¹²⁵ Sb	2.7 5yr	2189.19	²⁴⁰ Pu	6560.0 yr	3648.65
¹³¹ I	8 days	no data	²⁴¹ Pu	14.4 yr	4.38
¹³⁴ Cs	2.1 yr	36486.49	²⁴¹ Am	432.7 yr	437.84
¹³⁷ Cs	30.26 yr	72972.97	²⁴² Cm	162.8 days	29.1 &
			²⁴³ &	29.1 &	4.38
			²⁴⁴ Cm	18.1 yr	

Table 4.2. Chernobyl emissions: initial radionuclide activity as estimated by World Health Organisation (1989).



A



B

Figure 4.2. Chart A: Global ¹³⁷Cs fallout: shown as % of total cumulative to 1987. Data from Cambray *et al.* (1989). Chart B: Caesium -137 fallout at two sites in Scotland: shown as % of total cumulative to 2003. Data from AEA Technology (1960-1998) and DEFRA (1998-2003).

Location	Total ¹³⁷ Cs activity Bq/m ²	¹³⁷ Cs activity attributed to Chernobyl Bq/m ²
UK		
Holmrook, Cumbria	13000	10000
Lerwick, Shetland	6100	4600
Antrim, N. Ireland	4000	2200
Trawsfynydd, Gwynedd	3100	1850
Dounreay, Caithness	3000	1250
Eskdalemuir, Dumfries and Galloway	1300	820
South Brent, Devon	700	<40
Carmarthen, Carmarthenshire	610	43
Culham, Oxfordshire	370	<70
Ashbury, Wiltshire	330	25
N. Europe and Scandinavia		
Budapest, Hungary	13000	8800
Belgrade, Serbia	8900	7300
Bucharest, Romania	5600	4300
Warsaw, Poland	3600	2860
Bonn, Germany	1800	1550
Vienna, Austria	1600	1150
Helsinki, Finland	1400	990
Stockholm, Sweden	600	430
Remy, France	430	290
Moscow, Russia	370	210
Reykjavik, Iceland	66	7

Table 4.3. Spatial variation of ¹³⁷Cs radioactivity in soils in selected parts of the Northern Hemisphere. Measured in the top 5cm, and decay corrected to 03/05/86. Data from Cambray *et al.*, (1987).

Unlike the fallout from the nuclear weapons program, the Chernobyl contamination was not projected high into the stratosphere and was confined to the Northern Hemisphere (Figure 4.2A). The majority of the deposition occurred in the former Soviet Union and Northern Europe (Table 4.3). Over 60% of the fallout from the Chernobyl reactor fuel was deposited in the Ukraine (Kashparova *et al.*, 2003). Radio-caesium was a significant component of this fallout and some 10¹⁷ Bq of ¹³⁷Cs (Cambray *et al.*, 1987) is estimated to have been eventually dispersed throughout the Northern Hemisphere following the accident in 1986. The other caesium radioisotope involved, ¹³⁴Cs, has a shorter half-life and the activity in the sedimentary record quickly dropped below detectable limits (Appleby, 2001).

The deposition of Chernobyl fallout was very patchy and was primarily controlled by regional air flows and the precipitation patterns in the days following the accident (Smol, 2002; Kashparova *et al.*, 2003; Rezzoug *et al.*, 2006). There was a marked differential in the ¹³⁷Cs fallout levels received by some parts of North Wales and Northern England, and the rest of the region (Table 4.3). Likewise when the whole hemisphere is examined the data shows how some distal sites in the east and south

of the affected zone received higher doses than some of the more proximal areas in the north simply because of precipitation patterns during the critical period of 26th April to 6th May. Appleby (2001) expressed the opinion that the 1986 Chernobyl accident produced 'over an order of magnitude greater' ^{137}Cs deposition over some areas of the UK, Scandinavia and central Europe than the cumulative nuclear weapons fallout of that radionuclide. This contention is supported by the ^{137}Cs fallout data for Lerwick presented in Figure 4.2B which illustrates how the fallout of radioactive caesium in 1986 at that site was approximately three times the maximum ^{137}Cs activity recorded during the height of the nuclear weapons tests during the early 1960s (Cambray *et al.*, 1987).

The other fallout radionuclide considered here that offers some potential as a chronological marker is ^{241}Am (Appleby, 2001). It was not present in significant amounts in either the initial fallout from the nuclear weapons tests of the 1950s and 1960s, or the 1986 Chernobyl accident, but it can now also be used as a proxy for its parent, ^{241}Pu . Plutonium isotopes did form a significant part of the fallout from the nuclear test program and the Chernobyl accident (Krey *et al.*, 1976; Appleby *et al.*, 1991; UNSCEAR, 2000), and the majority of the ^{241}Am activity in present-day sediment archives is the result of the gamma decay of ^{241}Pu , which has a half-life of 14.4 yr (Thomson *et al.*, 2002; Pourchet *et al.*, 2003). Americium-241 activity in the present day sedimentary record had originally been regarded as only marking the deposition of sediments virtually contemporaneous to the timing of high-yield atmospheric nuclear tests (Appleby *et al.*, 1991; Appleby, 2001; Abril, 2004), but this situation has started to change. At locations affected by Chernobyl fallout the ^{241}Pu in this fallout has been decaying exponentially (See Chapter 3) to ^{241}Am , and radiometric dating principles predict that the maximum ^{241}Am activity recorded in sediments will be reached approximately 30 yrs after the first deposition of the parent ^{241}Pu (Pourchet *et al.*, 2003).

The fallout history of the two UK sites is essentially the same. Both south Wales and southern England received a significant dose of thermonuclear by-products in the 1950s and early 1960s, and were significantly effected by the Chernobyl plume in 1986 (Cambray *et al.*, 1987; Appleby, 2001). These signals should be recorded in both sequences, but because of local precipitation patterns during the late April and early May of 1986 the Chernobyl signal recorded at Carmarthen, some 25 km northeast from the Taf site, was comparatively low (Cambray *et al.*, 1987). In

contrast, the total radionuclide fallout on Iceland from all sources has been very low compared to the rest of Europe (Table 4.3), and there is some evidence that the Chernobyl fallout is not detectable in most Icelandic soil profiles (Pálsson *et al.*, 1994).

4.2.2. Radionuclide activity in the oceans. In addition to the atmospheric fallout of radionuclides from nuclear weapon tests and the Chernobyl accident there have been a number of local point sources of radioactive contamination that have introduced ^{137}Cs , ^{241}Pu and ^{241}Am directly into the oceans. Foremost amongst these are the deliberate discharges from nuclear reprocessing plants, notably Sellafield in the UK and the French plant at Cap de La Hague (Table 4.4). Deliberate radioactive effluent discharges have contributed more than 7 % of the total radioactivity inventory of the oceans. This is over twice the radionuclide activity in the oceans attributed to the Chernobyl accident and several magnitudes more than the combined activity attributed to other known nuclear accidents, including those involving crashed US bombers and sunken Russian submarines (Aarkrag, 2003).

Source	Year of peak discharge	Estimated maximum ^{137}Cs activity level during peak discharge year	Estimated total contribution to the ^{137}Cs loading of Northern European Seas surface waters in
		TBq	AD 2000 TBq
Global fallout	1963	145,000 (Surface air)	12,000
Chernobyl	1986	70,000 (Surface air)	6000
Sellafield	1975	5,200 (Sea water)	41,000
La Hague	1971	243 (Sea water)	1000
*Winfrith	1980	2.2 (Sea water)	7.7

Table 4.4. Caesium -137 contributions to northern European coastal waters 1952-1998. Data from Povinec *et al.* (2003) and *Thompson *et al.* (2002).

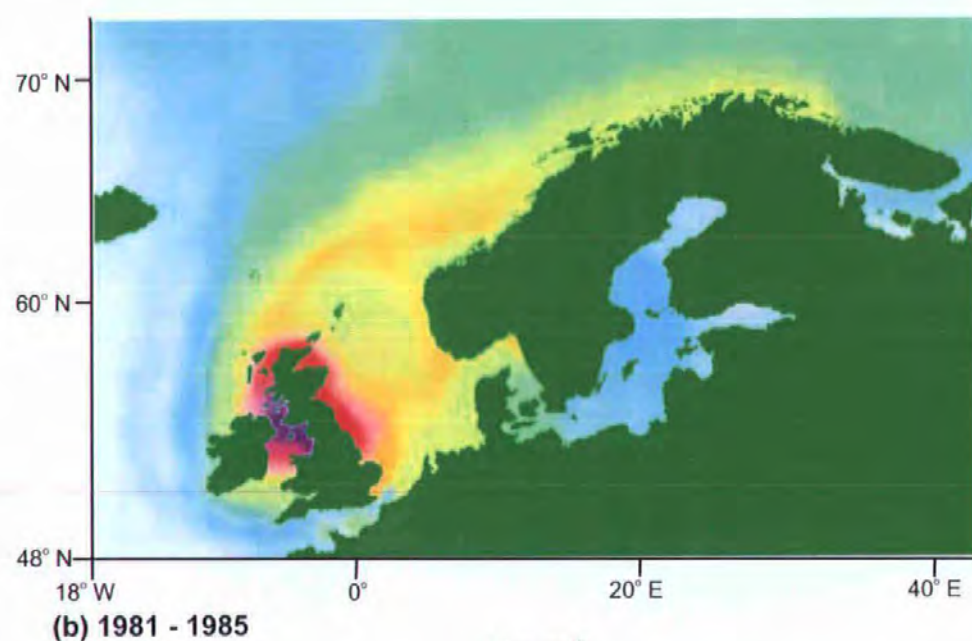
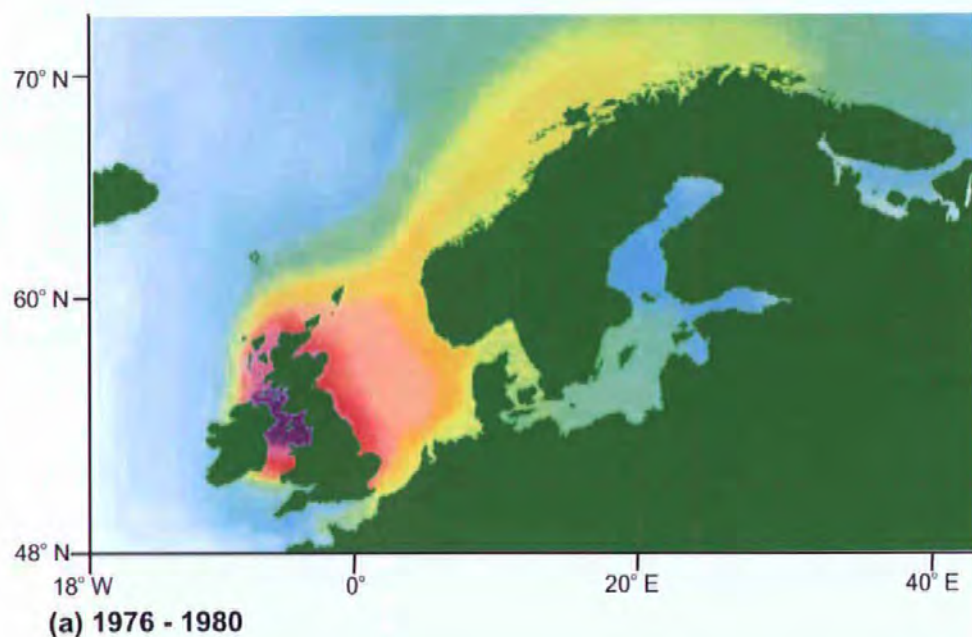
The Sellafield reprocessing plant, formally known as Windscale, in Cumbria began discharging radioactive effluent into the Irish Sea in 1952, and has been the dominant contributor (Table 4.4) to the radionuclide inventory of North Atlantic and northern European seawater (Povinec *et al.*, 2003). This activity has been both controversial and extensively studied (See Morris *et al.*, 2000 and references

therein). It peaked during the 1970s (UNSCEAR, 2000) and has now been significantly reduced, but between 1952 and the end of 1998 41 PBq (1 Petabecquerel = $1 \text{ Bq} \times 10^{15}$) of ^{137}Cs , 22 PBq of ^{241}Pu and 1 PBq of ^{241}Am were discharged directly into the sea along with over 35 PBq of other long-lived radionuclides (IAEA, 2001). The French La Hague plant has been discharging a similar set of radionuclides since 1966. However, the relative contribution from La Hague to the total radionuclide activity in the Northern European Seas is low. In the case of ^{137}Cs it is only 2 % of the Sellafield contribution.

Once released the fate of radionuclides depends on currents, sediments and water depth, and the characteristics of the individual nuclide (Morris *et al.*, 2000; Povinec *et al.*, 2003). Particle reactive nuclides discharged, like ^{241}Pu and ^{241}Am , quickly become incorporated into fine sediments and tend to remain close to the source. In the case of the Sellafield discharge, these particles have primarily remained incorporated in the muds of the Irish Sea basin. On the other hand, ^{137}Cs is conservative, and, being highly soluble in sea-water, it slowly disperses into the body of water it is released into. Mixing, by the circulation of ocean waters, and transport, by currents, result in low-level activity being detected some distance from the source. In the case of ^{137}Cs , the exchange of water to the North Atlantic from the Irish Sea has moved ^{137}Cs activity attributed to discharges from Sellafield up to the northern tip of Scotland, before it travels then down into the southern North Sea and further north toward the Arctic. This is shown clearly in the isoline maps published by Povinec *et al.* (2003) reproduced here in Figure 4.3. These maps also show how the water south of Iceland and in the eastern Norwegian Sea have been affected by this plume.

In addition to the Sellafield and La Hague reprocessing plants, the former UKAEA research and development site at Winfrith, near Wool in Dorset, is of special interest to this study. This site is only some 17 km west of the Arne Peninsula and is within the catchment of the River Frome which flows into Poole Harbour. It is now undergoing decommissioning, but when active between 1958 and 1995 it discharged small amounts of fission products and transuranic radionuclides via an offshore outfall in Weymouth Bay. These levels were low when compared with Sellafield and other contributors (Table 4.4), so the potential contribution from Winfrith to the radionuclide inventory of sites on the English Channel coast is minimal. The known ^{137}Cs emissions from Winfrith peaked at around 2000 GBq in

1980, but the alpha-emitting radionuclides in the effluent were not differentiated. It is known that they peaked at around 0.005 TBq in the period between 1972 and 1976 (Thompson *et al.*, 2002). Thomson *et al.* (2002) found low level ^{241}Am activity in salt-marsh sediments from Beaulieu Marsh, located approximately 65 km east of Winfrith. This signal appeared to broadly agree with the known history of alpha radiation in discharges from the former UKAEA site, but the deposition chronology suggested by the ^{137}Cs data from the same section was not in agreement.



Bq m⁻³



Figure 4.3. Caesium-137 activity in the surface waters of the Northern European Seas. (a) 1976 – 1980; (b) 1981 – 1985; (c) 1986 – 1990; (d) 1991 -1995. Reproduced from Povinec *et al.* (2003), their Figure 3.

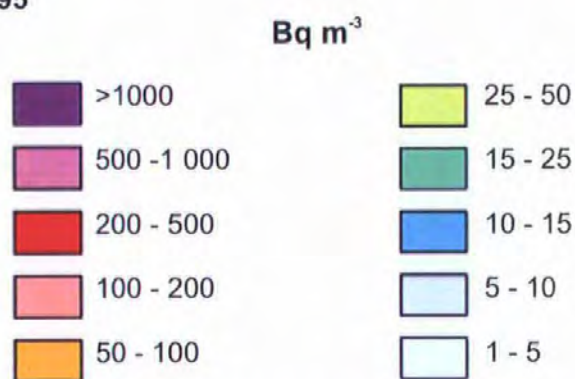
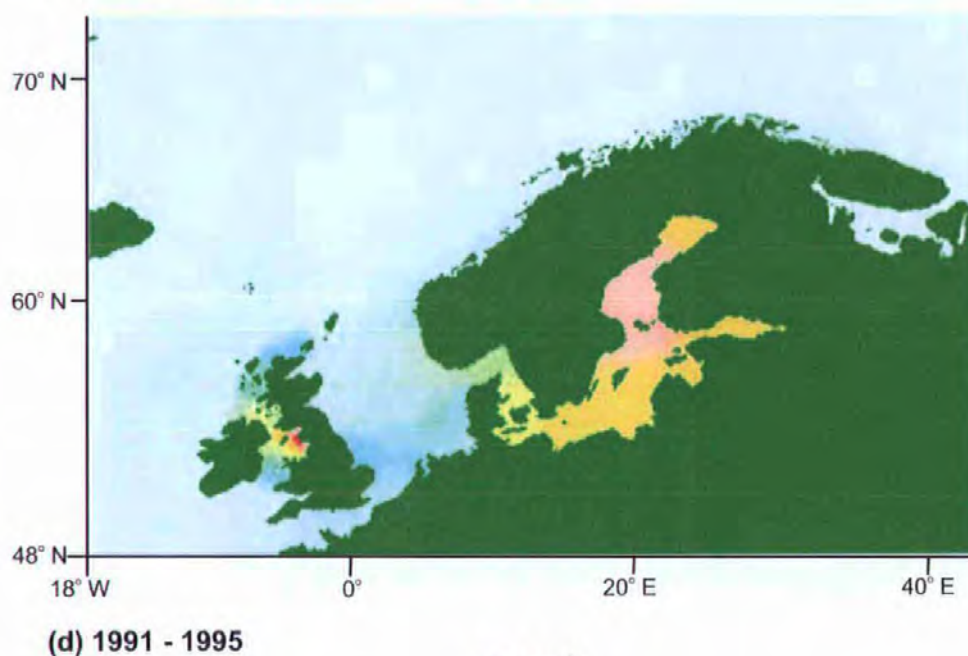
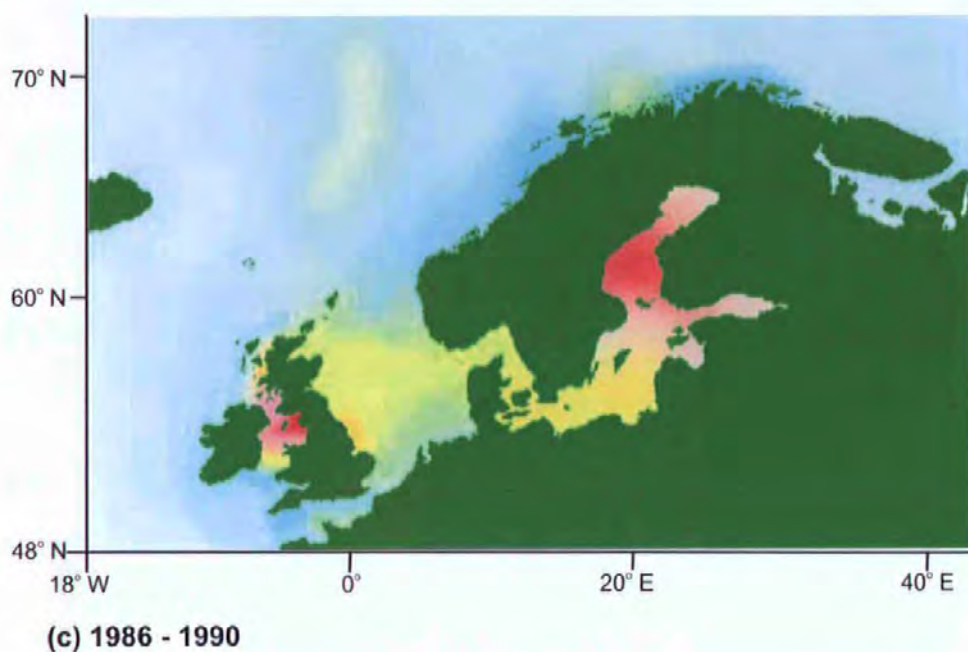


Figure 4.3 (Continued). Caesium-137 activity in the surface waters of the Northern European Seas. (a) 1976 – 1980; (b) 1981 – 1985; (c) 1986 – 1990; (d) 1991 -1995. Reproduced from Povinec *et al.* (2003), their Figure 3.

4.2.3. Dating salt-marsh sediments with non-carbon radionuclides. A number of recent studies have used ^{210}Pb and ^{137}Cs to date recent salt-marsh sediments, e.g. Gehrels *et al.*, (2002) in the Gulf of Maine, Haslett *et al.* (2003) on the Normandy coast, Temmerman *et al.* (2003) in the Scheldt estuary, Belgium and Bartholdy *et al.* (2004) in the Danish Wadden Sea. These studies indicate that in some sites this dating method can give acceptable results with fine grained intertidal sediments deposited during the last 100-120 years. These studies were concerned with sea level and the growth and retreat of salt-marsh environments, but ^{210}Pb and ^{137}Cs dating is also used in estuarine pollution studies, e.g., Plater *et al.* (1998) on the Tees, and Spencer *et al.* (2003) on the Medway in Kent. Thomson *et al.* (2002) used ^{210}Pb dating to help construct radionuclide pollution histories for UK salt-marsh sites in the Irish Sea and the Solent.

The results obtained by this present study using ^{210}Pb analysis supported by ^{137}Cs and ^{421}Am data at the Arne site are presented in the following sections. These are evaluated, and then the findings compared with those obtained by previous radionuclide work in the Taf estuary (W. R. Gehrels unpublished data) in Wales, and at the Viðarhólmi site (Gehrels *et al.*, 2006) in Iceland.

4.3. The Arne radionuclide analysis

4.3.1. Method. Undisturbed 1 cm slices were cut from the Arne ARN03 and ARN04 monoliths to create a complete sequential set for the top 50 cm of the sediment column. The individual surface areas of each slice were noted and, after drying and weighing, the dry bulk density of each slice calculated. The samples were sent to the Liverpool University Environmental Radioactivity Laboratory and analysed for ^{210}Pb , ^{226}Ra , ^{137}Cs and ^{241}Am using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby *et al.*, 1986). The total ^{210}Pb activity was determined directly by measuring gamma emissions at 46.5 keV. The samples were stored in sealed containers for three weeks to allow time for radioactive equilibrium to occur, and then the ^{226}Ra activity in the samples was determined indirectly by the measurement of the 295 keV and 352 keV γ -rays of its daughter isotope ^{214}Pb . These data were then used to calculate the supported fraction of the ^{210}Pb inventory by subtracting it from the total ^{210}Pb activity. Caesium - 137s and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV respectively. The detectors were corrected for the effect of self-absorption of low energy γ -rays within the sample (Appleby *et al.*, 1992), and their absolute efficiencies determined using calibrated sources and sediment samples of known activity.

4.3.2. Results. The total ^{210}Pb activity at the surface was found to be 88.7 Bq kg^{-1} , of which 24.2 Bq kg^{-1} was supported by the ambient ^{226}Ra activity in the sediments (Table 4.5). After increasing down profile to 155.4 Bq kg^{-1} at 4.5 cm the total ^{210}Pb activity rapidly declined, and below 25 cm was found to be close to equilibrium with the ^{226}Ra supported activity in the samples (Figure 4.4). The ^{226}Ra supported ^{210}Pb activity ranged from 17.6 Bq kg^{-1} (16.5 cm) to 34.5 Bq kg^{-1} (42.5 cm) with a mean of 24.6 Bq kg^{-1} (Figure 4.3). The ^{137}Cs activity versus depth curve shown in Figure 4.4 defines two peaks. The lesser peak, of 38.3 Bq kg^{-1} , was at 4-5 cm and the large peak, of 78.7 Bq kg^{-1} , was at 20-23 cm. There was some presence of ^{241}Am evident in the sediments upward from 23 cm but this activity declined below detection levels in the samples above 12 cm.

Depth		²¹⁰ Pb						¹³⁷ Cs		²⁴¹ Am	
		Total		Unsupported		Supported		Bq kg ⁻¹	±	Bq kg ⁻¹	±
cm	g cm ⁻²	Bq kg ⁻¹	±	Bq kg ⁻¹	±	Bq kg ⁻¹	±				
0.5	0.13	88.7	10.6	64.4	10.9	24.2	2.7	13.9	1.9	0.0	0.0
2.5	0.54	78.2	15.0	51.3	15.4	26.8	3.5	27.0	2.6	0.0	0.0
4.5	0.82	155.4	7.0	127.3	7.8	28.1	3.4	38.3	1.5	0.0	0.0
6.5	1.08	111.1	11.3	78.8	11.7	32.3	3.1	23.0	2.4	0.0	0.0
8.5	1.34	112.4	13.0	83.3	13.4	29.1	3.2	14.2	3.1	0.0	0.0
10.5	1.60	112.7	14.5	91.6	14.7	21.1	2.7	19.7	2.3	0.0	0.0
12.5	1.88	84.8	7.2	61.9	7.4	22.9	1.7	23.4	1.4	2.0	0.9
14.5	2.17	77.3	7.3	55.2	7.5	22.1	1.7	20.2	1.8	2.3	0.8
16.5	2.48	84.7	6.9	67.1	7.0	17.6	1.4	29.5	1.3	3.1	0.7
18.5	2.82	71.5	6.8	53.0	6.9	18.5	1.6	47.9	1.7	2.1	0.7
20.5	3.25	55.3	5.7	30.4	5.9	24.8	1.5	78.7	1.5	0.0	0.0
22.5	3.71	48.2	6.0	22.8	6.2	25.4	1.7	70.9	1.9	3.3	0.8
24.5	4.17	17.9	8.0	-4.6	8.2	22.5	1.9	29.2	1.7	0.0	0.0
26.5	4.60	26.1	5.8	2.8	6.0	23.4	1.6	11.2	1.4	0.0	0.0
28.5	5.03	40.0	6.2	19.2	6.4	20.7	1.5	7.6	1.1	0.0	0.0
32.5	5.87	34.9	4.3	14.9	4.3	20.0	0.8	2.4	0.6	0.0	0.0
36.5	6.79	30.1	4.7	4.0	4.8	26.1	1.0	0.1	0.6	0.0	0.0
40.5	7.80	31.9	4.4	3.7	4.5	28.2	0.9	0.5	0.6	0.0	0.0
42.5	8.36	31.7	3.4	-2.8	3.5	34.5	0.8	0.0	0.0	0.0	0.0

Table 4.5. Radionuclide concentrations in Arne salt-marsh sediments. Note: The negative unsupported ²¹⁰Pb values are calculation artefacts resulting from the combining of data and errors from the two analysis methods used, i.e. direct and indirect, and should be regarded as zeros.

The unsupported ²¹⁰Pb activities vary irregularly with depth (Figure 4.4) and this situation does not conform to the ideal exponential decline profile discussed in 4.1.2. Furthermore the maximum ²¹⁰Pb concentration occurs in the 4-5 cm section, not at the surface. Below this step the overall trend is one of exponential decline, suggesting that some of the sediments have accumulated at a relatively steady rate. However, there is abrupt fall to zero values and then a down profile recovery in the 24-27 cm section.

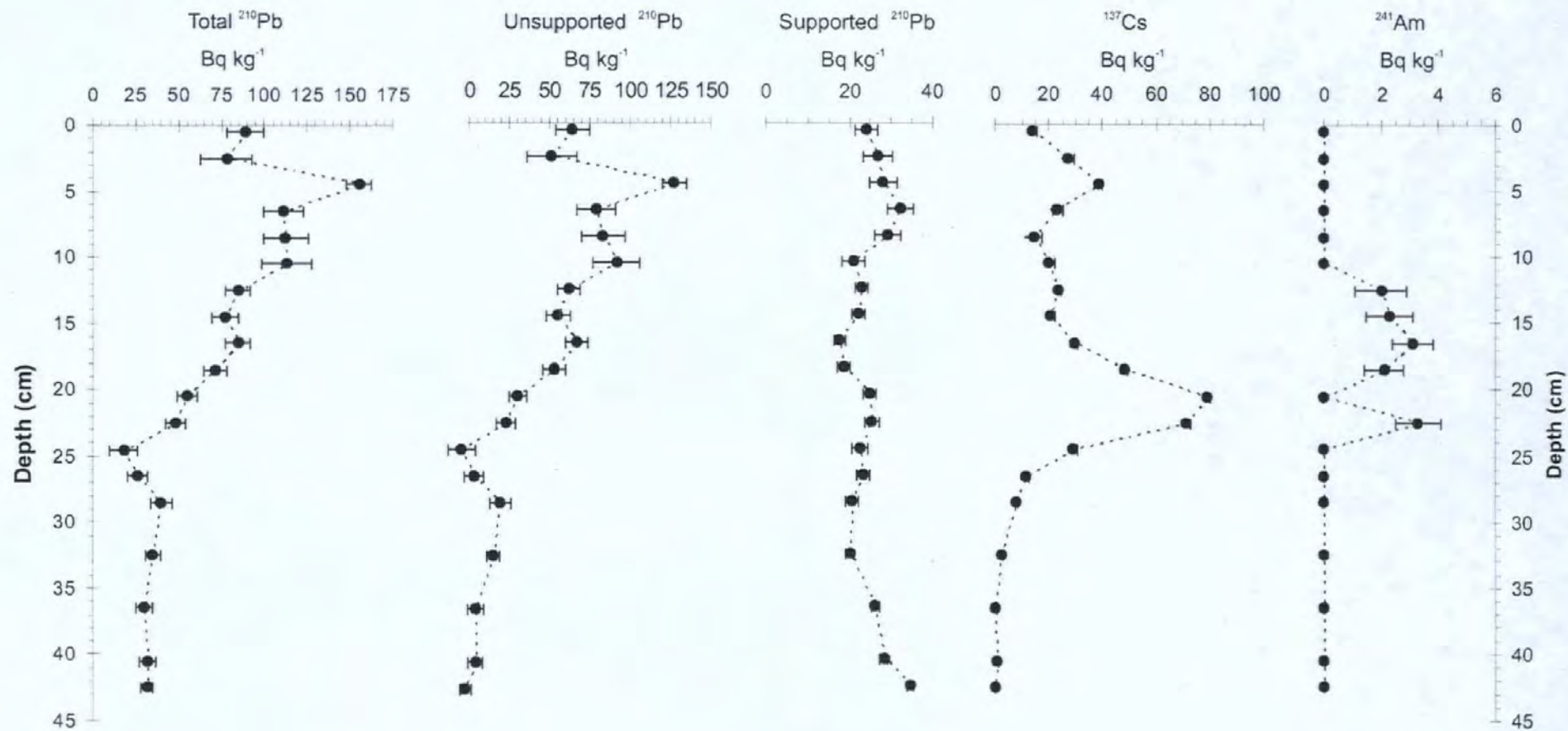


Figure 4.4. The Arne radionuclide data.

The low ^{210}Pb activity between 24 cm and 27 cm, and in the top 3 cm of the sequence, could indicate:

1. Variability in the rate of direct deposition of atmospheric ^{210}Pb to the local ground surface.
2. Removal of deposited atmospheric ^{210}Pb from the local ground surface, possibly by over-marsh water flows
3. An increase in other sedimentation during these times that has effectively diluted the concentration of fall-out lead.
4. Disturbance to the sediment record associated with, for example, storm events that have promoted the deposition of older, ^{210}Pb depleted, sediments in these horizons reworked from elsewhere.

These low ^{210}Pb activity issues will be considered later in this chapter, but what is apparent is that some episodic mechanism appears to have reduced the unsupported activity of ^{210}Pb in the sediments of some samples.

4.3.3. The Arne ^{210}Pb chronology. An irregular, non-monotonic ^{210}Pb profile, typically found in dynamic sedimentary environments, is considered to preclude the use of the simple CFCS model (Appleby, 2001). To confirm that this situation applied to the Arne sequence, the unsupported ^{210}Pb data are plotted on a logarithmic axis against depth (See Section 4.1.2). As expected this produced a non-linear plot (Figure 4.5). This procedure established the need for a more sophisticated model so the CRS (Appleby *et al.* 1978) method described in Section 4.1 was used (Table 4.6).

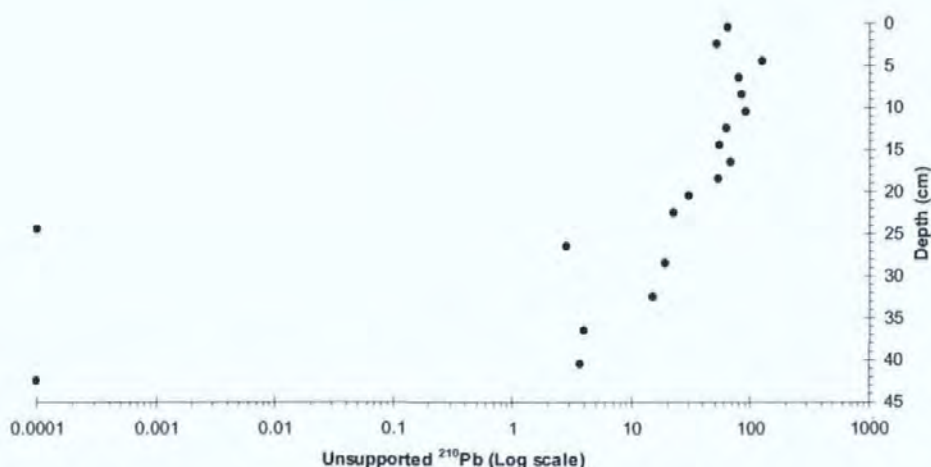


Figure 4.5. The Arne unsupported ^{210}Pb data plotted on a log scale against depth.

Depth		Date	Age		Accumulation rate	
cm	g cm ⁻²	AD	yr	±	cm yr ⁻¹	g cm ⁻² yr ⁻¹
0	0	2003	0.0	0	0.83	0.15
0.5	0.13	2003	0.2	0	0.71	0.71
2.5	0.54	2002	0.8	0	0.8	0.67
4.5	0.82	2000	3.2	0	0.83	0.12
6.5	1.08	1998	5.3	1	0.94	0.12
8.5	1.34	1995	8.4	1	0.66	0.09
10.5	1.6	1990	12.8	1	0.45	0.06
12.5	1.88	1986	16.8	2	0.50	0.07
14.5	2.17	1981	21.6	3	0.42	0.06
16.5	2.48	1973	29.6	5	0.25	0.04
18.5	2.82	1964	39.1	7	0.21	0.04
20.5	3.25	1956	47.3	10	0.24	0.05
22.5	3.71	1946	56.6	12	0.22	0.05
24.5	4.17	1946	56.6	10	NA	NA
26.5	4.6	1945	58.2	8	1.19	0.26
28.5	5.03	1928	74.8	12	0.12	0.03
32.5	5.87	1898	105.0	25	0.13	0.03
36.5	6.79	1877	126.3	30	NA	NA

Table 4.6. Arne CRS model (Appleby, 1978) chronology and accumulation rates.

The CRS model (Appleby, 1978) indicates that the sequence spanned approximately the last 125 years and suggested, as shown in Figure 4.6, that there had been two abrupt fluctuations in accumulation rates: one around 6.5 cm and one between 26.5 cm and 22.5 cm.

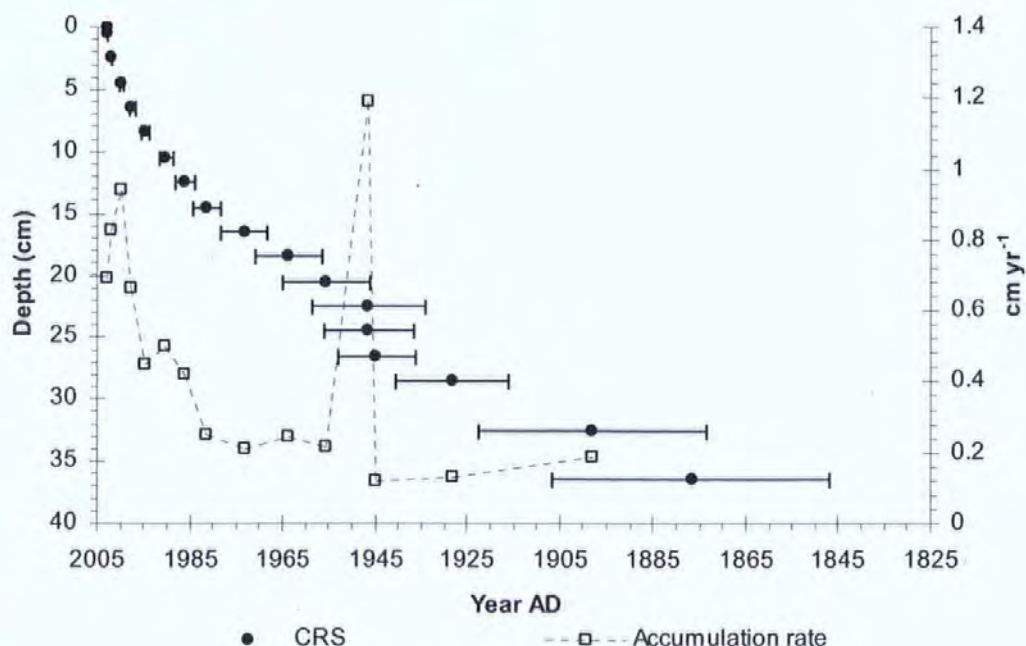


Figure 4.6. The Arne ²¹⁰Pb chronology obtained using the CRS model (Appleby *et al.* 1978). Dating errors propagated from the analytical uncertainty.

Although the non-monotonic character of the complete Arne ^{210}Pb record may jeopardise the use of a simple ^{210}Pb model, the curve between 4.5 cm and 22.5 cm has an approximate exponential shape in Figure 4.4. These data also plot with a near linear trend in Figure 4.5 therefore suggesting that this part of the sequence was deposited under relatively steady-state conditions. Under some circumstances the CIC model can be used to obtain an accumulation rate for an isolated section of a record (Appleby, 2001). Therefore, the CIC model was applied to the samples from 4.5 cm down to 22.5 cm. As a first step the natural logarithm of the unsupported ^{210}Pb data was plotted against the cumulative mass (Figure 4.7), and then the gradient was used to calculate accumulation rates and age estimates (Table 4.7).

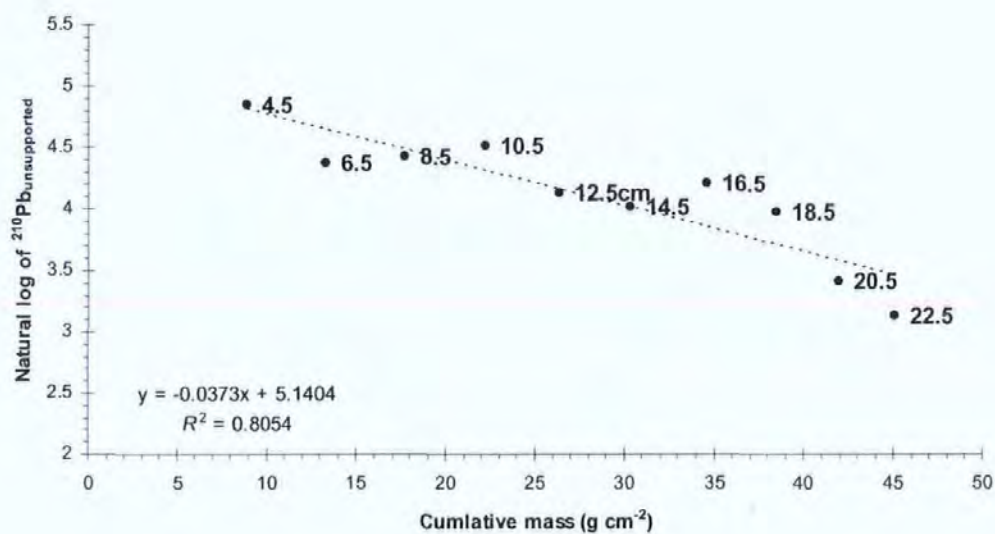


Figure 4.7. The natural logarithm ($\ln$) of the Arne unsupported ^{210}Pb against cumulative mass. Sample identifiers indicate depth in cm.

The results of this exercise do not agree with the results from the CRS model. The accumulation rate, expressed in cm yr^{-1} , suggested by the CIC model is higher than that calculated using the CRS model. This is most evident in the lower section of the sequence (Figure 4.8). The CIC model indicates that the sediments at 36.5 cm were deposited over 50 years later than the age obtained using the CRS model, but what this exercise does support is an apparent episode of increased sediment accumulation rate between 26.5 cm and 22.5 cm. To try and resolve the chronology the ^{137}Cs and ^{241}Am data are examined.

Depth cm	g cm^{-2}	Date AD	Age yr	$\pm$	Accumulation rate cm^{-1}	$\text{g cm}^{-2} \text{yr}^{-1}$
0	0	2003	0.00	0	0.50	0.83
0.5	0.13	2002	1.00	0	0.52	0.83
2.5	0.54	1998	4.87	0	0.34	0.83
4.5	0.82	1992	10.68	1	0.38	0.83
6.5	1.08	1987	15.91	2	0.38	0.83
8.5	1.34	1982	21.21	2	0.37	0.83
10.5	1.6	1976	26.62	3	0.40	0.83
12.5	1.88	1971	31.56	3	0.42	0.83
14.5	2.17	1967	36.36	4	0.40	0.83
16.5	2.48	1962	41.40	4	0.42	0.83
18.5	2.82	1957	46.16	5	0.49	0.83
20.5	3.25	1953	50.25	5	0.53	0.83
22.5	3.71	1949	53.99	5	NA	0.83
24.5	4.17	1949	53.99	5	1.62	NA
26.5	4.6	1948	55.23	6	0.57	0.83
28.5	5.03	1944	58.77	6	1.24	0.83
32.5	5.87	1941	62.00	6	2.41	0.83
36.5	6.79	1939	63.66	6	NA	NA

Table 4.7. Arne CIC model (Appleby, 2001) chronology and accumulation rate.

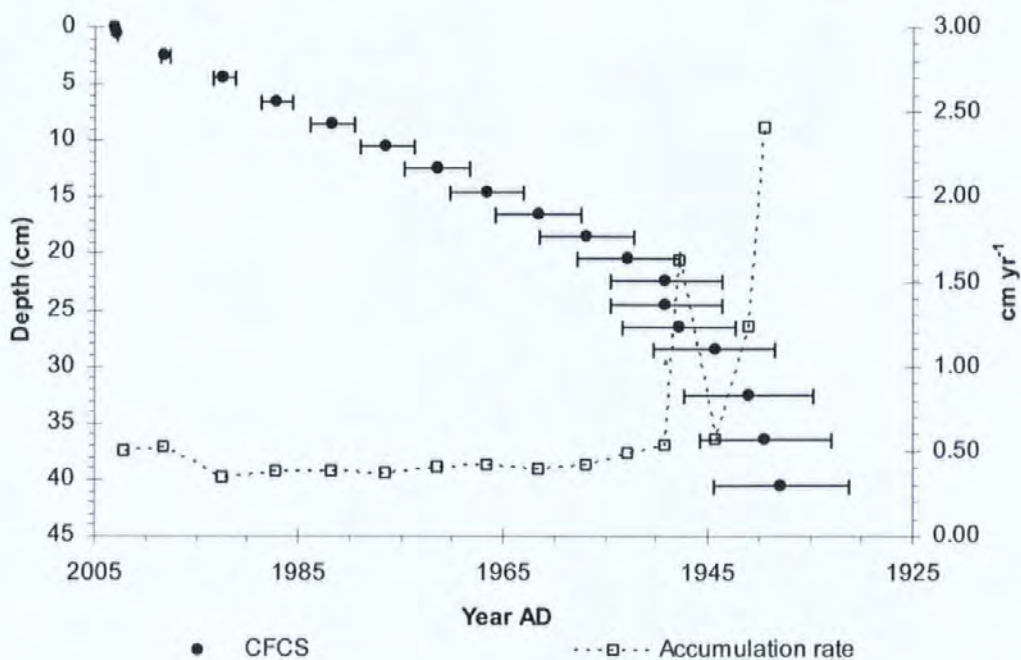


Figure 4.8. The Arne ^{210}Pb chronology obtained using the CIC model (Appleby *et al.* 1978; Appleby, 2001). Dating errors are propagated from the analytical uncertainty.

The major peak in ^{137}Cs activity is between 20 cm and 23 cm (Figure 4.4), and the curve has a single apex point of some 17 % of the total inventory. This is associated with a significant presence of ^{241}Am , and is therefore interpreted as marking the deposition of early 1960s nuclear weapons test fallout. Above this level there is a secondary peak in ^{137}Cs activity at 4.5 cm that represents just over 8% of the total inventory. Given the geographic location of the site and the level of activity in the sediments this signal is interpreted as marking the presence of radioactive fallout from the Chernobyl accident. If correct, this age is also in disagreement with dates obtained by the ^{210}Pb models for this depth. If the ^{137}Cs date of 1963 is used as a reference level it indicates a post-1963 ^{210}Pb flux of $99 \text{ Bq m}^{-2} \text{ y}^{-1}$. This is comparable to the level of the estimated atmospheric flux for this part of Europe (Preiss *et al.*, 1998; Appleby, 2001). The ^{137}Cs emissions from Winfrith (discussed in section 4.3.3) are not considered to be a significant factor because the minimum activity in the Arne sediments are too high for such low levels of activity to be detectable. In addition, the timing of the first ^{241}Am peak is wrong for it to be attributed to this source, and this would tend to confirm that the lowest Arne ^{137}Cs peak is from the early 1960s weapons test fallout.

The results from the ^{210}Pb models place 1963 at a depth of 16 -19 cm, significantly above the depth indicated by the ^{137}Cs record, and it is evident that ages derived from the Arne ^{137}Cs and ^{241}Am data do not closely agree with either the CRS or the CIC chronologies. One fundamental issue here is that ^{137}Cs was not in existence before the dawn of the nuclear age, and was only measurable in significant levels in the northern hemisphere atmosphere after 1954 (Smol, 2002). The second is that a signal exists in the activity of ^{137}Cs and ^{241}Am at depth in European sediment sequences that corresponds in most cases to the timing of the maximum nuclear test fallout in 1963 (See Section 4.2 for details). In the Arne sequence some 95 % of the ^{137}Cs inventory lies above 27.5 cm, and significant ^{137}Cs activity was found in samples from below 24.5 cm. This implies that the sediments at 27.5 cm are unlikely to be younger than 1954. However, the first detectable signal in the sediments is likely to slightly post date the first atmospheric detection date, so the deposition of the sediments at 26.6 cm, and above, probably took place after 1955, and a reasonable estimate of the deposition date of the sediment at 27 cm would be 1956. This indicates that the CRS model over estimates the deposition ages in these lower horizons.

One possible solution to resolve the disagreement between the Arne CRS ^{210}Pb chronology and the ^{137}Cs deposition dates is the composite correction method described by Appleby (2001). This approach uses one, or more, independent chronological markers (e.g., ^{137}Cs dates) to calibrate a modelled ^{210}Pb chronology. In the case of the Arne CRS ^{210}Pb chronology it was calibrated using a deposition date at 20.5 cm of 1963 as a reference point. This procedure dates the episode of increased accumulation to 1956-1959 (Table 4.8), and suggests a fairly uniform accumulation rates since that time up to about 2000, with a mean value of 0.47 cm y^{-1} (Figure 4.9).

Depth		Date	Age		Accumulation rate	
cm	g cm^{-2}	AD	y	$\pm$	cm y^{-1}	$\text{g cm}^{-2} \text{ y}^{-1}$
0	0	2003	0	0	0.83	0.15
0.5	0.13	2002	1	2	0.82	0.12
2.5	0.54	2000	3	2	0.80	0.17
4.5	0.82	1997	6	2	0.57	0.06
6.5	1.08	1993	10	2	0.64	0.09
8.5	1.34	1991	12	2	0.63	0.08
10.5	1.6	1987	16	2	0.49	0.06
12.5	1.88	1983	20	2	0.56	0.08
14.5	2.17	1980	23	3	0.52	0.08
16.5	2.48	1975	28	3	0.37	0.06
18.5	2.82	1969	34	4	0.34	0.06
20.5	3.25	1963	40	5	0.40	0.09
22.5	3.71	1959	44	5	0.65	0.11
24.5	4.17	1957	46	6	1.19	0.40
26.5	4.6	1956	47	6	1.60	0.39
28.5	5.03	1954	49	6	0.63	0.11
32.5	5.87	1946	57	8	0.47	0.11

Table 4.8. Arne ^{137}Cs corrected CRS chronology and accumulation rates (Appleby, 2001).

The result of correcting the CRS chronology using the ^{137}Cs 1963 reference point is shown in Figure 4.9. It can be seen how this procedure significantly reduced the ages suggested by the model for the lower horizons, and it was noted that the corrected chronology agrees closely with the date of 1956 for the 27 cm horizon estimated from the ^{137}Cs data. However, even with the 1963 ^{137}Cs correction, the CRS chronology still disagrees with the location of the ^{137}Cs peak assumed to be the signal of the 1986 Chernobyl accident. For comparison, all four age-depth solutions are shown in Figure 4.10. If the analytical uncertainty is considered above 26.5 cm there appears to be little difference between all four solutions. Below this level the CRS model progressively over estimates the deposition ages of the samples.

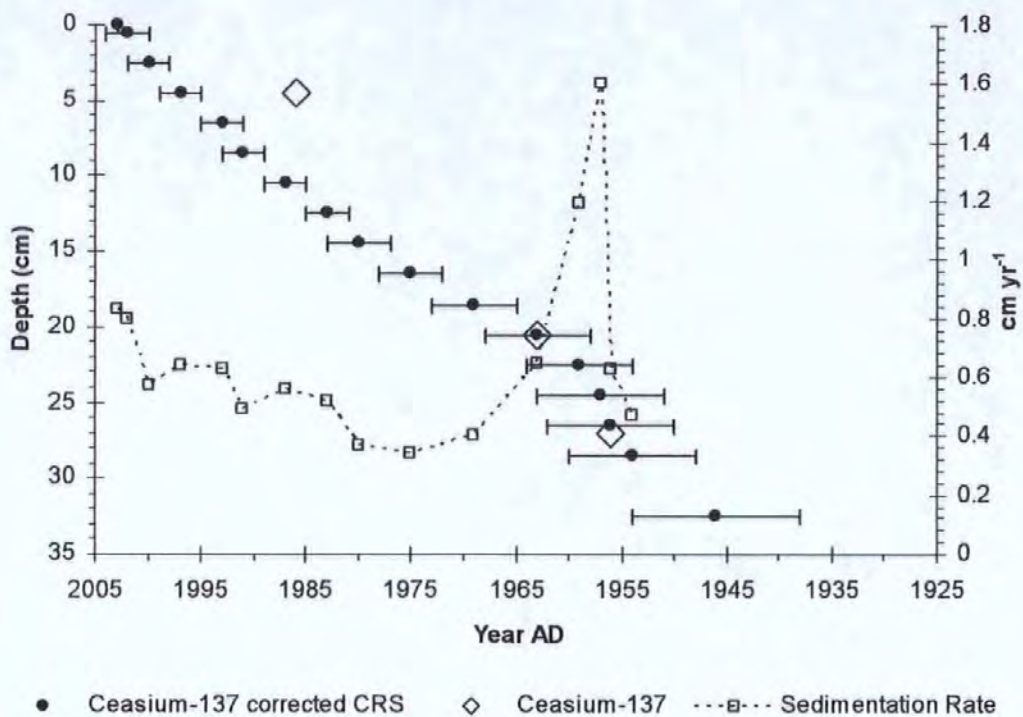


Figure 4.9. The Arne ^{210}Pb chronology obtained using ^{137}Cs corrected CRS model (Appleby, 2001). Dating errors propagated from the analytical uncertainty.. Ceasium-137 estimated dates of 1986, 1963 and 1956 are indicated by the open diamonds – see text for explanation.

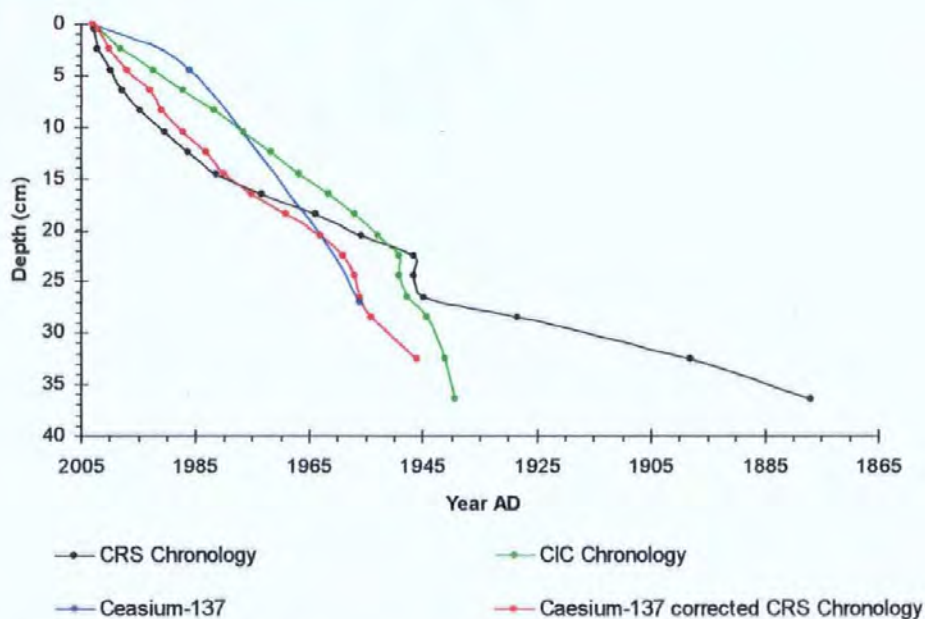


Figure 4.10. The four age-depth solutions obtained for the Arne sequence using radionuclide dating methods. Uncertainty ranges omitted to aid comparison.

4.4. Inter-site comparisons and evaluation

The radionuclide dating results from the Arne site will now be compared to results obtained at the Taf and Viðarhólmi sites by W. R. Gehrels (unpublished data) and Gehrels *et al.* (2006) respectively.

4.4.1. The Taf radionuclide analysis. As part of ongoing work in the Taf Estuary by members of the School of Geography, University of Plymouth (e.g., Gehrels *et al.*, 2001; Charman *et al.*, 2002; W. R. Gehrels, unpublished data) a ^{210}Pb and ^{137}Cs analysis was carried out on a core collected in 1998 (Table 4.9). The data set is limited and no analytical uncertainty was reported by the laboratory involved (Reading).

Depth		Unsupported ^{210}Pb	^{137}Cs
cm	g cm ⁻²	Bq kg ⁻¹	Bq kg ⁻¹
0.5	2.4	341.1	27.0
1.5	2.0	429.9	51.0
2.5	1.5	364.7	66.1
3.5	2.0	292.0	32.6
4.5	2.1	185.5	45.3
5.5	2.1	112.9	78.5
6.5	3.2	180.5	98.7
7.5	2.1	182.9	158.0
8.5	3.4	134.8	312.9
9.5	3.8	68.9	159.0
10.5	5.3	85.7	83.0
11.5	5.9	74.9	42.4
12.5	4.6	113.6	30.7
13.5	3.2	108.9	30.8
14.5	4.7	65.1	16.0
15.5	5.2	40.0	11.5
16.5	4.1	68.5	6.2
17.5	4.3	26.5	0.0
18.5	5.3	33.4	0.0
19.5	5.9	26.5	0.0
20.5	6.9	0.5	0.0
21.5	5.8	7.7	3.2
22.5	2.3	2.7	3.7
23.5	4.3	1.3	2.1
24.5	7.1	2.8	1.5

Table 4.9. Radionuclide data from the Taf site.

An initial inspection of the unsupported ^{210}Pb and ^{137}Cs curves (Figure 4.11) reveals an exponential decline in the unsupported ^{210}Pb data. The curve is punctuated by a number of 'steps'. Like the Arne, the Taf ^{137}Cs curve has a major peak at depth and a minor peak closer to the surface.

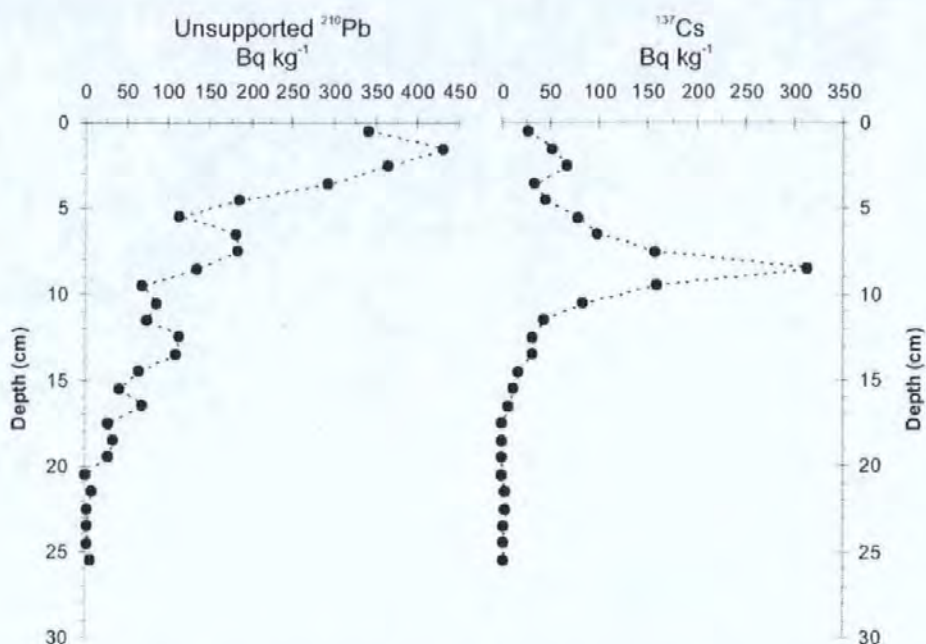


Figure 4.11. The Taf radionuclide data. No analytical uncertainty was reported by the laboratory involved.

The Taf radionuclide activity curve profiles are similar to the Arne curves but the absolute activity levels are considerably higher in the Taf sediments. The unsupported ²¹⁰Pb value near the surface (Table 4.9) is five times higher at the Taf site with a value of 341 Bq kg⁻¹. Likewise, the maximum value at depth for ¹³⁷Cs activity at the Taf site, 312 Bq kg⁻¹, is nearly three times higher than that described by the results from Poole Harbour, but the relative value of the minor ¹³⁷Cs peak to the maximum ¹³⁷Cs peak is reduced at the Taf. In the Arne record the minor peak reaches 48% of the height of the major peak, whereas in the Taf the minor peak maximum value is only 21 % of that achieved in the major peak.

The Taf unsupported ²¹⁰Pb data was first plotted on a log scale to check for possible linear trends (Figure 4.12). In common with the Arne data, when the complete data set was considered no overall trend was apparent, but the middle section did have some indication of steady-state deposition. Thereafter, the CRS model was used to model deposition ages using the whole data set, and a linear regression applied to the data from 1.5 cm to 19.5 cm to enable a mean accumulation rate to be calculated for this section using the CIC model (Table 4.10).

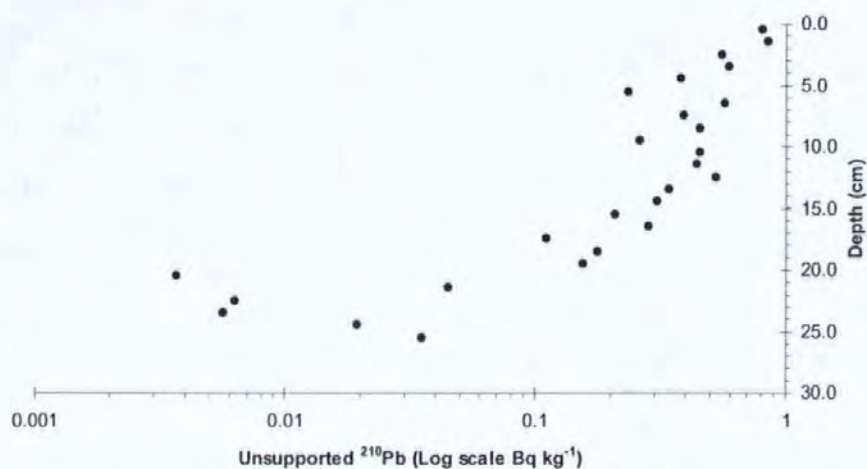


Figure 4.12. The Taf unsupported ^{210}Pb data plotted on a log scale against depth.

The CRS model (Figure 4.13) indicated that the base of the Taf monolith was deposited around 1823, and that since that date the mean accumulation rate has increased slowly overall, but has remained, in the main, between 0.15 cm yr^{-1} and 0.3 cm yr^{-1} . In contrast, the CIC model (Figure 4.14) produced a date of 1890 for the base of the sequence, and indicated a higher, and less stable, accumulation rate. However, the chronologies from both ^{210}Pb models were in some agreement as to the approximate location, i.e. between 9.5 cm and 11.0 cm, of the sediments deposited at the Taf site during the height of the 1960s nuclear weapons fallout in the Northern Hemisphere.

Depth		CRS model			CIC model		
		Age	Accumulation rate		Age	Accumulation rate	
cm	g cm ⁻²	AD	cm yr ⁻¹	g yr ⁻¹	AD	cm yr ⁻¹	g yr ⁻¹
0	0	1998	0.30	0.72	1998	0.39	0.92
0.5	2.4	1995	0.21	0.28	1995	0.47	0.92
1.5	2.0	1991	0.25	0.15	1993	0.60	0.92
2.5	1.5	1988	0.26	0.15	1992	0.45	0.92
3.5	2.0	1985	0.29	0.13	1989	0.45	0.92
4.5	2.1	1982	0.32	0.12	1987	0.44	0.92
5.5	2.1	1981	0.30	0.15	1985	0.29	0.92
6.5	3.2	1977	0.31	0.09	1982	0.43	0.92
7.5	2.1	1974	0.30	0.12	1979	0.27	0.92
8.5	3.4	1969	0.31	0.12	1976	0.24	0.92
9.5	3.8	1967	0.29	0.15	1971	0.17	0.92
10.5	5.3	1962	0.27	0.14	1966	0.16	0.92
11.5	5.9	1956	0.25	0.09	1959	0.20	0.92
12.5	4.6	1947	0.23	0.05	1954	0.29	0.92
13.5	3.2	1940	0.22	0.07	1951	0.20	0.92
14.5	4.7	1932	0.21	0.07	1946	0.18	0.92
15.5	5.2	1925	0.19	0.05	1940	0.22	0.92
16.5	4.1	1912	0.19	0.05	1936	0.22	0.92
17.5	4.3	1905	0.17	0.05	1931	0.17	0.92
18.5	5.3	1888	0.14	0.04	1925	0.16	0.92
19.5	5.9	1861	0.15	0.05	1919	0.13	0.92
20.5	6.9	1860	0.14	0.04	1911	0.16	0.92
21.5	5.8	1843	0.14	0.01	1905	0.40	0.92
22.5	2.3	1840	0.15	0.03	1903	0.21	0.92
23.5	4.3	1837	0.14	0.04	1898	0.13	0.92
24.5	7.1	1823	NA	NA	1890	NA	NA

Table 4.10. $\text{Taf}^{210}\text{Pb}$ derived chronologies and accumulation rates using the CRS and CIC models (Appleby *et al.* 1978; Appleby, 2001). No analytical uncertainty was reported by the laboratory involved therefore it is not possible to propagate these errors.

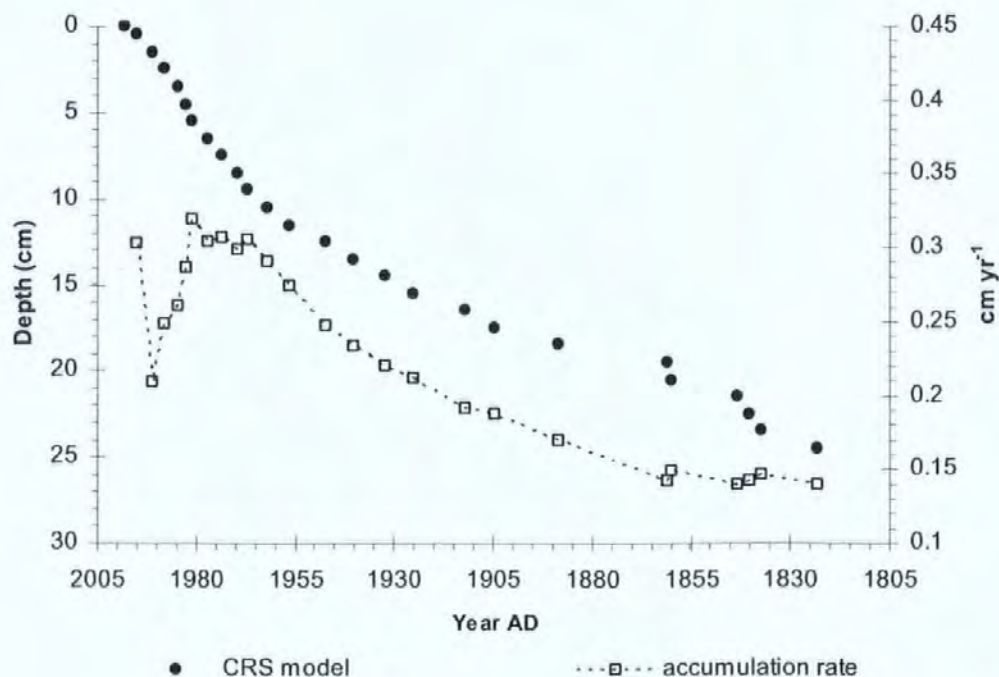


Figure 4.13. The $\text{Taf}^{210}\text{Pb}$ chronology obtained using the CRS model (Appleby *et al.*, 1978).

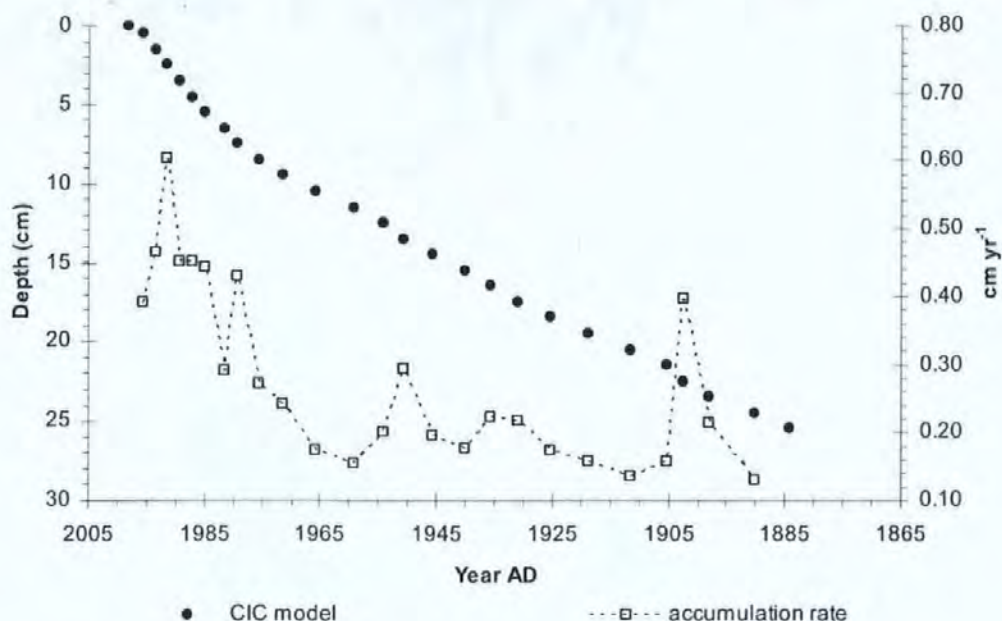


Figure 4.14. The Taf ^{210}Pb chronology obtained using the CIC model (Appleby, 2001).

In consideration of the Taf ^{137}Cs data, 98 % of the total inventory is found above 16 cm, and so the sample from 15.5 cm is therefore considered to mark the start of significant ^{137}Cs deposition in 1954-1956. Above this level the Taf curve has a well defined profile with a progressive rising limb, containing a small step between 14 cm and 12 cm. The rising limb terminates in a well defined major peak with the apex marked by a single data point of 312 Bq kg^{-1} at 8.5 cm, which represents some 21 % of the total ^{137}Cs inventory. This signal is interpreted as representing the deposition of fallout from nuclear weapons tests in 1963. This major peak is followed by a steady decline to levels that are less than 3 % of the inventory before an abrupt rise at 2.5 cm to activity levels that are approaching 10 % of the total ^{137}Cs activity found in the sequence. This lesser peak is tentatively interpreted as being the signal of the 1986 Chernobyl fallout in the Taf sediments.

Although there is not the added confirmation of ^{241}Am data, it is felt that the 1963 bomb test signal can be interpreted in this sequence with some certainty. The ^{137}Cs profile agrees with the known ^{137}Cs fallout history for this part of south Wales. Deposition of radionuclides from Chernobyl was light in this area resulting in a relatively depressed signal for this event compared to some other parts of Europe, including southern England (See Table 4.3). It was documented in 1986 that the contribution from Chernobyl to the total ^{137}Cs activity in Carmarthenshire was only

some 7 %. In contrast, further north in Gwynedd over 59 % of the local ^{137}Cs activity measured in 1986 was the result of fallout from the Russian reactor accident (Cambray *et al.*, 1987). This disparity in deposition inventories is the result of precipitation and air flow patterns during the critical days following the accident.

The robustness of the interpretation for the upper section of the sequence is also confirmed when the Taf ^{137}Cs data is examined alongside the two ^{210}Pb chronologies (Figure 4.13). The CRS model supports the proposed location of the Chernobyl signal, and there is agreement that the sediments from 11.5 cm were deposited in 1959-1960. This notwithstanding, below this level both the ^{210}Pb chronologies indicate older deposition ages for the sediment when compared to the ^{137}Cs data. The deposition date indicated by the ^{137}Cs data for the sample from 15.5 cm is 1956, but the CIC model suggests a date of 1940 for this level, and when the CRS model is used a date of 1925 is produced. However, given that the significant fallout of ^{137}Cs did not start until after 1954 (Appleby, 2001), it is unlikely that the deposition of the sediments at 15.5 cm could have occurred before 1956.

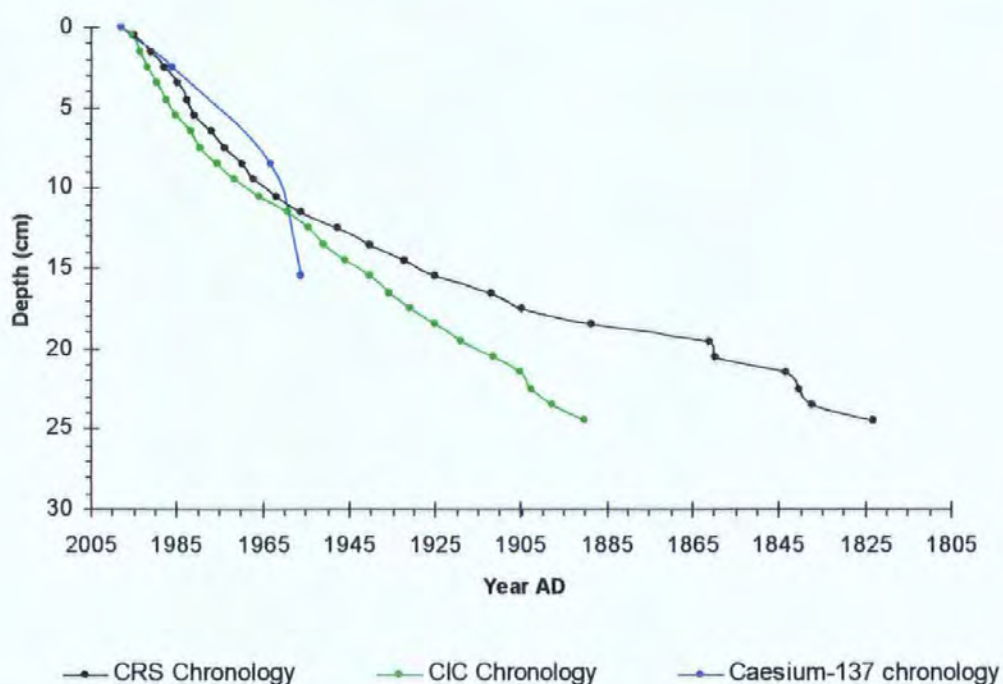


Figure 4.14. The three age-depth solutions obtained for the Taf sequence using radionuclide dating methods.

4.4.2. The Viðarhólmi radionuclide analysis. As part of the HOLSMEER Project (See Scourse *et al.*, 2006) recent sea-level change investigations have been carried out in northwest Iceland by Gehrels *et al.* (2006). This work included a radionuclide analysis on sediments from the Viðarhólmi site (Table 4.11).

Depth		²¹⁰ Pb						¹³⁷ Cs	
		Total	Unsupported		Supported (from ²²⁶ Ra)				
cm	g cm ⁻²	Bq kg ⁻¹	±	Bq kg ⁻¹	±	Bq kg ⁻¹	±	Bq kg ⁻¹	±
0.5	0.55	72.4	10.0	46.9	7.9	27.0	2.6	1.5	0.1
1.5	0.69	76.8	8.0	57.2	8.3	21.5	2.2	2.2	0.6
2.5	0.46	77.5	10.0	52.3	8.7	26.9	2.9	2.3	1.0
3.5	0.49	95.3	11.9	69.6	10.9	27.9	2.7	2.5	1.0
4.5	0.45	80.5	10.7	51.5	8.4	30.7	2.9	4.1	1.0
5.5	0.55	54.4	9.5	29.4	5.9	25.9	2.6	4.4	1.0
6.5	0.50	45.6	8.0	21.7	4.3	24.6	2.4	4.0	1.0
7.5	0.55	36.4	7.2	11.9	2.7	25.0	2.7	4.1	1.1
8.5	0.55	31.2	6.0	8.8	1.9	22.7	2.2	21.2	1.3
9.5	0.55	30.8	4.2	5.9	1.2	25.2	3.6	24.2	2.1
10.5	0.42	26.2	7.9	0.9	0.3	25.4	2.6	14.7	1.3
11.5	0.61	33.6	6.4	15.7	3.5	18.5	2.1	7.3	0.8
12.5	0.63	21.8	4.2	ND	ND	22.7	3.5	2.3	0.8
13.5	0.55	ND	ND	ND	ND	ND	ND	ND	ND
14.5	0.51	ND	ND	ND	ND	ND	ND	ND	ND
15.5	0.73	ND	ND	ND	ND	24.0	2.3	1.1	0.7
16.5	0.60	8.4	5.6	ND	ND	21.0	4.2	7.4	0.9
17.5	0.66	ND	ND	ND	ND	ND	ND	ND	ND
18.5	0.61	ND	ND	ND	ND	ND	ND	ND	ND
19.5	0.60	7.7	3.6	ND	ND	20.0	2.0	1.2	0.8
20.5	0.71	11.7	4.6	ND	ND	24.0	3.3	ND	ND
21.5	0.56	ND	ND	ND	ND	ND	ND	ND	ND
22.5	0.68	8.4	4.1	ND	ND	19.5	3.3	4.6	0.8
23.5	0.51	ND	ND	ND	ND	ND	ND	ND	ND
24.5	0.49	ND	ND	ND	ND	32.0	3.5	ND	ND
25.5	0.48	ND	ND	ND	ND	ND	ND	ND	ND
26.5	0.70	ND	ND	ND	ND	19.3	2.9	1.9	0.6
27.5	0.79	5.3	4.3	ND	ND	21.3	2.2	4.3	0.1
28.5	0.69	ND	ND	ND	ND	20.9	4.4	4.5	1.2

Table 4.11. Radionuclide concentrations in Viðarhólmi salt-marsh sediments. ND = No Data.

On first inspection, the radionuclide data from the Viðarhólmi analysis is notable by the depressed values obtained for both ²¹⁰Pb and ¹³⁷Cs activity when compared to the Taf data. The supported ²¹⁰Pb surface activity was measured at 27.0 Bq kg⁻¹, which is compatible with the Arne record (These data are not available for the Taf), but the unsupported ²¹⁰Pb activity is only 46.9 Bq kg⁻¹ in the surface sediments. This increases to 69.6 Bq kg⁻¹ at 3.5 cm, before quickly decaying down profile to 0.9 Bq kg⁻¹ at 10.5 cm. In addition both the radionuclide activities reported have an erratic and fragmentary record below 11.5 cm (Figure 4.15). This notwithstanding, to aid inter-site comparisons it was decided to follow the same approach as used with the other two data sets. Therefore, the unsupported ²¹⁰Pb data were first plotted against depth to test for any linear trends (Figure 4.16).

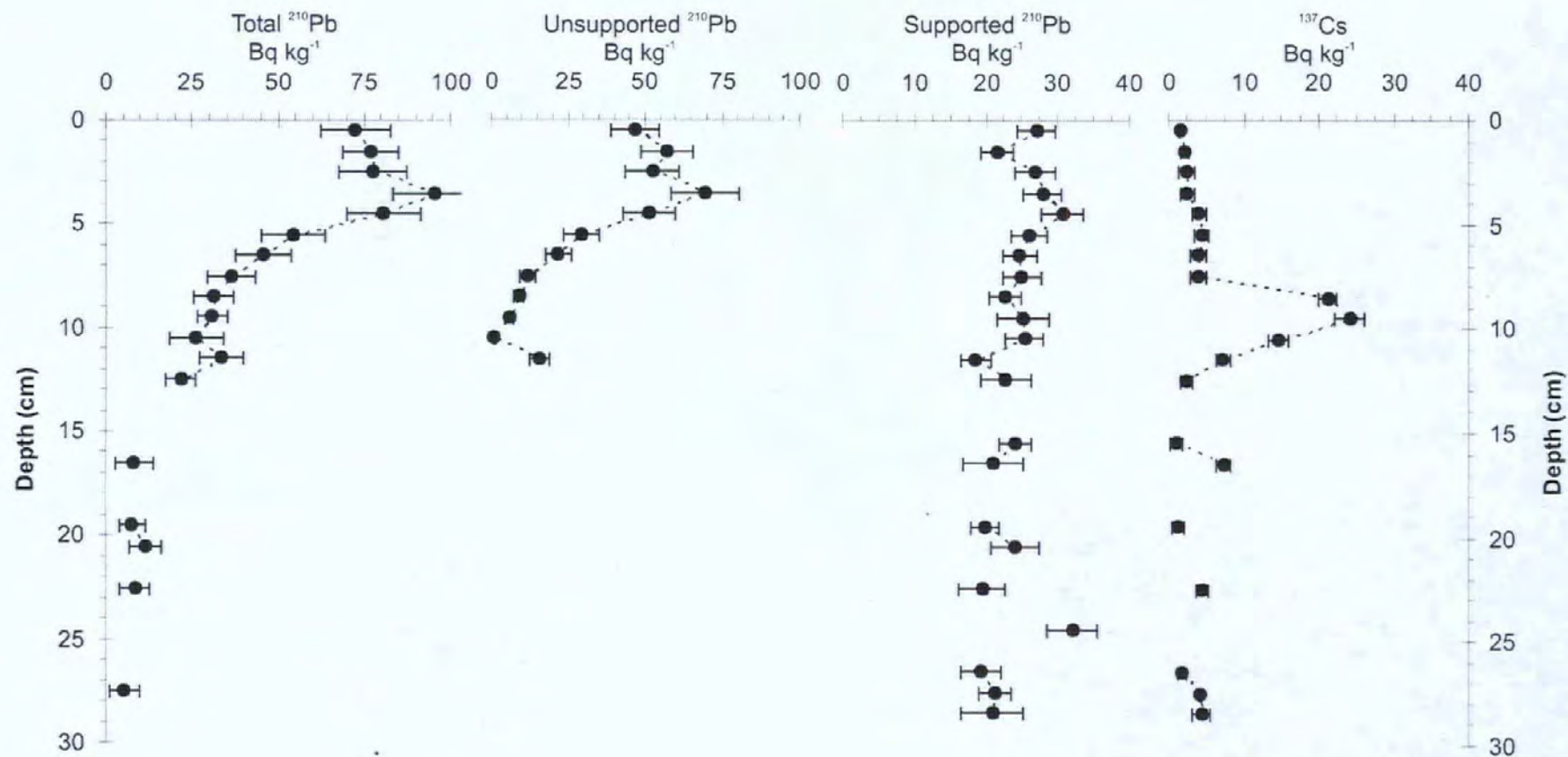


Figure 4.15. The Viðarhólmi ^{210}Pb and ^{137}Cs analysis.

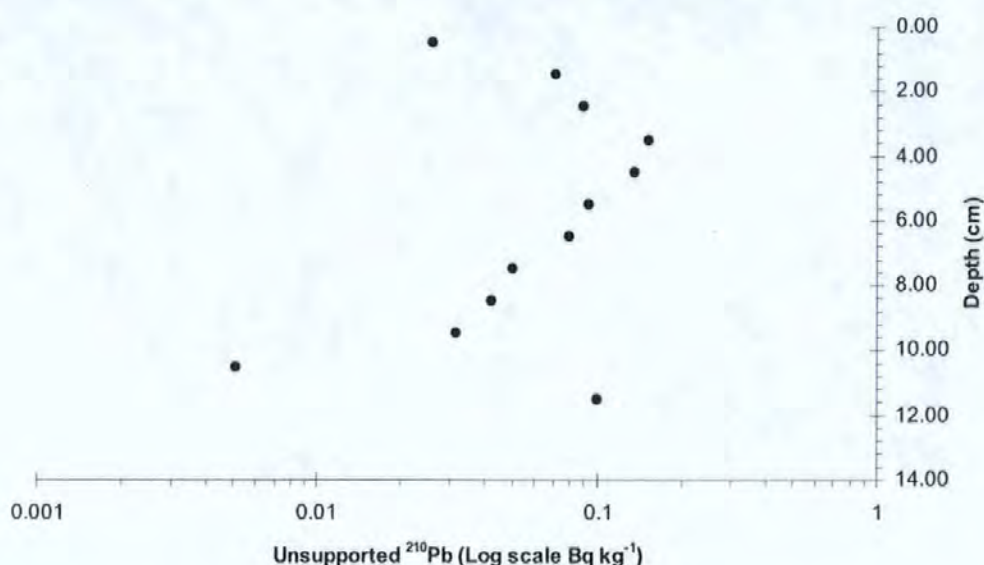


Figure 4.16. The Viðarhólmi unsupported ²¹⁰Pb data plotted on a log scale against depth.

Only 12 data points could be plotted in Figure 4.16 so this exercise is potentially not as reliable as when it was applied to the other two data sets. However, a similar result was obtained. When the complete data set is considered no overall linear trend is apparent, but the section from 3.5 cm to 9.5 cm does have some indication of steady-state deposition. This established, the CRS model was used to model deposition ages down to 10.5 cm, and a linear regression applied to the data indicated by Figure 4.16 to enable the use of the CIC model (Table 4.12).

Depth		CRS model				CIC model			
		Age		Accumulation rate		Age		Accumulation rate	
cm	g cm ⁻²	AD	±	cm yr ⁻¹	g cm ⁻² yr ⁻¹	AD	±	cm yr ⁻¹	g cm ⁻² yr ⁻¹
0	0	2001	0.00	1.04	0.57	2001	0.00	0.07	0.04
0.50	0.55	2000	0.01	0.27	0.33	1987	0.24	0.06	0.04
1.50	1.25	1997	0.11	0.13	0.22	1969	0.55	0.08	0.04
2.50	1.71	1993	0.18	0.06	0.14	1957	0.76	0.08	0.04
3.50	2.19	1985	0.43	0.04	0.11	1945	0.97	0.09	0.04
4.50	2.64	1976	0.75	0.03	0.10	1933	1.17	0.07	0.04
5.50	3.19	1967	0.84	0.02	0.09	1919	1.42	0.08	0.04
6.50	3.70	1958	0.98	0.02	0.08	1906	1.64	0.07	0.04
7.50	4.24	1950	0.95	0.02	0.08	1892	1.88	0.07	0.04
8.50	4.79	1941	0.98	0.01	0.08	1878	2.12	0.07	0.04
9.50	5.35	1933	1.16	0.01	0.08	1864	2.37	0.09	0.04
10.50	5.77	1931	1.04	NA	NA	1853	2.56	NA	NA

Table 4.12. Lead-210 chronologies for the Viðarhólmi site using the CRS and CIC models (Appleby *et al.*, 1978; Appleby, 2001).

The two chronologies produced by the ^{210}Pb models for the Viðarhólmi sequence are vastly different. The CRS result (Figure 4.17) suggests that the sediments at 5.5 cm were deposited in the 1960s whereas the CIC model (Figure 4.18) dates this level to 1919. This disagreement increased down profile, and by the bottom of the usable data series at 10.5 cm there was an approximate 75 year difference in the sediment deposition ages suggested by the two models.

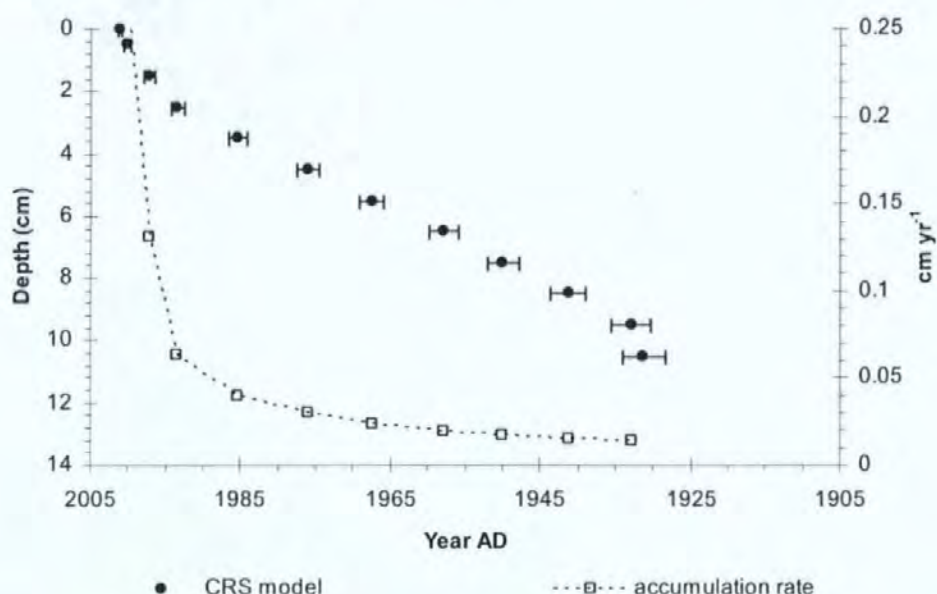


Figure 4.17. The results of using the CRS model (Appleby, 1978) on the Viðarhólmi sequence. Dating errors propagated from analytical uncertainty.

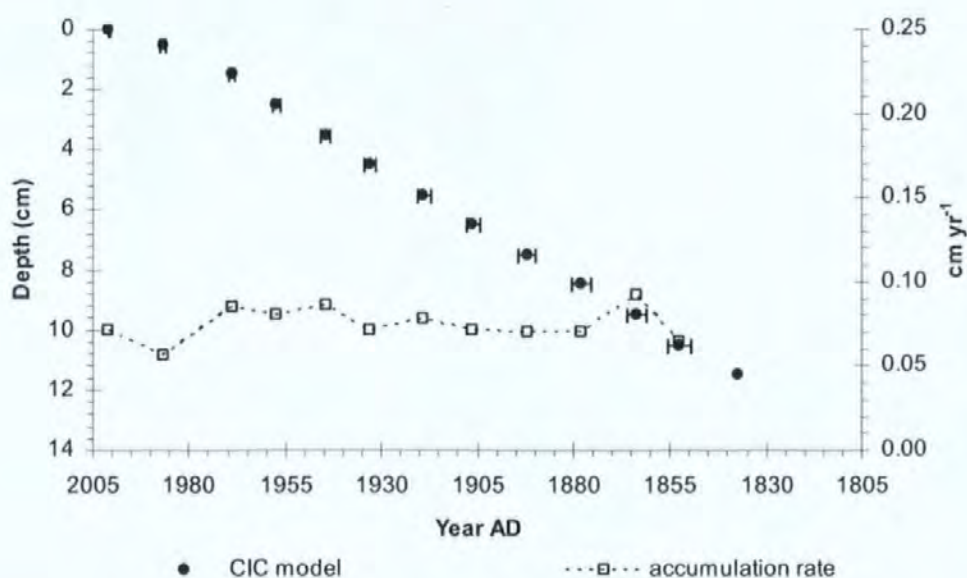


Figure 4.18. The results of using the CIC model (Appleby, 2001) on the Viðarhólmi sequence. Dating errors propagated from analytical uncertainty.

The situation can not be easily solved by consulting the ^{137}Cs data. There is a well defined peak of 24.18 Bq kg^{-1} at 9.5 cm, and some 38 % of the total ^{137}Cs inventory lies above this level. In this upper section the values drop quickly toward the surface to around 4 Bq kg^{-1} . This major peak has a progressive rising limb, suggesting this feature is not a single, short-term event, and the apex point value represents around 20 % of the total ^{137}Cs inventory in the sequence. Below this level, at 16.5 cm, there is a small isolated peak of around 7.37 Bq and sporadic low-level activity down to 28.5 cm. Unlike the Arne and Taf records this profile does not simply agree with the known history of ^{137}Cs fallout deposition for this region. It is not clear if the major peak represents the 1963 weapons peak. In fact, because there is a secondary peak at 16.5 cm, the peak at 9.5 cm could be interpreted as the 1986 Chernobyl signal. This issue will be explored further in the next section, but as a comparison exercise the major ^{137}Cs peak at 9.5 cm is assumed here to be the 1963 signal and therefore all three possible solutions suggested for the Viðarhólmi sequence using radionuclides are shown in Figure 4.19.

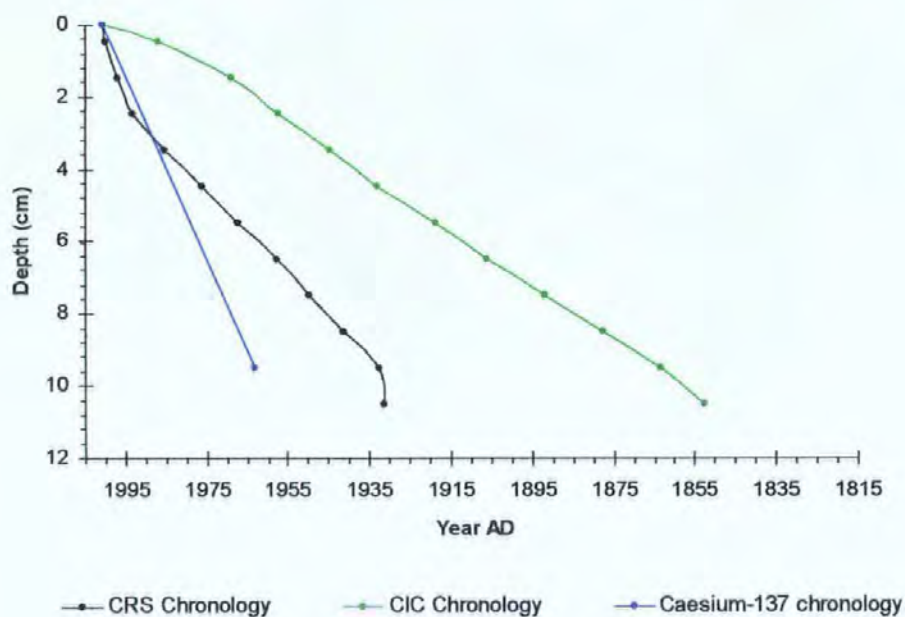


Figure 4.19. The three age-depth solutions suggested for the Viðarhólmi sequence using radionuclide dating methods.

4.5. Discussion and synopsis

4.5.1. Lead - 210. It is felt that the concerns about the use of non-verified and unsubstantiated ^{210}Pb chronologies, expressed by Smith (2001), Appleby (2001), Thompson *et al.* (2002) and others, are shown to be especially pertinent to salt-marsh sequences. The two ^{210}Pb models used with the Arne ^{210}Pb data produced very different results. This situation was much the same at the other sites, and the deposition ages derived from the other radionuclide data are not in agreement with the CRS or CIC chronologies. When the Arne data are considered in detail, it is only when the CRS chronology is 'corrected' using the 1963 ^{137}Cs marker that any close agreement becomes apparent between the ^{210}Pb chronology and the ^{241}Am data. However, given that the ^{137}Cs marker is assumed to signal the same events in 1962-1963 that had produced the peak in ^{241}Am data, this alignment was to be expected. It is also noted that, if the uncertainty in the CRS model is considered, there was no real advantage in using the ^{210}Pb data to model deposition ages for the Arne sequence. An accumulation rate could have been simply estimated using the ^{137}Cs and ^{241}Am age markers and projected back with equal, or possibly better, apparent reliability than the two 'uncorrected' ^{210}Pb chronologies. However, the use of ^{137}Cs to correct the CRS chronology did retain some extra detail that would be lost by just using the isolated fallout radionuclide markers.

The Taf data did produce two plausible ^{210}Pb chronologies that showed some agreement with each other, and the ^{137}Cs markers for 1986 and 1963, in the upper part of the sequence. This situation deteriorated in the lower section of the sequence with a marked deviation between the chronologies below 15 cm. The Icelandic ^{210}Pb results are not viewed to be reliable, and there is little agreement between the individual CRS and CIC chronologies, and both ^{210}Pb solutions, with the ^{137}Cs marker assumed to represent the 1963 weapons test signal.

If a single conclusion is to be drawn from this investigation into the use of ^{210}Pb as a dating tool for salt-marsh sediments it must be that the method and model that works well at one site is not guaranteed to work at another. One reason for this situation is the subtle differences in the physical characteristics of each individual site (e.g., sedimentation rate and lithology). All of the ^{210}Pb models demand some level of stability in the supply of the minerogenic fraction of the sediments, and the

constant permanent emplacement of ^{210}Pb within the sediment matrix. In a salt marsh minerogenic sediments are deposited by regular tidal inundations, and so changes in the tidal characteristics of a site will result in corresponding changes in the suspended sediment supply to the marsh surface. This will change the ratio between supported and the unsupported ^{210}Pb fraction. In addition, changes in tidal flow velocities, and episodes of marsh erosion, will influence the retention on the marsh surface of the ^{210}Pb deposited as fallout.

Simple fluctuations in sediment accumulation rates can, to some extent, be incorporated into the age modelling by the use of cumulative dry mass/unit area data and the CRS model (Appleby and Oldfield, 1978). However, these are factors that may not change the bulk density significantly, but may preferentially change the affinity of the sediment for ^{210}Pb . Other variables, that may need to be incorporated into the modelling, include changes in grain size (Maringer, 1996; Dellapenna *et al.*, 2003), subtle changes in sediment lithology and grain magnetic properties (McCubbin *et al.*, 2000).

Thompson *et al.* (2002) stated that ^{210}Pb derived accumulation rates for salt marshes 'should be viewed with some caution'. Pivotal to the success of the ^{210}Pb models commonly used to derive sediment deposition chronologies is the assumption that the unsupported ^{210}Pb fraction in the sediments under analysis has been deposited from one dominant source, and at one concentration ratio with the sediments. It is also hoped that once it has been deposited it has then remained undisturbed on the sediment surface. This situation may be found in a lake basin or a peat bog, but an accreting intertidal salt-marsh surface will be more complex. It will have some ^{210}Pb contributions associated with the sediments deposited by tidal flooding, and some particles deposited directly from atmosphere. Furthermore, over-marsh flooding may, in some situations, remove ^{210}Pb from the marsh surface previously deposited directly from the atmosphere. It is therefore evident that the basic dynamics of the intertidal salt-marsh environment may mean that the long-term steady-state deposition of ^{210}Pb from atmosphere is unlikely.

The robustness of chronologies derived from the analysis of radionuclides in sediment samples is entirely dependent on the reliability of the initial determination of activity levels. This in itself is somewhat dependent on the activity levels present in the samples. As with all geochemical analysis, if the concentration of the substance being assayed falls below a certain plateau then the analytical precession falls, and the uncertainty attached to the data grows. This is evident when the data

from the Viðarhólmi is examined. Unfortunately, because of its oceanic location and ice cover (See Section 4.1), Iceland has a low background level of unsupported ^{210}Pb . Disregarding all other factors, if the ambient level of ^{210}Pb activity is low it can preclude the use of ^{210}Pb as a dating tool. If the initial activity is low, the unsupported ^{210}Pb down profile activity will decrease below reliable detectable values before the inventory has covered 5-6 half lives. If the unsupported ^{210}Pb levels fall off too quickly the data will be unusable. To be reliably detected by gamma spectrometry the activity needs to be $> 10 \text{ Bq kg}^{-1}$. Any changes in values below that level are likely to be statistically meaningless (Appleby, 2001). This means that in situations like that found at Viðarhólmi a significant number of the lower data points could be discarded. In addition, if the unsupported activity falls below 10 Bq kg^{-1} too quickly the total fallout inventory will be underestimated. This means that the ages produced using the CRS, and similar ^{210}Pb models, will be correspondingly underestimated, and the chances of any reliable chronology produced using ^{210}Pb modelling is slim.

4.5.2. The artificial radionuclides. Caesium-137 is soluble in sea water and behaves conservatively in marine environments (Beks, 2000). In some instances it can be remobilised in salt-marsh sediments and migrate vertically. It is suggested (Kim *et al.*, 1997; Abril, 2004; Donders *et al.*, 2004) that this tendency for mobility can preclude the use of ^{137}Cs as an independent dating tool. The misalignment of the ^{137}Cs 1986 marker and the corrected CRS ^{210}Pb chronology may indicate that there has been some displacement of ^{137}Cs in the Arne sediments. This tendency could also explain the fragmentary occurrence of ^{137}Cs activity in the lower sections of the Viðarhólmi sequence. In some environmental situations, ^{137}Cs and other radionuclides are known to exhibit post-depositional mobility in saturated sediments (Abril, 2004). This mobility can degrade the precision of a ^{137}Cs record by blurring the introduction boundaries and reducing the amplitude of the maximum values.

Americium-241, in contrast is particle-reactive, and unlike ^{137}Cs , it is rapidly, and irreversibly, bound into particulate material after deposition (Clifton *et al.*, 1999). Lead-210, like ^{241}Am , is also non-conservative (Beks, 2000) in a marine environment, and is scavenged by particulate material. It binds to sediment grains, and, under normal circumstances, it does not go into solution. In theory this means that ^{137}Cs has the ability to migrate independently of both ^{241}Am and ^{210}Pb in sediment pore water. In this situation ^{137}Cs can be found in sediment horizons that were deposited before the time when this artificial radionuclide was first dispersed into the environment (Thompson *et al.*, 2002).

At the two sites where plausible chronologies could be constructed, the Arne and the Taf, there is some notable difference between the ^{210}Pb chronology on the one hand and the sediment depositional history indicated by the ^{137}Cs age-markers. Because of the reasons outlined above, this is not unique. Thompson *et al.* (2002) found significant variability in the alignment of the results of their ^{210}Pb chronologies and the age markers derived from ^{137}Cs at their Beaulieu Marsh and Wry Marsh sites, but could find 'no obvious explanation for the disparity'. Other salt-marsh studies have experienced difficulties when attempting to align ^{210}Pb chronologies and ^{137}Cs age markers (e.g., Kim *et al.*, 1997; Cochram *et al.*, 1998; San Miguel *et al.*, 2004; Gehrels *et al.*, 2006), but as yet there is not conclusive evidence that mobility in the pore water is always the simple explanation of the problem.

However, the presence of ^{241}Am in the Arne sediments between 12.5 cm and 22.5 cm is viewed as significant. The close association in the Arne sediments between the maximum of ^{137}Cs deposition, interpreted as 1963, and the level containing the ^{241}Am peak activity does confirm that any post depositional migration of ^{137}Cs has been minimal. There is a presence of low ^{241}Am activity above this level, and, although not conclusive in itself, this may be the result of the documented discharge of effluent containing low-level activity from the former UKAEA establishment at Winfrith (Thompson *et al.*, 2002). This alpha discharge started in the 1970s, and the peak of emissions pre-dates the 1986 Chernobyl fallout. In addition, the associated ^{137}Cs releases from Winfrith were negligible (Table 4.4). This material would have been rapidly dispersed in the English Channel and is very unlikely that this activity would have produced a signal in the Arne sediments. This supports the interpretation presented in 4.3 of the two ^{137}Cs activity peaks in the Arne sequence.

To use the timing of events signalled by the ^{137}Cs data the event must be reliably identified. At the Arne site the ^{137}Cs record conforms to the expected profile for a site in southern England. It starts with zero values and climbs steadily to a well defined lower peak, followed by a steady decline to near introduction levels before an abrupt increase to a sharp peak and subsequent steady decline to near introduction. The Taf record also shows good agreement with the documented history of ^{137}Cs deposition for south Wales. Unfortunately, in the case of the Viðarhólmi sequence, the profile could not be simply interpreted, and it is necessary to consider the dynamics of the ^{137}Cs pathway in more detail.

In common with the rest of Europe, Iceland received ^{137}Cs fallout from the nuclear weapons test program of the 1950s and 1960s, with the peak of this deposition occurring in 1963. This peak was not a single, sudden event but was the culmination of a steady increase that started in 1960, and was spread over the next three years (Figure 4.2). In contrast, the 1986 Chernobyl accident suddenly produced elevated atmospheric levels in a matter of hours over the proximal parts of Northern Europe. In the UK the ^{137}Cs concentration in air at Chilton in 1986 rose from $<0.001 \text{ mB kg}^{-1}$ during the period of 21st to the 28th of April to 58 mB kg^{-1} during 28th of April to 5th May, and a similar rapid increase was monitored at all stations in Western Europe that were in the path of the fallout plume during the first days following the accident (Cambray *et al.*, 1987). Although the abruptness of the increase did reduce with time and distance its influence was still effectively instantaneous. By 1st of September 1986 the ^{137}Cs concentration in the air at Chilton had dropped to $0.0022 \text{ mB kg}^{-1}$.

The data for Reykjavik in Table 4.3 suggest that the signal of the Chernobyl accident will be most likely be below detection levels or nonexistent in most Icelandic sediment sequences. This supposition is supported by measurements of ^{137}Cs activity taken by Pálsson *et al.*, (1994) in Icelandic soils, lichens and reindeer meat in 1990-1992. They found that the total ^{137}Cs activity in Iceland in 1990-1992 was comparable to values in other parts of Scandinavia before the Chernobyl accident, and that there was only one zone of significantly enhanced activity in the soil profiles they analysed. Given this information, and the extended width of the major ^{137}Cs peak at 9.5 cm in the Viðarhólmi sequence, it is felt that it is not the result of Chernobyl fallout, and an alternative interpretation must be sought.

In addition to fallout from nuclear weapons tests, and some small possible contribution from the Chernobyl accident, Iceland has also been receiving contamination via the marine pathway (Óafsdóttir *et al.*, 1999). Table 4.4 ranks Sellafield as the dominant source of ^{137}Cs in the northern European seawater, but the data presented in Figure 4.3 indicate that the activity in the sea around Iceland from 1976 to 1995 has never been above 5 Bq m^{-3} . Óafsdóttir *et al.* (1999) suggest transportation times to Iceland for radionuclides discharged from Sellafield to be in the order of 14-17 years. As the peak ^{137}Cs discharge from Sellafield was in 1975 it follows that if this source was going to influence significantly the ^{137}Cs activity in the sea off Iceland, an increase in the local activity would be evident in the period

preceding the situation portrayed in Figure 4.3 (d). No such change is apparent, and, after consideration of the data published by Povinec *et al.* (2003), it is concluded that contributions from Sellafield to the Viðarhólmi ^{137}Cs inventory will have been negligible, and it is most likely that the peak at 9.5 cm is a signal of the maximum deposition of weapons test fallout in 1963.

4.5.3. Synopsis. In this chapter three chronologies were obtained from the Arne site using ^{210}Pb analysis. These results, and the deposition rate calculated from ^{137}Cs and ^{241}Am data, have been presented and discussed. The Arne results were then compared those obtained at the other two sites featured in this thesis. Each site had subtly differing results, and the agreement between the methods was somewhat limited, or poor, in some parts of the sequences. It is felt that the important issues highlighted by this chapter fall into three basic categories.

1. Issues associated with the ^{210}Pb models used, their selection, inherent limitations of use and need for validation.
2. The reliable interpretation of ^{137}Cs records and the identification of the signals of specific events.
3. The implications of low activity levels in the sediments, analytical detection levels and age uncertainties.

Chapter 5

Palaeomagnetic dating

The first sections of this chapter will give an introduction to the concept of the Earth's geomagnetic field, how it changes through time, and how this can be used to date materials. The process in which the palaeomagnetic signal is preserved will be examined, and the subject of palaeomagnetic calibration curves and some issues surrounding potential uncertainties will be discussed. Section 5.2 describes how palaeomagnetic dating was tested on material from the three study sites, and presents the results of these investigations.

5.1.1. Palaeomagnetic dating.

5.1.1. Palaeomagnetism and palaeomagnetic dating. An in-depth review of all aspects of environmental magnetism and palaeomagnetism is outside the scope of this chapter, and the reader is directed to the many texts that are available on the background theory of environmental magnetism, palaeomagnetic dating and archaeomagnetic dating. Many of the classic 'standard' environmental magnetism books contain useful explanatory material on sediment-based palaeomagnetic dating methods. These include Tarling (1983), Thompson and Oldfield (1986), and in particular Butler (1992) which also covers the topic of polar reversals and longer-term magnetic stratigraphy. In addition to these 'pure magnetic' texts the chapter by Thompson in Berglund (1986) covers the theory of regional master curves to calibrate the data and other key aspects, and a noteworthy review paper is Dekkers (1997) which makes links between environmental magnetism and the key principles controlling the remanent magnetization of sediments.

Technical explanations on remanent magnetization and how it is measured are in the QRA technical guide on environmental magnetism (Walden *et al.*, 1999). This guide also gives a good introduction to magnetic susceptibility and magnetic measurements. Unfortunately, there is a lack of good up-to-date technical guides specifically on magnetic dating methods, apart from the recent comprehensive publication on archaeomagnetic dating by English Heritage (English Heritage, 2006).

Palaeomagnetic dating is an indirect, or 'event', dating method that uses magnetic stratigraphy to create a chronology. Over centennial to millennial time scales during the Holocene the record of small changes in the direction and the intensity of the geomagnetic field, or secular variations (SV), offers a means to establish the age of suitable recent sediments and some archaeological artefacts. Over longer 'geological' time scales the timing of past polar reversals in the Earth's geomagnetic field can be used to provide low resolution age-estimates. Using subtle signals preserved in ancient sediments and igneous rock deposits, these reversals, or geomagnetic polarity inversions, can be used to correlate geological sequences with established geochronologies using magnetostratigraphy. However, total polarity inversions are rare events, and the last one occurred around 0.73 M yr ago when the Matuyama magnetic time period, or chron, ended and the present chron, the Brunhes, started.

Palaeomagnetic dating of minerogenic sediments is very similar in its concept, and is closely related to, archaeomagnetic dating. Much of the recent research and development has been interdisciplinary. In the United Kingdom the initial palaeomagnetic and archaeomagnetic dating studies started over 50 years ago (e.g., Cook and Belshé, 1958), but it was not until the 1970s that the real potential of geomagnetism as a dating tool for 'soft' sediments of Holocene age was more widely recognised by the palaeoenvironmental community (See Mackereth, 1971; Molyneux *et al.*, 1972; Thompson, 1978; Thompson and Turner 1979; Creer, 1981; Turner and Thompson, 1981). During the preceding two decades magnetic dating was associated primarily with archaeological studies, or it was used to create long-term geological chronologies and study igneous rocks. This changed somewhat after the publication of the regional palaeomagnetic master curves derived from the analysis of sediment sequences from three UK lakes (Turner and Thompson, 1981), and the production of a limited Irish master-curve (Thompson and Edwards, 1982).

5.1.2. The Earth's geomagnetic field. The Earth's geomagnetic field is generated by complex dynamo process within the liquid outer core, but in simplistic terms it can be conceptualised as being produced by a straight bar magnet located in the centre of the planet. At present the effective axis of this best-fitting dipole magnet is offset from the axis of the Earth's rotation. This means that the north and south geographic poles and the north and south magnetic poles are not located in the same place. This situation is not constant through time, and the geomagnetic field can change in both strength and direction over time periods that range from milliseconds to millions of years (Table 5.1).

Geomagnetic changes	Duration (years)
Changes in the average frequency of polarity inversions	5×10^7
	10^7
Time interval between successive polarity inversions	10^6
	10^5
	10^4
Intensity and direction fluctuations of both dipole and non-dipole (induced) fields creating secular variations	10^3
	10^2
11-year sunspot cycle	10^1
Annual variation	$10^0 > 10^{-1}$
Diurnal variation	10^{-2}
Magnetic storms	10^{-3}
Micropulsations	10^{-4}

Table 5.1. Timescales of change in the Earth's geomagnetic field (after Thompson 1978).

The best description of the present geomagnetic field is provided by a geocentric dipole that has an angle of $\sim 11.5^\circ$ with the rotation axis. Approximately 80 % of the geomagnetic field activity can be explained by the best-fitting eccentric or inclined geocentric dipole model (Figure 5.1). The remaining 20 %, or the nondipole field activity, is created by localised turbulence in the outer core and the movement of charged particles in the upper atmosphere. It can be determined by subtracting the

best-fitting dipolar field from the observed geomagnetic field (Butler, 1992). The ability of the best-fitting eccentric dipole to describe the geomagnetic field depends on location on the Earth's surface. At some locations, the best-fitting eccentric dipole perfectly describes the geomagnetic field, but in other areas there are some significant contributions from the nondipole field. This is why the actual magnetic pole and the virtual geomagnetic pole, as assumed by the inclined dipole model, are in different locations (Figure 5.1).

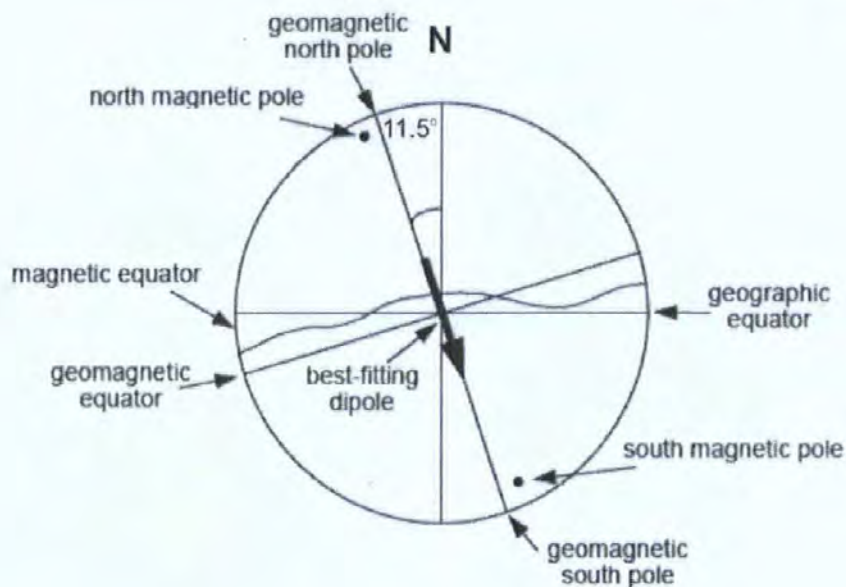


Figure 5.1. The arrangement of the present day inclined geocentric dipole model. Reproduced from Butler (1992).

At any one point in time the strength and direction of the Earth's geomagnetic field can be described by three components:

1. **Declination.** The measured difference in the apparent angle between magnetic north and geographic or 'true' north.

2. **Inclination.** The observed angle of dip of the local prevailing magnetic field from horizontal within the range of 0° , at the magnetic equator, to 90° , at the magnetic poles.
3. **Intensity.** This is the strength of the prevailing geomagnetic field. The present day field strength at the poles is twice that at the equator. It is defined as the torque required to prevent a free swinging magnetic needle returning to the angle of magnetic dip when it has been rotated through 90° .

The geomagnetic field for 2005 is shown in Figure 5.2. These maps were drawn using a compilation of data from observatories scattered around the world using the BGS World Magnetic Model (WMM2005). It shows the propagation of declination values from the poles and the displacement of the inclination of the geomagnetic equator. This situation is constantly changing on a number of timescales, as summarised in Table 5.1, but it is the short-term annual, decadal and centennial changes that are of most interest for palaeomagnetic dating studies. Since the mid-1800s, observations in London and Paris have indicated that the geomagnetic field has changed in direction by about 0.25° and has varied in intensity by about 0.05% each year (Tarling, 1983).

The timing and magnitude of secular variation observed in Paris is similar to that in London but the global patterns of secular variation differ between continents. This reflects the size and eccentric location of the nondipole sources of geomagnetic field within the Earth (Butler 1992). Turner and Thompson (1981) concluded that changes in SV in the nondipole activity in the UK over the last 10,000 years were not periodic, and that the magnitude of the swings in both declination and inclination has decreased since the start of the Holocene.

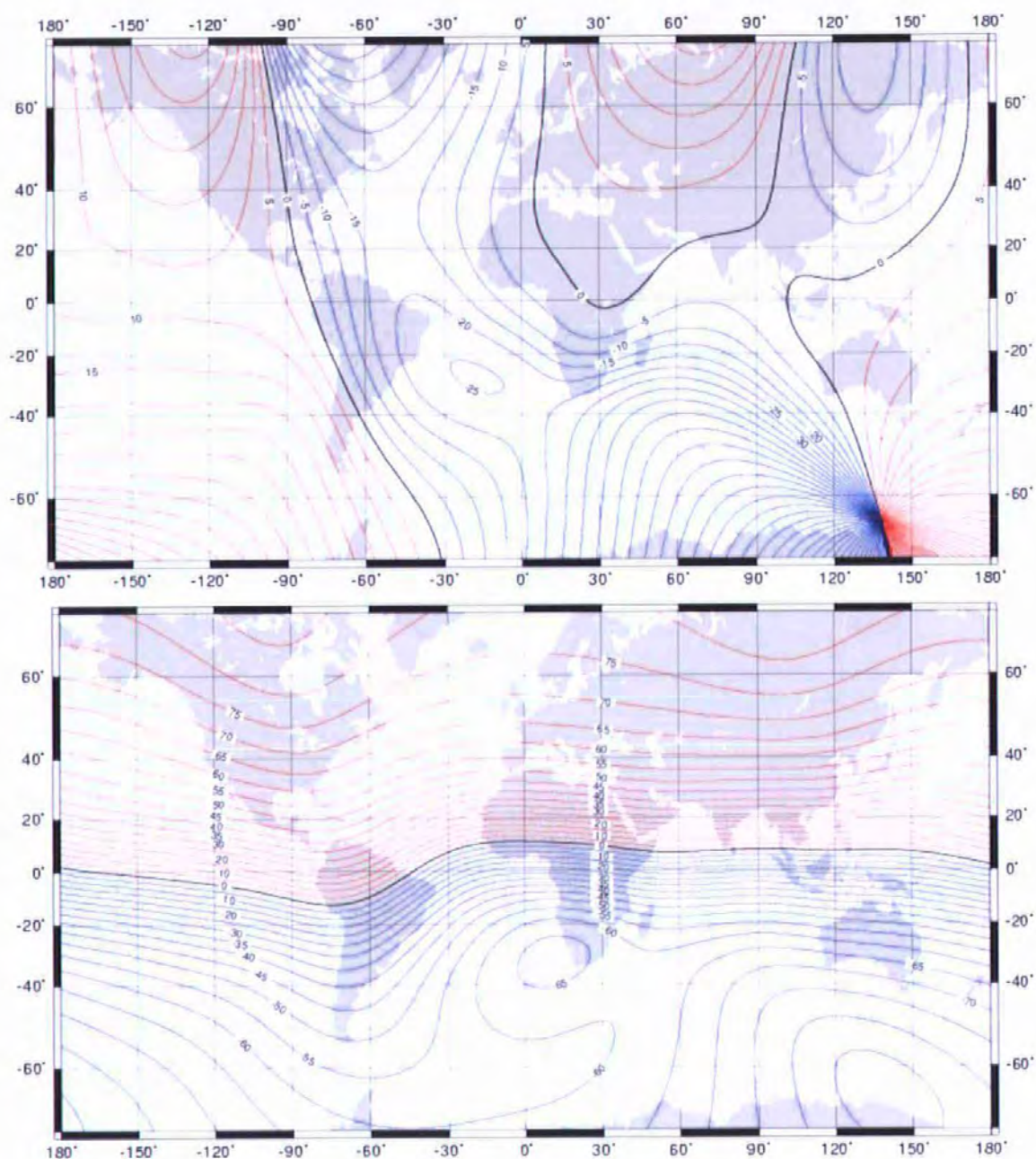


Figure 5.2. Declination (Top) and inclination (Bottom) world maps for 2005 (McLean *et al.*, 2004). Mercator projection using the BGS / NOAA World Magnetic Model (WMM2005).

5.1.3. Natural remanent magnetism. Palaeomagnetic and archaeomagnetic dating uses the record of geomagnetic SV, recorded as a natural remanent magnetism (NRM) in magnetically susceptible minerals. The most common magnetically susceptible minerals are the iron oxides magnetite, maghaemite and haematite. These occur in most soils and clays, and as trace components in many types of rock (Thompson and Oldfield 1986). If these susceptible materials are subjected to a prolonged magnetic field they can acquire their own permanent magnetisation, or a magnetic remanence, proportional to the strength of the ambient magnetic field. The remanence will persist after the removal of the active field, and it can be measured thousands of years later. This magnetic characteristic has both strength, or intensity, and direction. These components are combined to describe the NRM preserved in the sediments and can be used to estimate the geomagnetic field that had been prevailing. The original geological applications of magnetic studies concerned igneous rocks. While magma is still molten crystals in the melt can move until they are locked in place as the rock cools. This enables NRM to be used to correlate between igneous rock deposits, and it is often used to determine the ages of volcanic lavas (i.e. Rolph, 1987; Tanguy *et al.*, 2003; Arrighi *et al.*, 2005).

A tangible NRM signal is not always left in the sediment. If certain conditions are met, preferential alignment of the magnetic axes of lithic grains can occur and be preserved. The alignment will correspond to the force lines of a persistent ambient magnetic field (Turner and Thompson 1981). Depositional remanent magnetisation (DRM) can be left when magnetically susceptible waterborne minerogenic sediments are de-watered and consolidated. If sediment grains are free to rotate in zero, or low flow conditions, they will attempt to align their effective magnetic axis with the prevailing magnetic field. They will then settle to form a deposit magnetised parallel to the ambient geomagnetic force field. This will often be observed as a trend to the long axis in a majority of the grains, but the magnetic axes may not always correspond to the morphological axes of all the grains. The effective magnetic grain size of individual sediment particles is not dependent on the physical size of each sediment grain but on the amount of magnetically susceptible minerals present in each grain.

The proportion of magnetically susceptible minerals present in the sediment will influence the NRM intensity preserved, and the degree of smoothing that is displayed by the data. Creer (1981) states that the recorded signal is subjected to a degree of inherent smoothing that is influenced by:

- Post-depositional grain rotation and compaction.
- Chemical changes.
- Possible bacterial action.

As more sediment accumulates above each layer, or it is de-watered, the pore space is reduced and increasing friction between the grains will eventually lock the magnetised particles in place. As sediment accumulates upwards, a stratigraphic sequence of magnetic layers is created that will carry a record of the changes in the Earth's magnetic field through time. This record will be preserved as long as the grains are not 'liberated' and realign themselves. Even if the grains are locked, the intensity component of the NRM is not acquired instantaneously, and Austin and Lowe (1989) take the view that in lacustrine environments magnetic locking may take from a few days to several hundred years after deposition. The physical lock-in period will be influenced by the sediment morphology, grain size and other environmental factors. Stockhausen (1998) proposed that changes in sedimentation rates will be reflected in lock-in times because of the time required for a sufficient weight of sediment build up to trap the underlying grains. Therefore, in some environments an unknown time lag may exist between sediment deposition and lock-in. Batt (1999) expresses concern that this uncertainty is a potential problem when dating sediments using palaeomagnetism. However, a recent experimental study using marine sediments and revisable magnetic fields has indicated that an existing magnetic alignment in mobile sediments can respond to a change in the ambient magnetic field in a matter of hours (Katari *et al.*, 2000). This study also found that under the experimental conditions bioturbation had a limited effect on NMR mean alignment. Katari *et al.* (2000) found that, below the surface, bioturbation only reduced the vector intensity, and the pre-existing mean magnetic vector direction was preserved.

5.1.4. Palaeomagnetic dating and salt-marsh environments. In summary, for palaeomagnetic dating to produce satisfactory results in salt-marsh sediments the key conditions are:

- Substantive magnetic susceptibility and correct grain size. The grains must be fine and contain magnetic minerals, typically haematite and magnetite.
- A post-depositional period of mobility. In sediments grains must be free to move and rotate long enough for magnetic alignment to occur. This usually means they are held in suspension at the sediment-water interface or in water filled voids.
- Once magnetically locked or aligned the material must remain *in situ*. There must have been no significant post-deposition disturbance of the sediments.

The primary question to be answered is 'To what extent will a tangible NRM be preserved in a salt-marsh environment?' This depositional environment may not meet the criteria outlined above for the conditions in a viable site for the use of palaeomagnetic dating. In an abyssal environment the sediment-water interface is often diffused, and grains some centimetres below the bed surface are still mobile enough to be influenced by the comparatively weak geomagnetic forces. It is a low energy environment so there will be zero, or very low, water flows. Therefore any alignment forces will be weak and post depositional disturbance will be minimal. In contrast, salt-marsh sediments are subject to cyclic flooding and exposure, over-marsh and sub-marsh flows and disturbance by plant growth (See Chapter 1). Some areas of a salt-marsh environment can be subjected to significant alternating tidal flows. These could be powerful enough to override any geomagnetic alignment of the sediment thus precluding the use of palaeomagnetic dating. Fortunately, the area of a salt marsh that is most likely to provide a good sea-level record is also the zone of the marsh that is subjected to the least tidal flow, i.e. the upper high marsh.

As described in Chapter 2 the favoured zone for sea-level studies in a salt marsh is the very highest marsh zone at the upper extreme of marine influence. Under normal conditions the high marsh zone is only flooded at the top of spring tides so it is only during these events that fine minerogenic sediment will be transported into the high marsh zone. The lowest tidal flows occur during the slack-water period at

the top and bottom of the tidal cycle. As the tide approaches high water, the incoming flood will rise over the marsh surface, slowing in velocity as it approaches the maximum height of that particular high tide. The material deposited at this point will be fine grained material because that will be all that will be left in the water column, and the deposition of sediment in the high marsh will be from a static, or near static, flow. Therefore, the only time the grains on the high marsh surface are held in suspension is during slack water. In the classical model of salt-marsh deposition (e.g., Pethick, 1984) there is a net onshore transport of grains. Once deposited on the high marsh the sediments normally remain in place because the outgoing flow does not accelerate above the re-entrainment velocity before the ebbing tide has exposed the high marsh surface (See Alan, 2000). This implies that a high salt-marsh environment may fulfil the 'low flow criteria' necessary for the grains not to be disturbed and realigned after deposition, but the question remains as to whether the grains are in suspension, and mobile, for a sufficient period for geomagnetic alignment to occur.

5.1.5. Calibration and master curves. To transform, or calibrate, the NRM data from the sediment sequence, or artefact, under examination into chronological dates reference data sets are needed to produce a master curve. The NRM data are then matched to the master curve and ages allocated to the samples. In archaeomagnetic dating it is usual to have a number of sub-samples from one artefact, and a single mean age is obtained for the artefact from the calibration of the values. In most sediment-based magnetic studies a data curve is produced from a sequence of contiguous samples taken from a sediment section or core. In this situation the data set is calibrated by being 'wiggle matched' to a master curve. Palaeomagnetic calibration curves must have an acceptable precision in the magnetic domains and have good age control. It is also desirable for the curve reference location to be within a radius of 500 km of the site (Prof. Don Tarling, personal communication) that is being dated, or some difference in the event chronology may be apparent (Schnepp and Lanos, 2006). However, there will still be synchronicity in the timing of the major SV features beyond that zone. Creer (1981) compared European and North American records of geomagnetic SV and concluded that there was 'a reasonably secure correlation of inclination variations across the North Atlantic'. In addition, agreement has been noted between the UK palaeomagnetic master curve (Turner and Thompson, 1981) and at sites in both the Tyrrhenian Sea off southern Italy (Iorio *et al.*, 2004) and Sweden (Snowball and Sandgren, 2002).

The most reliable form of calibration curves are those that are constructed from data sets derived from a series of fully documented field measurements. Fortunately, an instrumental record for declination, inclination and intensity exists for London (Figure 5.3d) that spans most of the last 400 years (Malin and Bullard, 1981), and a number of similar historic records exist, admittedly in more fragmented and abbreviated forms, for a number of other the European cities including Paris and Rome (Thompson, 1986; Alexandrescu *et al.*, 1996). In addition, for the very recent period it is now possible to access real-time data on-line from a world-wide network of observatories, and obtain the predictive output of different geomagnetic models (USGS, 2006). An example of this is Figure 5.3e. This declination curve is a prediction for declination changes at the location of the Viðarhólmi site in Iceland. It is constructed in part from the British Geological Survey (BGS) geomagnetic models for period 1600 to 1890 which were developed from the work of Barraclough (1974, 1978) and others. This prediction has then been amalgamated with information from the International Geomagnetic Reference Field (IGRF) and the Definitive Geomagnetic Reference Field (DGRF) using the GEOMag interface available via the USGS National Geomagnetism Program web site (USGS, 2006).

Beyond the temporal range and spatial coverage of instrumental records other reference data must be use. There are a number of archaeomagnetic calibration curves that have been produced by the repeated analysis of suitable artefacts of known ages. The 'standard' curve used in the UK today was originally published by Clark *et al.* (1988) (Figure 5.3a) and subsequently updated by Batt (1997, 1998). It covers most of the last 2900 yr, and was compiled from direct observations of the UK geomagnetic field over the last four centuries (Malin and Bullard, 1981), combined with over 100 measurements from independently dated archaeological features (See English Heritage, 2006). The vectors were all adjusted to Meriden in Warwickshire (52.43°N, 1.62°W) before the construction of the data set to remove spatial variation affects. This data set is being expanded as part of ongoing work to improve the coverage (English Heritage, 2006). Outside the UK there are now a number of European (i.e. France, Bucur, 1994; Hungary, Márton, 1996; Germany, Schnepf and Pucher, 2000; Bulgaria, Kovacheva *et al.*, 1998; Italy, Gallet *et al.*, 2002) and American (La Belle and Eighmy, 1997; Bowles *et al.*, 2002; Lengyel and Eighmy, 2002) archaeomagnetic data sets.

The original UK SV master curve (Figure 5.3b) (Turner and Thompson, 1981) was compiled from 10 cores taken from Loch Lomond (Scotland), Windermere (N England) and Geilonydd (Wales). This data set was later extended back to the late Glacial using a palaeomagnetic record obtained from Llyn Gwernan, North Wales (Austin and Lowe, 1989). In the last decade, fuelled in some way by the rise of the 'multi-proxy approach' in palaeoenvironmental and palaeoclimate research, there has been a resurgence of interest in magnetic records and a number of studies have produced well-dated palaeomagnetic data sets.

Several lake-based studies in Europe have used varves to improve the age control of their data. In Germany, Stockhausen (1998) used varves to help date 13000 yr of SV records from three maar lakes, and a study in Italy by Brandt *et al.* (1999) used a combination of varve counting, AMS ^{14}C dates and tephra horizons to constrain palaeosecular variations during the Late Pleistocene and Holocene. In Fennoscandia recent work has cross-dated past SV events with varve chronologies in Sweden (Snowball and Sandgren 2002) and Finland (Saarinen 1999; Ojala and Saarinen 2002). This palaeomagnetic chronology from Finland (Figure 5.3c) was later used by Kotilainen *et al.* (2000) to date sediments in the Baltic Gotland Deep.

The precision and accuracy of the palaeomagnetic and archaeomagnetic dating method is very dependent upon the quality of the master-curve chronology used as a calibration tool. The age control of the magnetic data in archaeomagnetic reference curves are a combination of ^{14}C dating, archaeological provenance dates and contemporary documented reports. In many cases there may be two or more independent age estimates, or the date will be constrained and bracketed by 'prior events'. The present UK archaeomagnetic reference curve developed from Clarke *et al.* (1988) is considered to have a practical limit of around 50 years on the maximum resolution of dates at the 95 % confidence level (English Heritage, 2006). The work of Batt (1997,1998) has refined this record, and gone some way to quantifying the uncertainties attached to this master chronology.

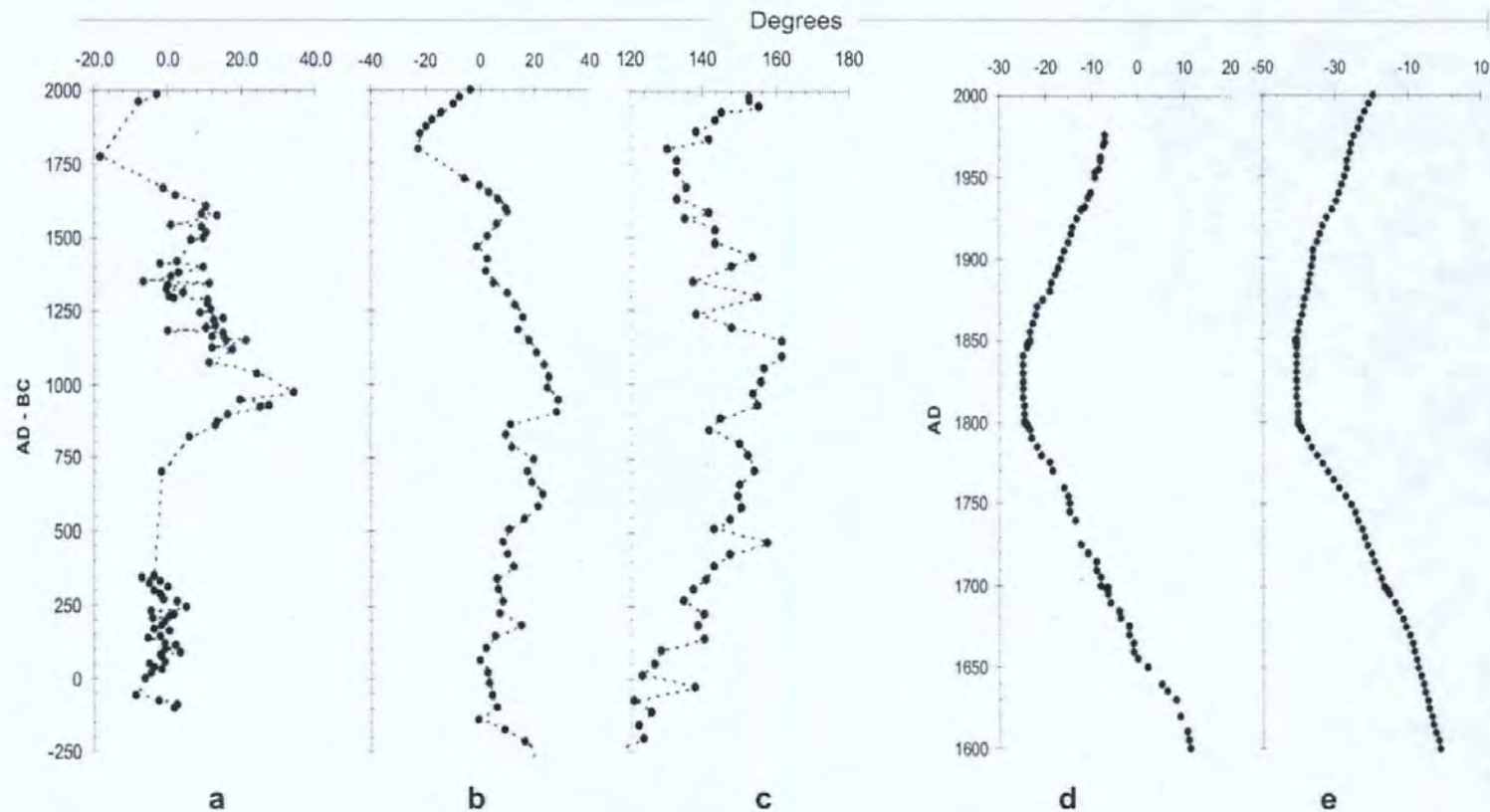


Figure 5.3. Five examples of declination reference curves. a) The UK archaeomagnetic declination record published by Clark *et al.* (1988); b) The UK master curve of Turner and Thompson (1981); c) Finish varved lake record published by Ojala and Saarinen (2002); d) Observed declination at London since 1570 compiled by Malin and Bullard (1981); e) Modelled composite declination curve for Viðarhólmi, Western Iceland from GEOMag (2006). See text for explanation (Section 5.1.5).

The UK sediment-based palaeomagnetic master curve chronology is heavily reliant on ^{14}C dates produced from the analysis of bulk sediments, and in the original form published by Thompson and Turner (1981) there was no age-uncertainty attached to it. An appreciation of the potential errors involved is important when using data sets that pre-date the use of ^{14}C AMS dating to calibrate palaeomagnetic data. During some time periods the modern generation of calibration programs and calibration curves can produce different dates for ^{14}C dates when compared to the calibration used in the 1970s and 1980s. Of the original 30 ^{14}C dates used by Turner and Thompson (1981) to construct their UK master-curve only 19 were later accepted as reliable due to reversals and inconsistencies (Saarinen, 1999). The uncalibrated ^{14}C age error of the Turner and Thompson (1981) ^{14}C dates was given as in the range of ± 55 to ± 330 ^{14}C yr., with a mean of ± 96 ^{14}C yr. To estimate what uncertainty should be attached to the UK master curve chronology some of the raw ^{14}C dates that were published in 1981 were calibrated using CALIB 5.0 (Stuiver *et al.*, 2005) and the IntCAL 04 calibration curve (Reimer *et al.*, 2004). Table 5.2 presents the results of calibrating eight of the younger Turner and Thompson (1981) ^{14}C dates.

The type of organic carbon sample available can change the precision of the dates obtained. A number of studies have commented on the lack of precision that is often unavoidable when using bulk sediments for samples. Age differences of > 2000 yr have been found when the AMS dates obtained on individual macrofossils are compared with dates from contemporaneous bulk sediment ^{14}C dates (See Snyder *et al.*, 1994; Barnekow *et al.*, 1998; Björk *et al.*, 1998). Saarinen (1999) points out that this can introduce a significant stratigraphic error to the final palaeomagnetic chronology. If a sedimentation rate of 1 mm yr^{-1} is assumed then a 10 cm thick sample potentially degrades the precision of an un-calibrated ^{14}C date by ± 50 yr, and this uncertainty would then be propagated via the calibration process adding potentially an extra >120 yr to the range between the upper and lower Cal BP dates.

Turner and Thompson (1981) Site	Lab sample code	Thickness of core sample (cm)	¹⁴ C yr BP	Turner and Thompson (1981) yr Cal BP	Calib 05 2 σ age range yr Cal BP	Relative probability	Median age: yr Cal BP
Lomond	GU 0.85-0.99	14	231 $\pm$ 55	315	133 - 228	0.35	226
Lomond	GU 0.17-0.27	10	643 $\pm$ 52	600	544 - 673	1.0	606
Lomond	GU 1.4-1.54	14	1838 $\pm$ 59	1760	1614 - 1896	1.0	1773
Windermere	SRR 0.91-1.11	20	1930 $\pm$ 120	1870	1565 - 2152	0.997	1878
Geirionydd	SRR 1.76-1.96	20	2670 $\pm$ 60	2850	2712 - 2897	0.972	2790
Lomond	GU 2.07-2.35	28	2712 $\pm$ 78	2890	2713 - 3005	0.989	2830
Windermere	SRR 1.16-1.36	20	2680 $\pm$ 140	2855	2360 - 3082	0.978	2796
Geirionydd	SSR 2.25-2.45	20	3025 $\pm$ 60	3295	3061 - 3375	0.99	3229

Table 5.2. Recalibration of eight ¹⁴C dates selected from those used for the UK master curve chronology of Turner and Thompson (1981). Calibration using Calib 5.0 (Stuiver *et al.*, 2005) and the IntCAL 04 calibration curve (Reimer *et al.*, 2004). Lab codes are GU = Glasgow University; SSR = Scottish Universities Research Reactor Centre.

The issues highlighted above suggest that a palaeomagnetic date on sediment deposited between 2000 yr and 3000 yr BP with a calibrated age of 2850 cal BP derived using the original Turner and Thompson (1981) UK master curve could in fact be >500 yr younger when all the potential uncertainties are incorporated. This may go some way to explain non-systematic age differences observed between features in the Snowball and Sandgren (2002) Swedish record and the UK master-curve of Turner and Thompson (1981). The Swedish study found that the sequence of palaeomagnetic features was similar in both records, but there was some increasing deviation of >500 yr with the timing after 3500 cal BP. This supports the proposal that that when the primary chronology of a PSV master-curve has been constructed using ¹⁴C analysis of bulk sediment the subsequent reference curve may produce an overestimate of age when compared to a SV record that is dated by a more robust incremental chronology (e.g., varves).

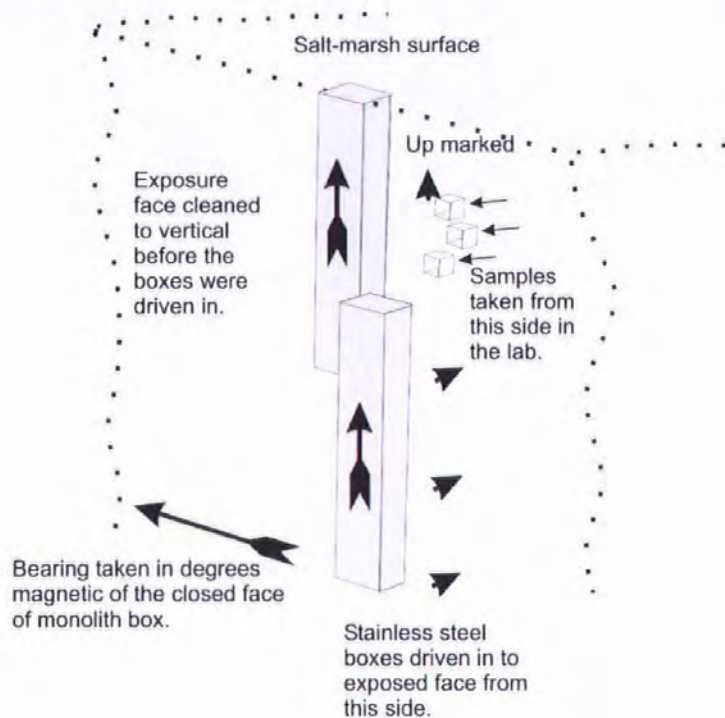
A further factor that must be considered when comparing different sets of palaeomagnetic data is that the sediment sequences used to construct chronologies may not have been oriented to azimuth. In these circumstances the absolute range and direction of the declination data is lost and the data is read as relative to the sequence mean. The sequence and timing of excursions and deviations in the records will be correct, but the range and absolute values of the declination recorded are not directly comparable. In all three of the records discussed here derived from lake sediments (UK - Turner and Thompson, 1981; Finland - Saarinen 1999 and Ojala and Saarinen 2002; Sweden - Snowball and Sandgren 2002) the declination data were published as 'relative to mean'. In contrast, the UK archaeomagnetic calibration curves (e.g. Clarke *et al.*, 1988) contain a 'real', absolute, record of the past declination values that would have been recorded in Meriden, Warwickshire, at specific times during the last three millennia.

5.2. Investigation of palaeomagnetic dating

5.2.1. Methodology. The application of palaeomagnetic dating was investigated at all three sites. Only one sequence was analysed from the Icelandic site, but to check the repeatability of the initial result from the Taf Estuary site (Taf-02) a replicate section (Taf-03) was obtained in 2003 and analysed. The 2003 pit was dug at the same ground surface elevation, 10 m west of the 2002 pit. In the case of the Arne Peninsula site a duplicate (Arne-04) monolith, cut abutting the location of the first monolith, was analysed to confirm the results from the 2003 samples (Arne-03). The sediment monoliths were orientated to azimuth (Figure 5.4a), and the sampling method was based on that used by Ellis and Brown (1998). In the laboratory sequential overlapping samples were taken from the sediment monoliths in aligned standard 6 cm³ plastic palaeomagnetic sample boxes. To reduce matrix disturbance the surface was incised with a stainless steel blade before the plastic boxes were pressed into the sediment blocks. As shown in Figure 5.4b the sampling track was along the mid line of the monolith, and the faces of the boxes marked to preserve the orientation noted in the field.

The NRM declination, inclination and intensity values were determined on the individual samples at the Southampton Oceanographic Centre (SOC) using a 2-G Enterprises cryogenic magnetometer controlled by custom software. Each sample was subjected to alternating field (AF) demagnetization using an in-line static 3-axis AF demagnetization system at a succession of peak fields up to 60 milliTesla (mT). After the NRM analysis was completed, the volumetric low-field magnetic susceptibility (K) was measured on the samples in the University of Plymouth Physical Geography Laboratory using a Bartington Instruments MS2 meter coupled to a Bartington MS2B dual frequency sensor and controlled by MULTISUS V2.0 software.

Some screening and refining of the raw palaeomagnetic data was needed before they could be used. The first task was to evaluate the robustness of the raw NRM vector data. After each of the demagnetization steps the NRM vectors and intensity value were determined in each sample. Typically, if a sample is carrying a strong stable component there should be a smooth and progressive decay in the intensity values without any reversals. Ideally there will be a common directional trend evident. This is demonstrated by the examples shown in Figure 5.5 and Figure 5.6a. The shape of these demagnetization curves is directly related the stability of the NRM in the samples.



a



b

Figure 5.4. The magnetic sample orientation. (a) The method of orienting the monolith and the samples. (b) The individual plastic sample boxes. Arrows indicate 'sample up'.

This in turn is influenced by the intensity component of the NRM. The NRM intensity and the directional vectors start to stabilise after being demagnetised at 10mT. This indicates that the viscous component is weak, and there is a significant stable NRM present after demagnetization at 20mT - 60mT. The orthogonal vector component plots for these three samples from the Icelandic section show how a linear trend in the declination and inclination vectors can be defined when the NRM signal is reasonably stable, and of a sufficiently high intensity. In contrast, the effect of low intensity on the stability of the NRM can be seen in Figure 5.6b and in Figure 5.7. In these latter two samples from the Arne the intensity reversals and the chaotic vector directions are indicative of very weak or non-existent stable NRM and non-stable viscous components. This association of chaotic vectors with low intensity is evident on inspection of the data from these six samples presented in Table 5.3.

When coherent remanence values were produced, the system software was used to identify the characteristic NRM (Ch-RM) vectors using principal component analysis (PCA). This was carried out on sub-group of up to five of the data points selected from the demagnetization curve as being stable. It is considered desirable for the vectors to be 'anchored', as in Figure 5.5, so the PCA was used to construct a best-fit line that followed the trajectory of the selected data points, and also intersected the origin. To evaluate the uncertainty associated with the Ch-RM vectors the maximum angular deviation (MAD) was calculated in conjunction with the PCA. The lower the MAD the more reliable the PCA result is assumed to be, but any results with MAD values above 15° are regarded as unreliable (See Butler, 1992; Channell, 2006). It should be noted that English Heritage in their 2006 archaeomagnetic dating guide recommends all samples with MAD values > 3° to be treated with caution (English Heritage, 2006). Therefore, any data associated with > 3° MAD values were treated as potentially unreliable, and all the samples that did not have any stable NRM components after being demagnetized were rejected at this stage (Figure 5.7).

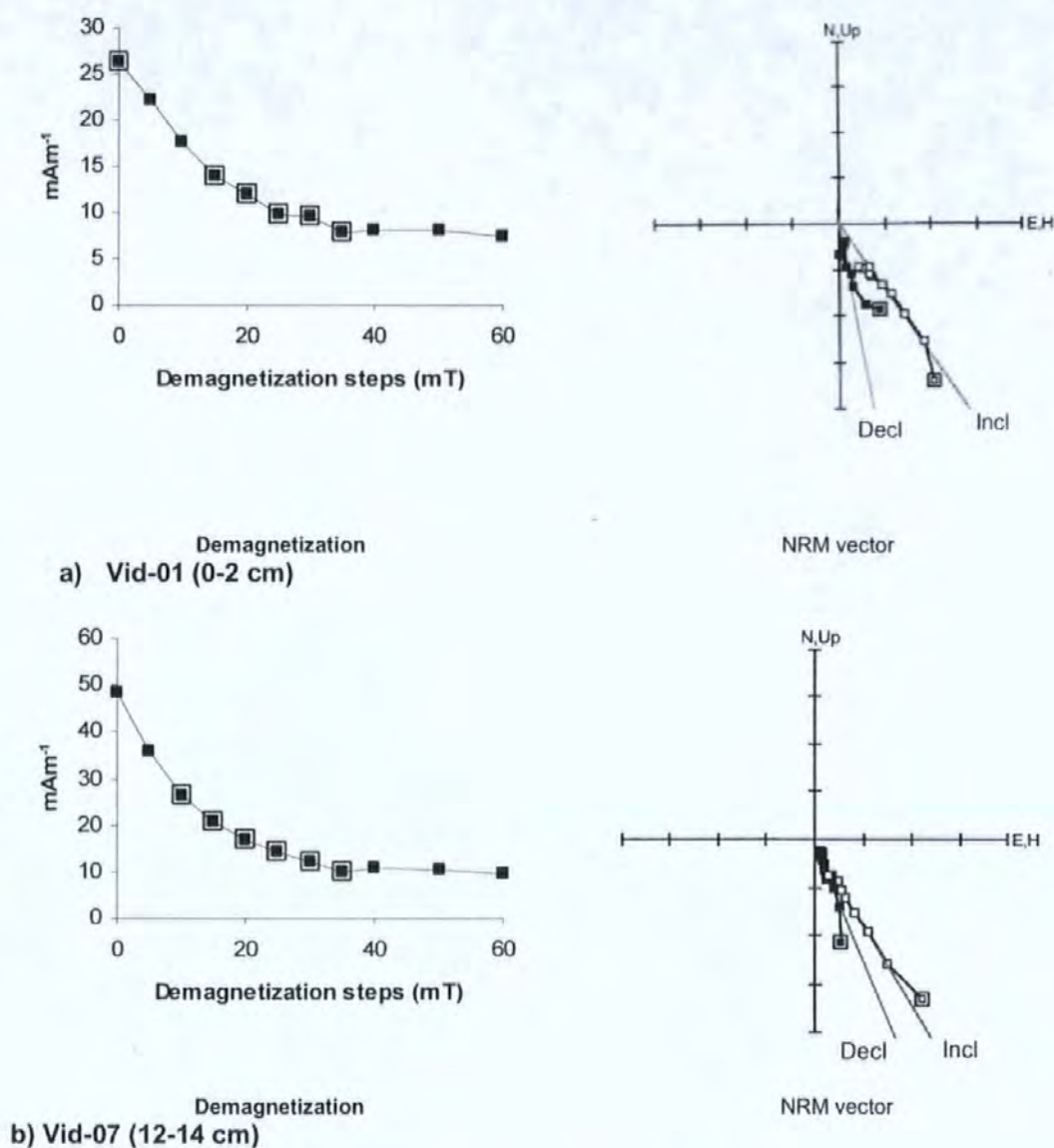


Figure 5.5. Demagnetization and NRM vector plots for samples Vid-01 (a) and Vid-07 (b). Note differing scales in the demagnetization plots. Scale is arbitrary in the vector plots. Declination vector is shown relative to 'N, Up' point. Inclination vector is shown relative to 'E, H' point. The values selected for PCA are boxed in the demagnetization plots. PCA results are (a) Vid-01 (0-2 cm) Declination (Decl) 164.4°; Inclination (Incl) 52.0°, MAD 2.5° and (b) Vid-07 (12-14 cm), Decl. 161.4°, Incl. 61.5°, MAD 1.7°. The two demagnetization plots presented here show the characteristic smooth decay curve associated with samples that contain a weak viscous component and a significant stable component. The presence of a significant stable component, and the robustness of these data, is confirmed by the low PCA MAD value.

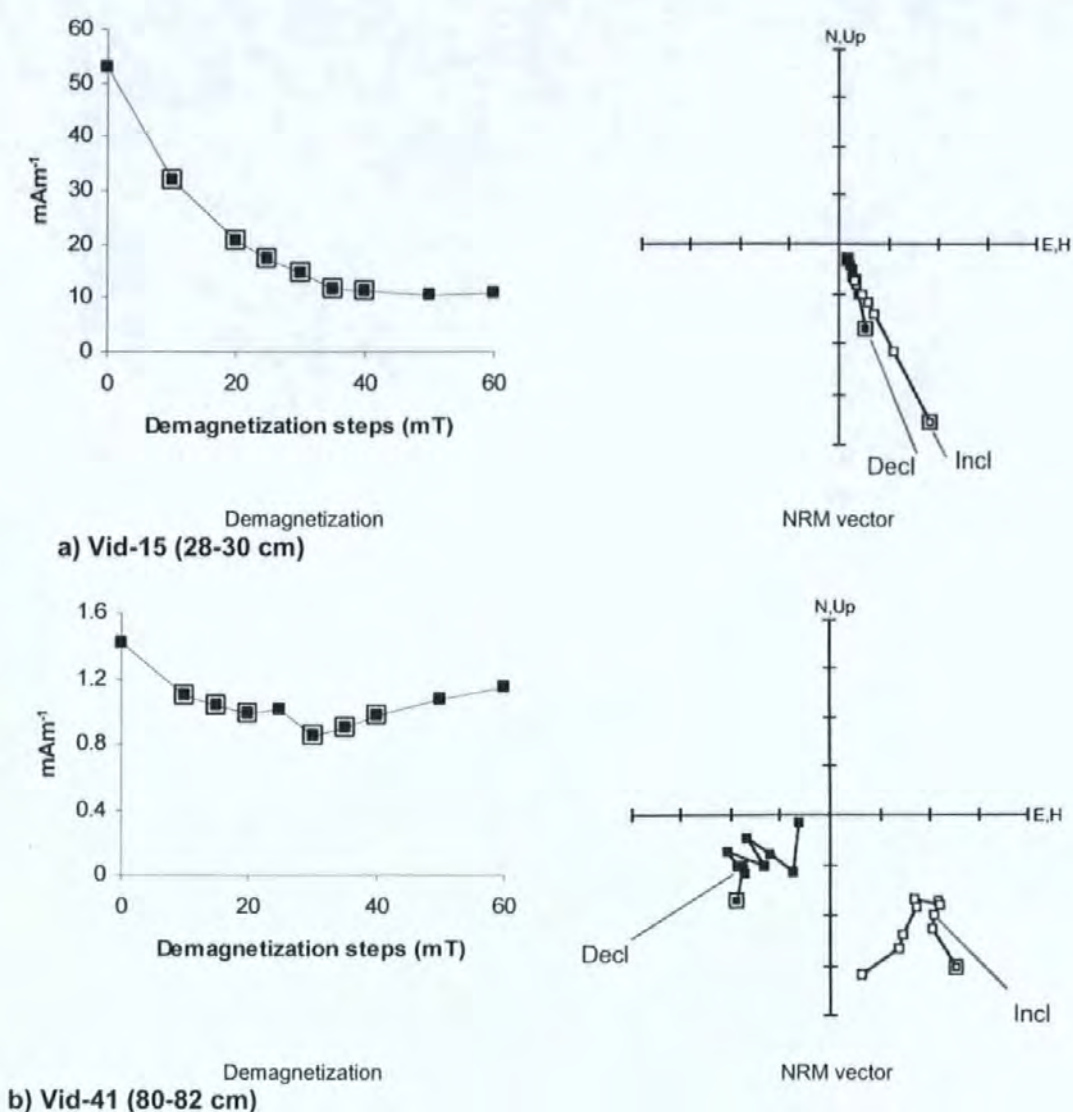


Figure 5.6. Demagnetization and NRM vector plots for samples Vid-15 (a) and Vid-41 (b). Note differing scales in the demagnetization plots. Scale is arbitrary in the vector plots. Declination vector is shown relative to 'N, Up' point. Inclination vector is shown relative to 'E, H' point. The values selected for PCA are boxed in the demagnetization plots. PCA results are (a) Vid-15 (28-30 cm) Declination (Decl) 156.7°, Inclination (Incl) 63.5°, MAD 1.5° and (b) Vid-41 (80-82 cm) Decl. 237.9°, Incl. 44.3°, MAD 4.2°. The plots for Vid -15 (a) show a strong stable NRM component and well defined vectors that pass through the origin. The robustness of these data is confirmed by the low PCA MAD value. This is in contrast to the plot from Vid-41 (b). In this sample the maximum NRM is > 2.0 mA⁻¹, and the associated plot has a poorly defined decay curve. This indicates the presence of a significant viscous component and a weak stable component, and is reflected by the higher MAD value from the PCA, and the detachment of the NRM vectors from the origin.

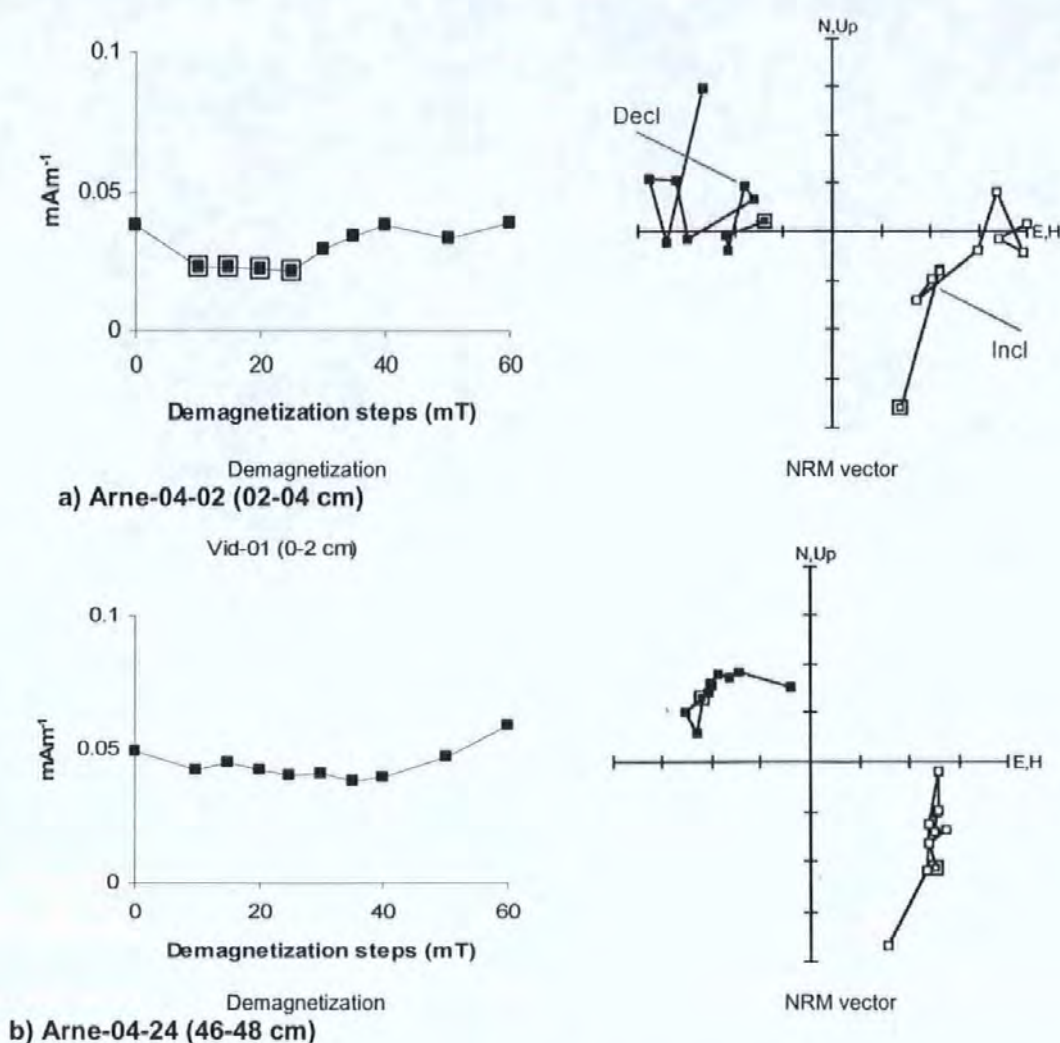


Figure 5.7. Demagnetization and NRM vector plots for samples Arne-04-02 (a) and Arne-04-24 (b). Note differing scales in the demagnetization plots. Scale is arbitrary in the vector plots. Declination vector is shown relative to 'N, Up' point. Inclination vector is shown relative to 'E, H' point. The values selected for PCA are boxed in the demagnetization plots. PCA results are (a) Arne-04-02 (02-04 cm) Declination (Decl) 278.0°, Inclination (Incl) 27.0°, MAD 16.3° and (b) Arne-04-24 (46-48 cm) no result. Both the above samples failed to meet the required criteria (See text). The total NRM intensity is $< 0.5 \text{ mAm}^{-1}$ in both samples, and this value is below the reliable operation limit of the magnetometer. PCA was attempted on some of these weak samples when a trend could be observed in the demagnetization plots. The results presented here for Arne-04-02 (a) are typical. The very high MAD value confirms that the principle NRM vectors produced are unreliable in samples with very low NRM levels. No PCA was attempted on Arne-04-24 (b). Samples that showed this type of reversal during demagnetization and very low total NRM intensities are all rejected.

Sample	Demagnetization (mT)	Declination (degree)	Inclination (degree)	Intensity (mAm ⁻¹)
Vid-01 (0-2 cm)	0	118.3	65.3	26.3
	5	149.8	60.1	22.1
	10	162.4	53.7	17.6
	15	163.0	50.7	14.0
	20	162.7	50.0	11.9
	25	165.7	52.1	9.79
	30	168.4	55.9	9.64
	35	165.4	54.9	7.79
	40	166.0	55.5	8.03
	50	159.2	53.1	8.1
	60	144.1	71.5	7.41
Vid-07 (12-14 cm)	0.0	165.7	56.1	48.2
	5	160.2	60.0	35.9
	10	159.2	60.4	26.4
	15	164.8	61.0	20.8
	20	163.9	62.5	16.7
	25	160.2	63.1	14.1
	30	158.1	61.8	12.0
	35	162.5	64.1	10.1
	40	162.6	67.6	10.7
	50	150.0	67.8	10.4
	60	149.1	70.8	9.59
Vid-15 (28-30 cm)	0.0	161.9	62.8	52.7
	10	158.6	63.0	32.0
	20	158.3	62.8	20.8
	25	153.7	63.9	17.3
	30	151.9	64.2	14.8
	35	155.0	65.4	11.7
	40	150.8	65.2	11.1
	50	146.6	63.8	10.5
	60	149.7	68.3	10.7
Vid-41 (80-82 cm)	0.0	227.2	50.1	1.42
	10	239.7	48.2	1.09
	15	236.1	43.9	1.03
	20	241.6	39.0	0.98
	25	250.2	39.7	1.01
	30	232.3	45.4	0.85
	35	254.2	46.7	0.9
	40	237.3	58.8	0.97
	50	213.8	62.9	1.07
	60	257.3	78.8	1.15
Arne-04-02 (2-4 cm)	0.0	277.5	68.8	0.0375
	10	267.7	19.8	0.0226
	15	259.9	20.9	0.0228
	20	298.0	25.8	0.0219
	25	292.8	39.2	0.0216
	30	266.9	7.9	0.0291
	35	288.5	-13.6	0.0336
	40	288.4	6.4	0.0381
	50	266.1	2.7	0.0332
	60	317.8	-2.1	0.0387
Arne-02-24 (46-48 cm)	0.0	300.1	40.0	0.0492
	10	284.3	34.5	0.0427
	15	292.1	26.9	0.0453
	20	304.2	29.7	0.0425
	25	307.9	21.9	0.0403
	30	308.1	20.7	0.0408
	35	313.9	4.1	0.0382
	40	316.8	27.9	0.0397
	50	321.9	42.7	0.0474
	60	346.0	66.7	0.0590

Table 5.3. Demagnetization steps and NRM results for six selected samples. Vector plots associated with these data are shown in Figure 5.5, Figure 5.6 and Figure 5.7. Values in **bold** were selected for the PCA.

Once the raw data had been screened the declination values were rotated to align the box face ('sample north') that the raw magnetometer results were referenced to, with the geographical 'site north'. For example in the case of the Icelandic site this meant the addition of 169.75° to the declination values. This was calculated from the observed magnetic bearing of the monolith of 299° and the declination for the site in 2003 of 18.75° as shown in Figure 5.8. After rotation the declination values were converted into $\pm 180^\circ$ notation.

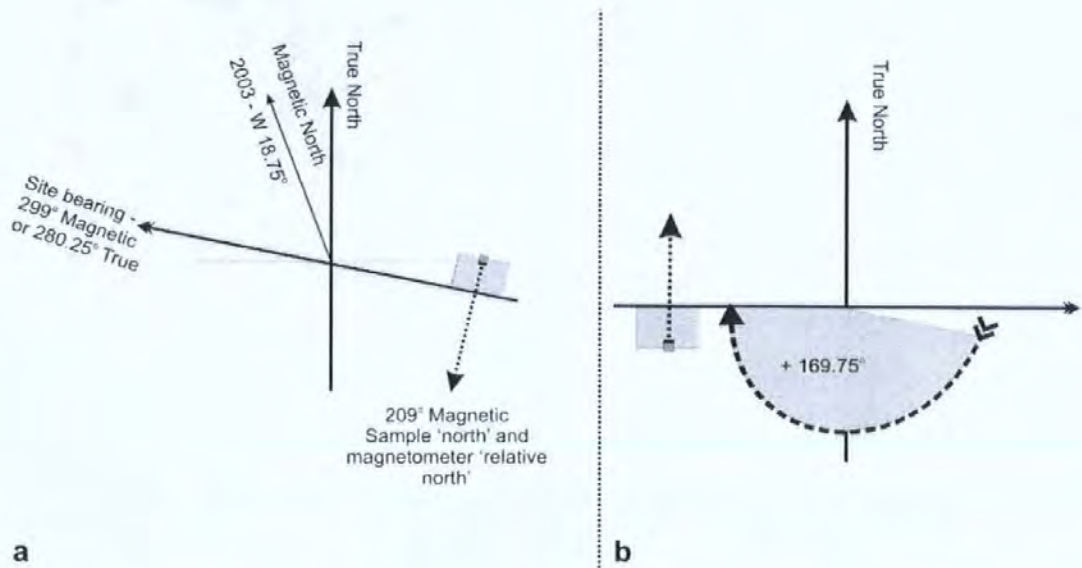


Figure 5.8. Schematic diagrams showing the method used to rotate the declination data to True North. Magnetic bearing and correction value shown here is that used for the Icelandic Viðarhólmi 2003 sequence. Panel a: The sediment monolith is represented by the larger grey rectangle. The plastic sample box is shown inserted into the open face of the monolith box. The magnetometer determines the NRM declination vectors relative to the open side of the plastic sample box; i.e. the face that receives the lid. Therefore the magnetic bearing for a zero vector or the 'sample north' is the site bearing less 90° . Panel b: To align the magnetometer results with True North a clockwise rotation must be applied. This is calculated in two steps:

1. $360^\circ - 280.25^\circ = 79.75^\circ$ - This rotates the monolith face bearing to True North.
2. $79.75^\circ + 90^\circ = 169.75^\circ$ - This rotates the monolith face bearing to True East and 'sample north' to True North.

The next stage in evaluating the magnetic data was to determine if the absolute measured values, and the variability in the declination and inclination records, could have been produced by the known history of geomagnetic SV in the North Atlantic region of north-western Europe during the late Holocene. To facilitate this task, descriptive statistics for three regional late Holocene SV records were calculated (Table 5.1). These data indicated that a range of variability of $>80^\circ$ could be expected in the declination data and $>20^\circ$ in the inclination data. Table 5.3 illustrates how the absolute values are dependent on geographic location, but the range of variability in the data is not dissimilar between sites.

	Curve 1 – UK			
	40 - 1000 yr BP		40 - 4000 yr BP	
	Declination (Degrees)	Inclination (Degrees)	Declination (Degrees)	Inclination (Degrees)
Maximum (Max)	25.1	75	50.9	75.2
Minimum (Min)	-24.0	56.9	-24.0	56.9
RV	49.1	18.1	74.9	18.3
Mean	3.8	64.3	19.1	68.8
SD	14.7	5.8	17.4	4.7
	Curve 2 – Finland		Curve 3 – Sweden	
	20 - 4000 yr BP		400 - 4000 yr BP	
	Declination (Degrees)	Inclination (Degrees)	Declination (Degrees)	Inclination (Degrees)
Max	111.7	78.6	88.6	83.1
Min	48.1	63.4	13.4	75.3
RV	63.6	15.2	75.2	7.7
Mean	88.6	70.6	47.9	79.7
SD	12.2	3.7	16.5	2.4

Table 5.4. Descriptive statistics calculated for three Northern European and Scandinavian palaeomagnetic 'master curves' derived from sedimentary records. RV = range of variability and SD = standard deviation. Palaeomagnetic data from (1) the Turner and Thompson (1981) UK palaeomagnetic master curve (Values used are rotated to 52.43° N 1.62° W (Meriden, UK)), (2) varved lake record from Finland, 61.8° N 24.4° E (Ojala and Saarinen, (2002) and (3) varved lake record from Sweden 64.0° N 19.6° E (Snowball and Sandgren, 2002).

5.3. Palaeomagnetic results

In the next three sections the magnetic data for each site are presented, plotted against depth. The declination data is also shown as rose-style radial plots produced using WindRose®, a software program available free at <http://www.enviroware.com> designed for plotting wind directions. The full palaeomagnetic data tables for the five sample sets are contained in Appendix 2.

5.3.1. The Taf magnetic results. The intensity signal preserved in some of the Taf samples is too low for the reliable measurement of the direction vectors. This is very evident with the samples from above 20 cm in both of the Taf sample sets, and, apart from the sample from 10 cm in the Taf-02 sequence, these are all excluded. However, the analysis did produced 40 coherent NRM determinations from the Taf-02 51 samples (Figure 5.9), and a similar number from the replicate Taf-03 section (Figure 5.10).

The declination and inclination data from the two Taf sequences are very variable, and in both instances there is a wide spread of values around the mean (Table 5.5). The absolute ranges of the NRM vector data from the respective Taf-02 and Taf-03 sequences are 86.5° and 52.2° for declination and 34° and 37.5° for inclination. When the means are examined the inclination measured in the two sequences is very similar, but when the declination values are compared the Taf-03 samples have a lower mean and a smaller range of variation. This is reflected by the SD values in Table 5.5.

Taf-02 n = 40	Declination (Degrees)	Inclination (Degrees)	Intensity (mA m ⁻¹)	MAD (Degrees)	K (SI)
Max	102.00	79.80	1.13	18.66	11.20
Min	15.50	45.80	0.34	1.30	1.20
RV	86.5	34.0	0.79	17.36	10.0
Mean	56.00	59.48	0.59	7.13	7.14
SD	20.37	9.46	0.22	4.06	2.22
Taf-03 n = 37					
Max	79.60	75.90	2.84	20.90	10.32
Min	27.40	38.40	0.26	1.00	3.80
RV	52.2	37.5	2.58	19.9	6.52
Mean	50.83	58.53	0.89	7.25	7.16
SD	13.65	9.42	0.62	5.60	1.79

Table 5.5. Descriptive statistics for the Taf 2002 and Taf 2003 magnetic data sets. RV = range of variability and SD = standard deviation.

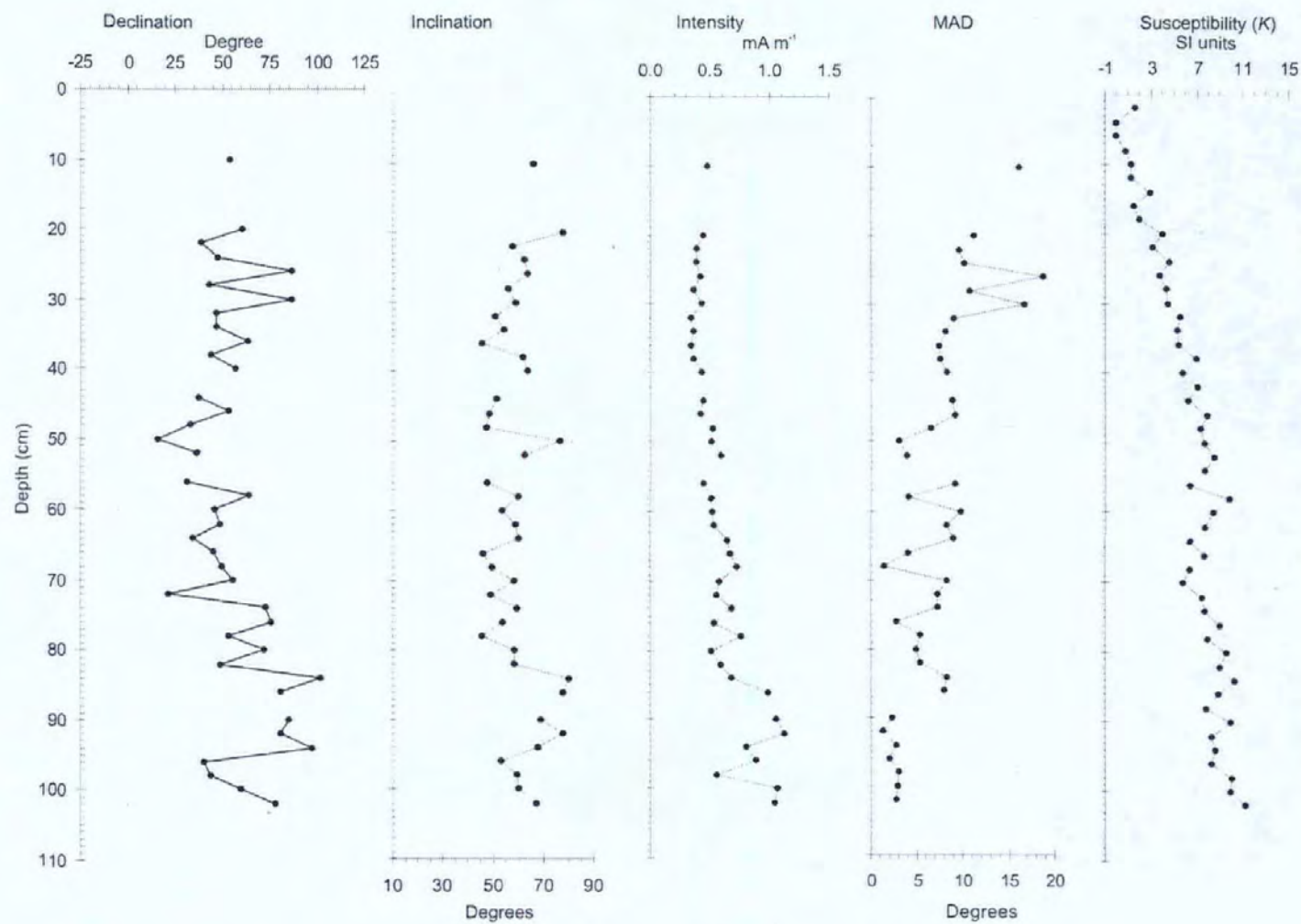


Figure 5.9. Taf-02 NRM and magnetic susceptibility results.

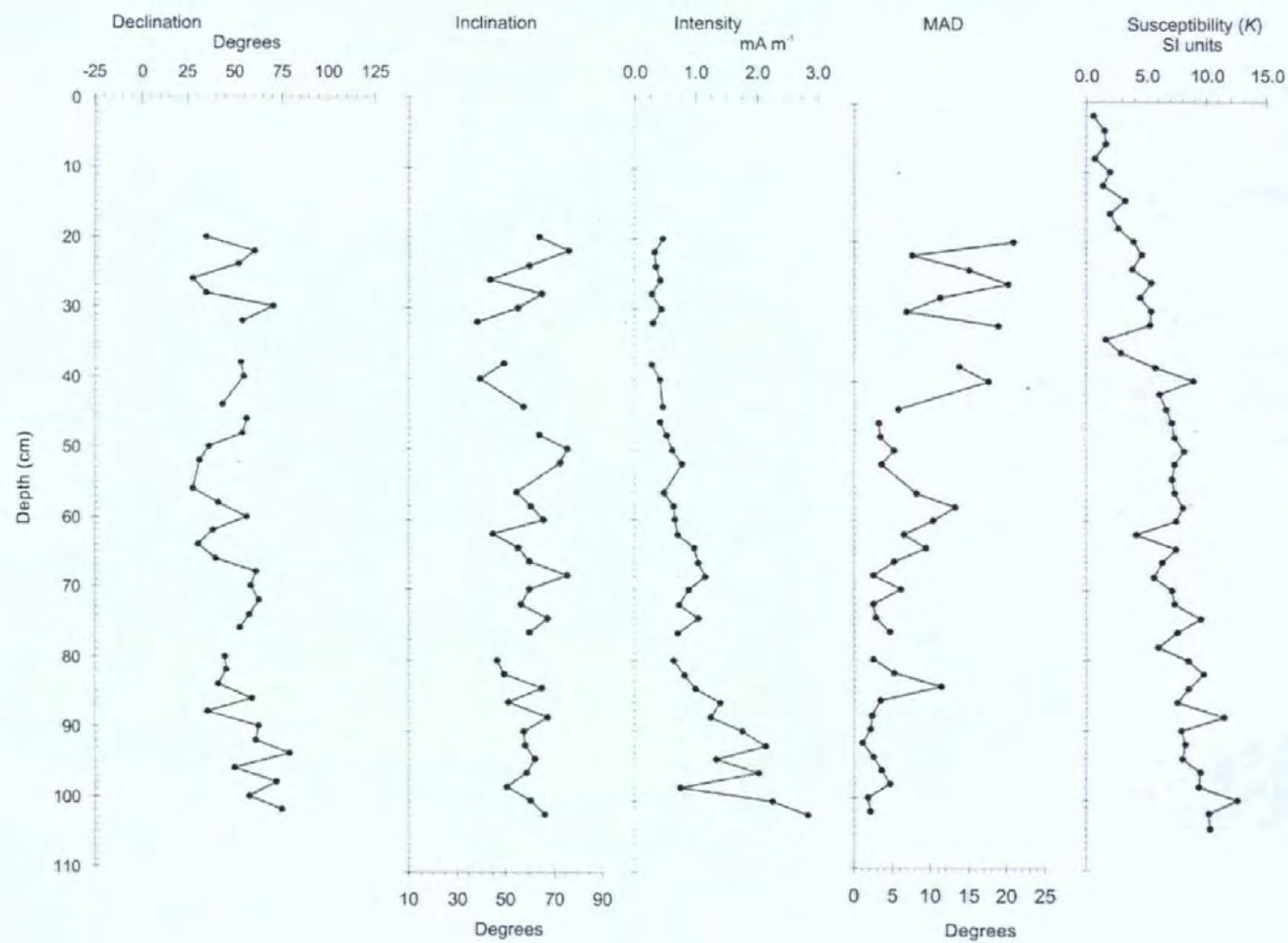
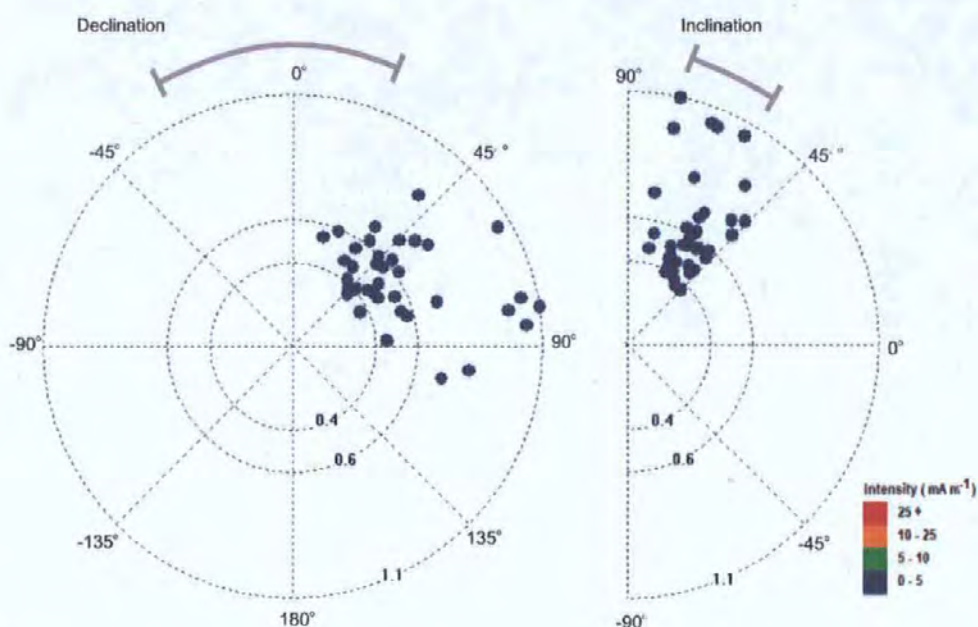


Figure 5.10. Taf-03 NRM and magnetic susceptibility results.

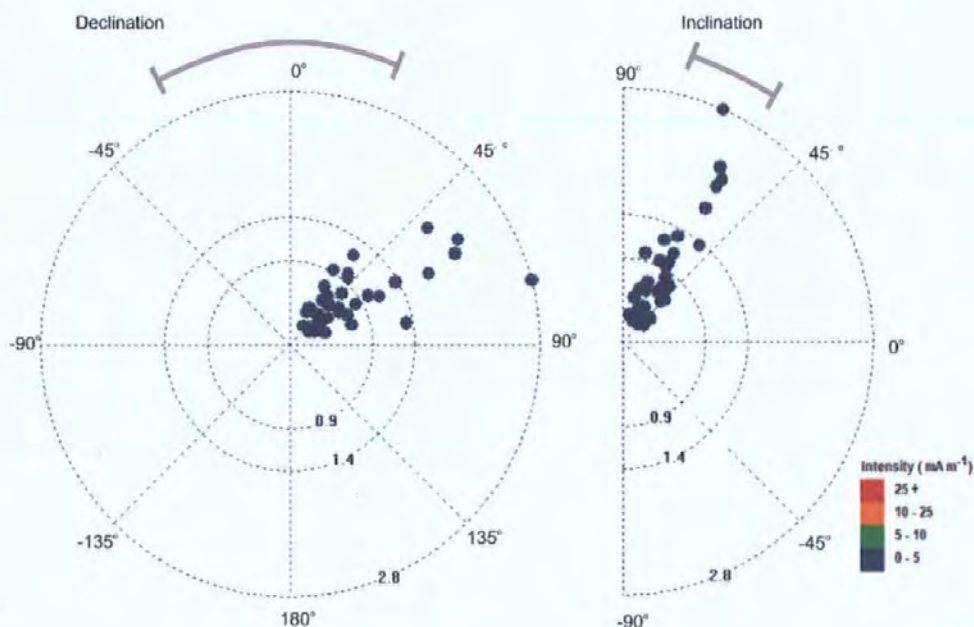
The relative declination RV values are not excessive, 86.5° (Taf-02) and 52.2° (Taf-03), but many of the Taf inclination values, and most of the declination results, are outside the range of declination and inclination values expected for the site (Figure 5.10). The mean declination of both sections is some 30° east of the expected range and the inclination variability is larger than that calculated for the three Holocene SV records examined in Table 5.3. As shown in Figure 5.11, both the inclination means are approximately 10° lower than the inclination expected for this geographic location. The mean intensity values measured are $<3 \text{ mA m}^{-1}$, with an overall decline toward the surface in both the Taf-02 and Taf-03 sequences. This decline toward the surface is also apparent in the K data. These values decrease from 11.2 SI 102 cm (Taf-02) and 10.3 SI (Taf-03) to near zero at the surface.

Data analysis. A Pearson product moment correlation matrix was constructed (Table 5.6 and Table 5.7) for each sequence. The Taf grain size and organic carbon data (Chapter 2) were included in this analysis. The Pearson analysis for the Taf-02 data (Table 5.6) suggests a relationship between intensity and K ($r = 0.616$; $p = 0.00$), and shows significant correlation for both of these variables with the MAD values. In addition, a strong significant correlation is found between intensity and clay ($r = 0.771$; $p = 0.00$) and K and organic carbon ($r = -0.786$; $p = 0.00$). Similar correlations between intensity, K , clay and the MAD values are found in the Taf-03 data but at slightly lower significances than those found in the Taf-02 data (Table 5.7).

To test further the relationship between intensity and K , the three grain size fractions and organic carbon % multiple regression analysis was used. In both the Taf data sets clay was found to be the best predictor for intensity (Taf-02, clay r^2 (adj) 0.58; Taf-03, clay r^2 (adj) 0.38). If the predictability of the K value was combined in the Taf-03 analysis r^2 (adj) 0.50 was achieved. None of the other variables were found to be significant as a predictor for intensity.



Taf-02



Taf-03

Figure 5.11. Radial plot of the Taf 2002 and 2003 NRM vector data. The concentric arcs show the intensity (mA m^{-1}) at intervals of 33%, 50% and 100% of the maximum value. The thick grey arcs show the estimated range of natural variability for geomagnetic SV during the last 4000 yr in South Wales. This range was estimated using the UK master curve of Turner and Thompson (1981).

	dec	inc	int	MAD	K	OrgC.	Sand	Silt
inc	0.469 0.002							
int	0.396 0.011	0.368 0.019						
MAD	0.044 0.786	-0.005 0.976	-0.589 0.000					
K	0.241 0.134	0.133 0.415	0.616 0.000	-0.748 0.000				
OrgC	-0.065 0.690	0.117 0.473	-0.382 0.015	0.612 0.000	-0.786 0.000			
Sand	0.067 0.681	-0.096 0.554	-0.396 0.011	0.379 0.016	-0.320 0.044	0.132 0.417		
Silt	-0.498 0.001	-0.285 0.075	-0.395 0.012	0.172 0.288	-0.378 0.016	0.273 0.089	-0.482 0.002	
Clay	0.460 0.003	0.385 0.014	0.771 0.000	-0.523 0.001	0.684 0.000	-0.405 0.010	-0.401 0.010	-0.610 0.000

Cell Contents: Pearson correlation
P-Value

Table 5.6. Pearson correlation matrix of the Taf-02 magnetic data and the associated grain size and organic carbon data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, K = magnetic susceptibility, OrgC = organic carbon %.

	dec	inc	int	MAD	K	OrgC.	Sand	Silt
inc	-0.046 0.789							
int	0.373 0.023	0.160 0.344						
MAD	-0.385 0.019	-0.355 0.031	-0.564 0.000					
K	0.301 0.071	-0.077 0.653	0.596 0.000	-0.494 0.002				
OrgC.	-0.158 0.350	0.081 0.633	-0.536 0.001	0.604 0.000	-0.692 0.000			
Sand	-0.098 0.562	-0.354 0.032	-0.327 0.048	0.405 0.013	-0.275 0.099	0.329 0.047		
Silt	-0.155 0.361	0.256 0.126	-0.272 0.103	0.032 0.852	-0.124 0.465	0.114 0.502	-0.548 0.000	
Clay	0.265 0.113	0.121 0.475	0.631 0.000	-0.471 0.003	0.423 0.009	-0.472 0.003	-0.521 0.001	-0.428 0.008

Contents: Pearson correlation (r value) n = 37
P-Value

Table 5.7. Pearson correlation matrix of the Taf-03 magnetic data and the associated grain size and organic carbon data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, K = magnetic susceptibility, OrgC = organic carbon %.

The Taf-03 magnetic analysis was designed to verify the Taf-02 data. An inspection of Figure 5.9, Figure 5.10 and Table 5.5 does indicate some level of agreement between the Taf data sets. In addition, there was some visual agreement between the overall trends of the NRM intensity data and the magnetic susceptibility (*K*) data. To test these observations, and evaluate the level of repeatability of the magnetic analysis correlations were sought between the two Taf data sets (Table 5.8). Very significant correlations were found between the pairs of intensity data ($r = 0.923$, $p = 0.000$) and the pairs of *K* data ($r = 0.738$, $p = 0.000$) but not between the pairs of vector data. The declination data did show weak positive correlation ($r = 0.363$, $p = 0.027$) but there was no significant relationship between the two sets of inclination data ($r = 0.162$, $p = 0.337$).

	02dec	02inc	02int	02MAD	02K	03dec	03inc	03int	03MAD
02inc	0.467 0.004								
02int	0.387 0.018	0.356 0.030							
02MAD	0.068 0.687	-0.018 0.914	-0.592 0.000						
02sus	0.254 0.130	0.205 0.223	0.654 0.000	-0.712 0.000					
03dec	0.363 0.027	0.016 0.926	0.295 0.076	-0.284 0.088	0.245 0.143				
03inc	-0.280 0.093	0.162 0.337	0.189 0.264	-0.218 0.195	0.027 0.875	-0.046 0.789			
03int	0.374 0.022	0.339 0.040	0.923 0.000	-0.587 0.000	0.667 0.000	0.373 0.023	0.160 0.344		
03MAD	-0.085 0.615	-0.105 0.535	-0.647 0.000	0.604 0.000	-0.600 0.000	-0.385 0.019	-0.355 0.031	-0.564 0.000	
03K	0.146 0.388	-0.023 0.894	0.528 0.001	-0.605 0.000	0.738 0.000	0.301 0.071	-0.077 0.653	0.596 0.000	-0.494 0.002
Contents: Pearson correlation (r value)					$n = 37$				
P-Value									

Table 5.8. Pearson correlation matrix of the Taf-02 and the Taf-03 magnetic data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, *K* = magnetic susceptibility, OrgC = organic carbon %.

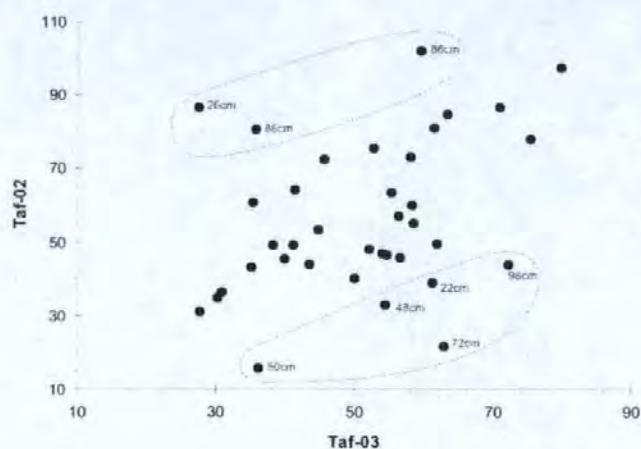


Figure 5.12. Biplot of the Taf-02 and Taf-03 declination data and the outliers removed.

Eight data points are identified as outliers in the declination data (Figure 5.12) of which six are also outlying in the inclination data. After these eight were removed the correlation analysis was repeated (Table 5.9). This time there is significant correlation between the pairs of declination data ($r = 0.746$, $P = 0.000$) and weak

correlation between the pairs of inclination data ($r = 0.335$, $P = 0.076$). There is some improvement to the correlations between the pairs of intensity data ($r = 0.937$, $P = 0.000$) and the pairs of K data ($r = 0.738$, $P = 0.000$). In addition, the correlation of the MAD values with both the intensity and K values is strengthened.

	03dec	03inc	03int	03MAD	03K	02dec	02inc	02int	02MAD
03inc	-0.110 0.569								
03int	0.450 0.014	0.321 0.089							
03MAD	-0.340 0.072	-0.276 0.148	-0.609 0.000						
03sus	0.279 0.143	-0.036 0.853	0.632 0.000	-0.506 0.005					
02dec	0.746 0.000	0.030 0.878	0.370 0.048	-0.308 0.104	0.322 0.089				
02inc	0.230 0.230	0.335 0.076	0.362 0.053	-0.112 0.563	-0.025 0.896	0.479 0.009			
02int	0.412 0.027	0.293 0.123	0.937 0.000	-0.694 0.000	0.588 0.001	0.402 0.031	0.357 0.057		
02MAD	-0.204 0.289	-0.183 0.342	-0.680 0.000	0.566 0.001	-0.582 0.001	-0.218 0.257	-0.079 0.684	-0.708 0.000	
02K	0.208 0.279	0.142 0.464	0.690 0.000	-0.579 0.001	0.738 0.000	0.330 0.080	0.138 0.474	0.680 0.000	-0.752 0.000
Contents: Pearson correlation (r value)					$n = 29$				
P-Value									

Table 5.9. Pearson correlation matrix of the Taf-02 and the Taf-03 magnetic data after removal of the outliers. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, K = magnetic susceptibility, OrgC = organic carbon %.

Taf data analysis: summary and evaluation. The structure apparent in the data, and the correlations between the two independent data sets, indicate that the magnetic analysis of the Taf sediment sequences has detected a tangible and, to some extent, reproducible NRM record. However, the lithology of the sediments is not conducive to magnetisation, and thus the measured NRM intensities were low in the majority of the samples. The high MAD values confirm that this has reduced the reliability of some of the PCA results. When the horizontal direction vector data is considered there are some issues with these data.

Although the range of change is not inconsistent with the variability expected in a late Holocene SV record from South Wales, the absolute mean value of the declination vectors is not aligned with the expected sector. The inclination angles are significantly depressed toward the horizontal in both sequences. This is taken to indicate some systematic gravitational post-depositional alignment of the platy grains during dewatering and subsequent compaction. There is excessive scatter in the Taf-02 inclination data. This, and the subsequent poor replication in the independent Taf-03 analysis, suggests that the absolute values of the inclination record are probably inadequate for palaeomagnetic dating.

An initial inspection of the declination data suggested that these were also of little value as a means of constructing a robust chronology. None of the data were in the expected sector of declination vectors for a late Holocene sequence from South Wales. This notwithstanding, the declination data are not chaotic. The radial plots (Figure 5.11) suggest that in both sequences the declination data have a systematic eastward bias of some 30° to 50° . Given the proximity of the monolith site (Chapter 2) to the Taf estuary channel this systematic bias is most likely the influence of regular over-marsh water flows during ebbing spring tides. Tidal conditions high enough for over-marsh flows to take place at the site would produce a flow with a strong east-west component.

Tidal alignment would not change significantly through time, and therefore is unlikely to be responsible for the short-term variability in the NRM data. The presence of this variability suggests that it is likely that there has been some modulation of the local tidal flow alignment by the geomagnetic SV declination component, and the resulting vectors are an amalgamation of the two processes. This means that although the absolute alignment of the magnetic grains in the Taf sediments can not be explained solely by geomagnetic forces, the relative variation in the declination record does

reflect the SV history and may offer some potential as a chronological tool. This aspect will be explored further in section 5.4.

5.3.2. The Arne magnetic analysis results. A total of 59 samples from the two Arne monoliths produced NRM values but these results (Figure 5.13) were chaotic with excessive scatter in the directional data. Many of the samples did not produce vector plots that were anchored to the origin and a high proportion were discarded at this stage. The Arne-04 analysis was abandoned on the magnetometer after 20 samples because it was obviously not replicating the Arne-03 results and was producing meaningless NRM vector data.

The variability in the declination values (Table 5.10) exceeded 340°, and the inclination data contained some values that could not have been produced at this site by the geomagnetic field at any time during the Holocene. The NRM intensity levels were mainly below 1 mA m⁻¹, and the *K* levels measured in the majority of the samples were very low. The only significant structure evident in the magnetic data was a positive excursion in the *K* record between 40 cm and 50 cm. This was detected in both the Arne-03 and Arne-04 sequences, and it is assumed to be the product of some local pulse of magnetically susceptible sediment.

Arne-03 n = 30	Declination (Degrees)	Inclination (Degrees)	Intensity (mA m ⁻¹)	MAD (Degrees)	<i>K</i> (SI)
Max	166.70	87.00	5.52	12.20	65.60
Min	-178.00	-71.30	0.02	0.80	-0.40
RV	344.7	158.3	5.5	11.4	66.0
Mean	-18.44	45.45	0.88	5.51	8.01
SD	130.36	32.06	1.41	3.55	15.28
Arne-04 n = 29					
Max	169.40	79.30	1.77	18.80	33.10
Min	-179.50	-23.40	0.02	1.90	0.00
RV	348.9	102.7	1.75	16.9	33.1
Mean	-11.01	41.54	0.32	10.45	5.55
SD	149.66	25.86	0.53	5.55	9.52

Table 5.10. Descriptive statistics for the Arne 2003 and Arne 2004 magnetic data sets. RV = range of variability and SD = standard deviation.

Radial plots were constructed for the two sets of Arne data (Figure 5.14). These confirmed the poor agreement between the measured data and the alignment, and the absolute range of values that could be expected in a NRM record of SV for a period during the last millennium from a site in southern England.

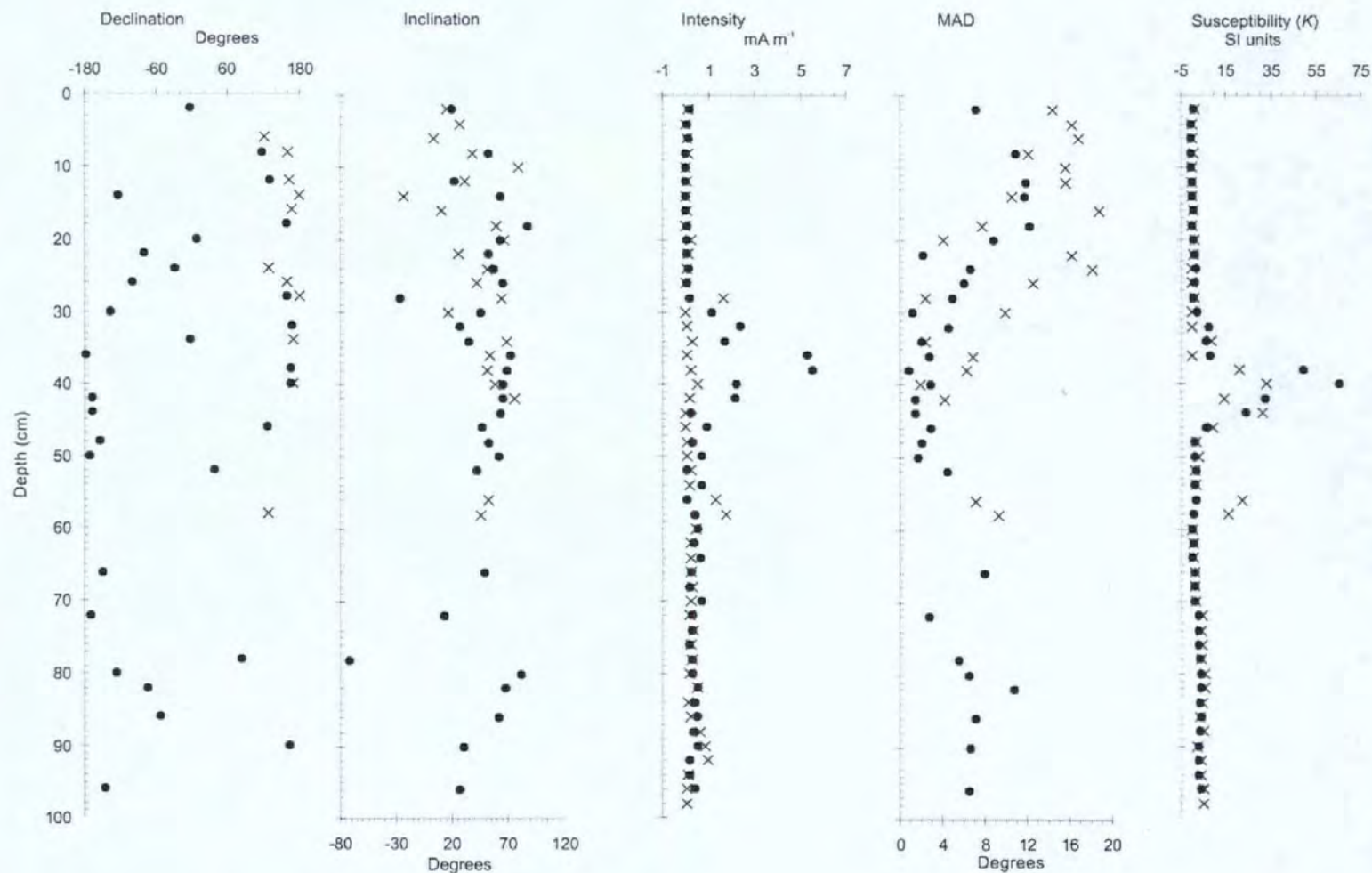
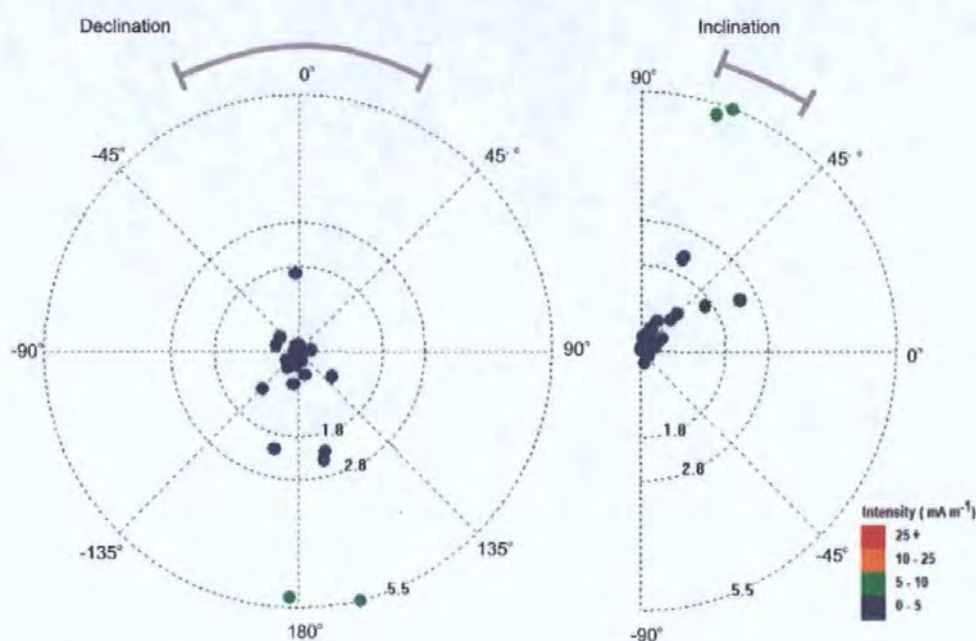
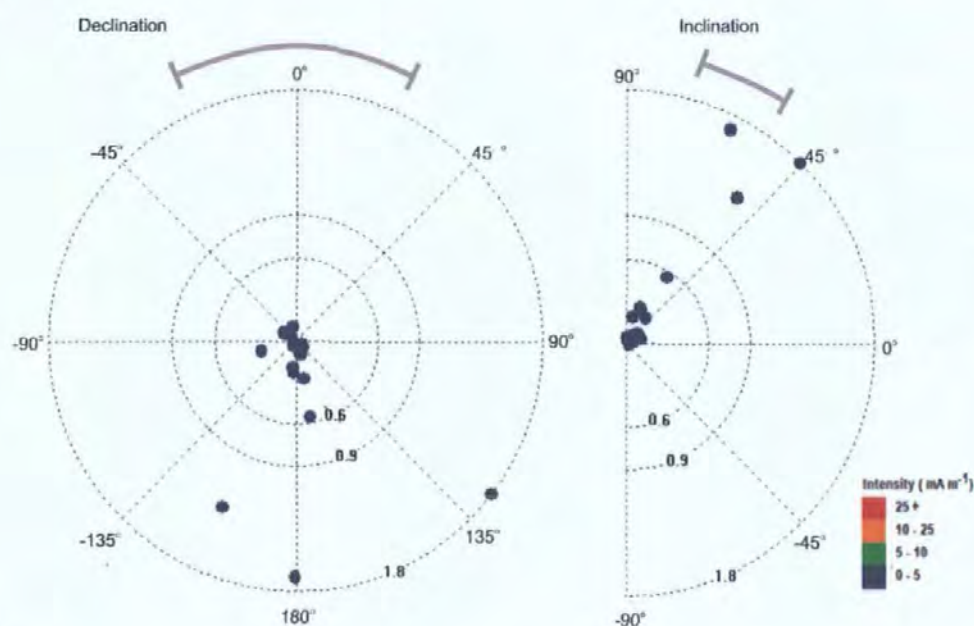


Figure 5.13. The Arne NRM and magnetic susceptibility results. The filled symbols show the Arne-03 data and the crosses show the Arne-04 data.



Arne-03



Arne-04

Figure 5.14. Radial plot of the Arne 2003 and 2004 NRM vector data. The concentric arcs show the intensity (mA m^{-1}) at intervals of 33%, 50% and 100% of the maximum value. The thick grey arcs show the estimated range of natural variability for geomagnetic SV during the last 1000 yr in Southern England. This range was estimated for the last 400 yr using the British Geological Survey (BGS) geomagnetic models for 1600 to 1890, the International Geomagnetic Reference Field (IGRF) and the Definitive Geomagnetic Reference Field (DGRF) models (GEOMag 2006) all calibrated to the location of the Arne site. The estimates for the previous 600 yr were produced using the UK master curve of Turner and Thompson (1981).

Data analysis. A Pearson correlation analysis on the Arne-03 data (Table 5.11) shows that there is no significant correlation between the grain size fractions, or the organic carbon %, and the magnetic data. There is significant correlation between *K* and intensity ($r = 0.598$, $p = 0.000$). Weak correlation is found between the MAD values and *K* ($r = -0.439$, $p = 0.015$) and intensity ($r = -0.477$, $p = 0.008$), with a trend for the higher MAD values to be associated with the lowest *K* and intensity values.

	dec	inc	int	MAD	<i>K</i>	OrgC.	Sand	Silt
inc	0.192 0.308							
int	-0.028 0.884	0.214 0.257						
MAD	-0.067 0.724	0.042 0.828	-0.477 0.008					
<i>K</i>	-0.083 0.664	0.234 0.213	0.598 0.000	-0.439 0.015				
OrgC.	-0.121 0.525	0.168 0.375	0.040 0.832	0.171 0.365	-0.066 0.729			
Sand	-0.015 0.936	-0.208 0.269	-0.241 0.200	0.136 0.475	-0.162 0.393	-0.676 0.000		
Silt	0.028 0.882	0.197 0.296	0.244 0.195	-0.114 0.549	0.149 0.431	0.678 0.000	-0.995 0.000	
Clay	-0.046 0.809	0.232 0.218	0.199 0.292	-0.217 0.249	0.197 0.297	0.579 0.001	-0.895 0.000	0.846 0.000
Contents: Pearson correlation (r value)				$n = 30$				
P-Value								

Table 5.11. Pearson correlation matrix of the Arne-03 magnetic data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, *K* = magnetic susceptibility, OrgC = organic carbon %.

To test for any reproducibility between the two data sets correlation analysis was carried out on 16 paired results from the two Arne data sets (Table 5.12). This confirmed the poor reproducibility of the Arne NRM vector data, but showed a very significant correlation between the two sets of *K* data ($r = 0.979$, $p = 0.000$). It confirmed the correlation between the *K* values and intensity, and the relationship of these two variables with the MAD values.

	03dec	03inc	03int	03MAD	03K	04dec	04inc	04int	04MAD
03inc	-0.068 0.804								
03int	-0.135 0.619	0.279 0.296							
03MAD	-0.207 0.441	-0.009 0.974	-0.628 0.009						
03K	-0.131 0.628	0.288 0.279	0.610 0.012	-0.539 0.031					
04dec	0.209 0.437	-0.017 0.949	0.130 0.631	-0.223 0.407	-0.195 0.470				
04inc	-0.449 0.081	0.031 0.909	0.329 0.213	-0.304 0.253	0.336 0.203	-0.216 0.421			
04int	-0.226 0.400	-0.688 0.003	-0.029 0.914	-0.182 0.499	0.138 0.609	-0.150 0.580	0.361 0.169		
04MAD	0.595 0.015	0.042 0.878	-0.454 0.077	0.315 0.234	-0.497 0.050	0.098 0.717	-0.570 0.021	-0.529 0.035	
04K	-0.166 0.540	0.211 0.433	0.530 0.035	-0.486 0.056	0.979 0.000	-0.240 0.372	0.363 0.168	0.185 0.493	-0.544 0.029
Contents: Pearson correlation (r value)					n = 16				
P-Value									

Table 5.12. Pearson correlation matrix of the Arne-03 and Arne-04 magnetic data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, K = magnetic susceptibility, OrgC = organic carbon %.

Arne data analysis: summary and evaluation. The lack of structure in the vector data, the excessive range of the variability in the values and the poor correlations between the two data sets, indicate that this analysis has not detected a reliable NRM record in the Arne sediments. In many of these samples the declination and inclination vectors measured are outside the range of possible values that could be produced by the influence of the geomagnetic field. In addition, the values are not replicated between the two data sets, and there are some negative inclination vectors measured. This suggests that when it was possible to measure any vertical alignments they were only from the rotation of platy grains by gravity during dewatering and sediment compaction. There is some correlation found between the K values and intensity, and both these variables are found to be co-varying with the MAD values in the samples that have a NRM result sufficiently substantive to allow the use of PCA.

There was no evidence of any structured or non-random horizontal NRM component. Some structure would have been expected if there had been any sediment alignment by over-marsh water flow. This indicates that the apparent measured vectors were from chaotic grains, or the K values were so low that NRM intensity signal preserved was below the detection level of the magnetometer. The

Arne results, therefore, do not warrant any further consideration for palaeomagnetic dating.

5.3.3. The Viðarhólmi magnetic analysis results. All of the 70 samples from the Icelandic salt-marsh sequence produced tangible NRM data with low MAD values ($<8^\circ$) and substantive K values. Figure 5.15 shows how the results form two distinct 'units' above and below the pumice layer that bisects this sequence around 60 cm. Below this horizon the declination and inclination data were very variable, whereas above the division there is more apparent structure in the data.

Below 110 cm in the lower unit the declination data is noisy and characterised by a series of excessive oscillations. There is an overall positive trend with a negative trough between 110 cm and 100 cm. Above this a negative eastward trend is established between 98 cm and 72 cm, before a short series of more positive values below the pumice layer. The inclination data in this lower unit are noisy. There is a negative trend defined between 96 cm and 78 cm and subsequent positive trend to 62 cm. The intensity and K values are relatively low, but remain steady throughout this part of the sequence with small discrete peaks at 126 cm, 118 cm, 92 cm and 62 cm. The maximum MAD values in the Vid-03 section are in this lower unit between the base and 104 cm.

The declination record above the pumice layer is well structured. At 56 cm there is a positive rise to a westward maximum at 54 cm before an eastward loop to a well defined minimum at 40 cm. Above this point there is a positive westward swing that continues to the surface with some small fluctuations. The inclination data has an overall downward trend from 56 cm up to the surface, with some minor abrupt steps and one extreme positive point at 8 cm. As in the lower unit, the intensity and K values have similar profiles displaying a steady rise from 52 cm to 16 cm. The values then fall toward the surface, but remain significantly higher than the values measured on the samples immediately above the pumice layer. In the upper unit the MAD values fluctuate around the mean with a small downward trend toward the surface.

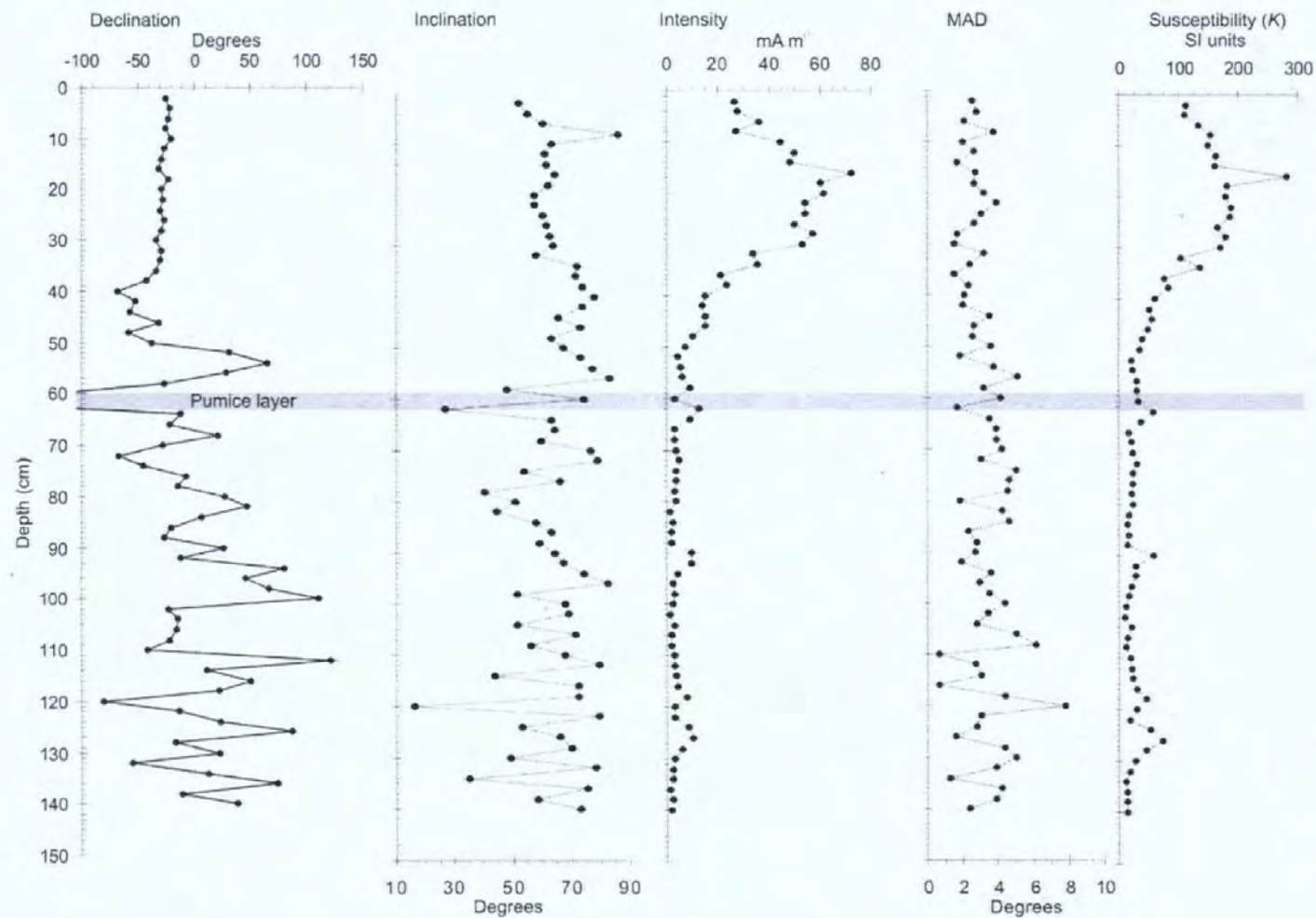


Figure 5.15. The Viðarhólmi NRM and magnetic susceptibility results.

Descriptive statistics have been calculated for each of these units (Table 5.13). The samples spanning the pumice layer, 58 cm to 60 cm and 60 cm to 62 cm, have been omitted from these calculations, and from the Pearson correlation analysis later in this section.

Vid-03 n = 68	Declination (Degrees)	Inclination (Degrees)	Intensity (mA m⁻¹)	MAD (Degrees)	K (SI)
0 cm to 58 cm					
Max	65.25	85.90	72.20	5.10	282.3
Min	-68.15	48.20	4.13	1.50	21.1
RV	133.40	37.70	68.07	3.60	261.2
Mean	-25.55	65.66	32.30	2.69	113.5
SD	26.58	8.98	20.39	0.83	67.1
60 cm to 140 cm					
Max	122.05	82.30	10.20	7.80	73.8
Min	-80.85	16.40	1.42	0.60	10.2
RV	202.90	65.90	8.78	0.20	63.6
Mean	8.23	61.77	3.99	3.49	24.5
SD	46.41	13.99	2.62	1.41	13.6

Table 5.13. Descriptive statistics for the Viðarhólmi 2003 magnetic data set. RV = range of variability and SD = standard deviation.

Table 5.13 shows there is a wide range of absolute variability in the declination and inclination data from both the upper and lower Vid-03 units. These ranges appear excessive when compared to the expected ranges shown in Figure 5.16, but an inspection of the means of the vector values shows that a significant proportion of the data is within, or close to, the expected range of values. Figure 5.16 illustrates how all the declination data associated with intensity values $> 25 \text{ mA m}^{-1}$ plot within the expected sector. The inclination vector values are slightly depressed, and in a similar manner to the declination results, there is a trend for the samples with the highest intensity values to plot closer to the expected range in Figure 5.16.

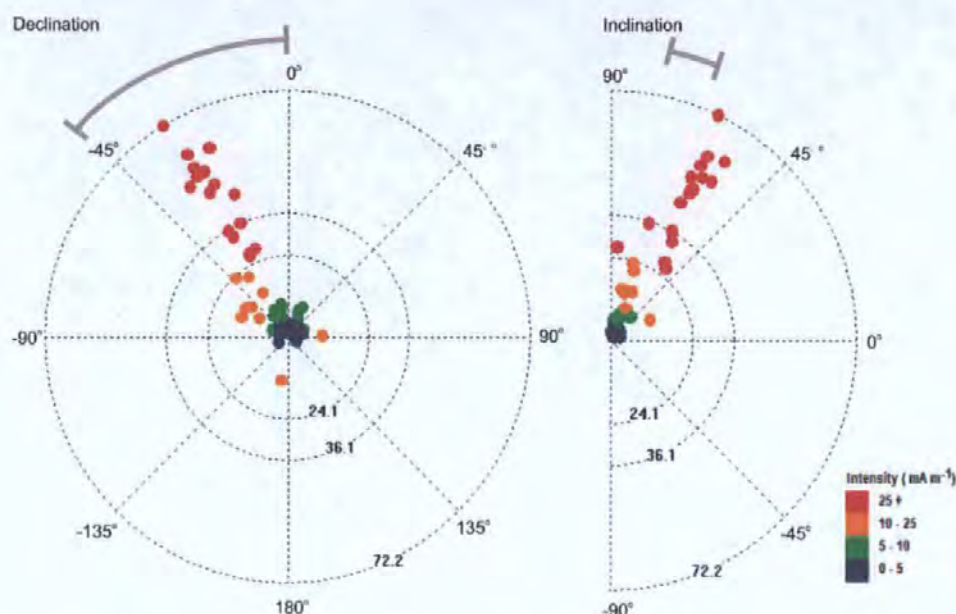


Figure 5.16. Radial plot of the Viðarhólmi 2003 NRM vector data. The concentric broken lines show the intensity (mA m^{-1}) at intervals of 33%, 50% and 100% of the maximum value. The thick grey arcs show the estimated range of natural variability for geomagnetic SV during the last 2000 yr in Iceland. This range was estimated for the last 400 yr using the British Geological Survey (BGS) geomagnetic models for 1600 to 1890, the International Geomagnetic Reference Field (IGRF) and the Definitive Geomagnetic Reference Field (DGRF) models (GEOMag 2006) all calibrated to the location of the Viðarhólmi site. The estimates for the previous 1600 yr were produced using the UK master curve of Turner and Thompson (1981) and the Scandinavian records of Ojala and Saarinen (2002) and Snowball and Sandgren (2002).

Data analysis. The Pearson correlation matrix (Table 5.14) shows a very significant correlation between intensity and the K values ($r = 0.981$, $p = 0.000$), and correlations between some of the grain size components, organic carbon % and intensity (e.g., sand and intensity, $r = 0.490$, $p = 0.000$; clay and intensity, $r = 0.518$, $p = 0.000$; clay and organic carbon, $r = 0.362$, $p = 0.002$). Significant correlation ($r = 0.419$, $p = 0.000$) was also found between intensity and declination, but a weaker negative correlation was apparent between the MAD values and both intensity ($r = -0.314$, $p = 0.009$), and the K values ($r = -0.296$, $p = 0.014$).

A regression analysis using the three grain size variables, organic carbon % and the variability in the K values as predictors for intensity yields K values r^2 (adj) 0.96, and when the K values are combined with clay r^2 improves to 0.97. However, if the K values are excluded the predictive power of the alone is r^2 (adj) 0.26. If the clay is combined with the organic carbon r^2 0.69 is indicated.

	dec	inc	int	MAD	K	OrgC.	Sand	Silt
inc	0.026 0.833							
int	0.419 0.000	-0.026 0.832						
MAD	-0.029 0.816	-0.246 0.043	-0.314 0.009					
K	0.392 0.001	-0.004 0.974	0.981 0.000	-0.296 0.014				
OrgC.	-0.027 0.824	0.118 0.336	-0.426 0.000	0.140 0.254	-0.479 0.000			
Sand	0.356 0.003	0.076 0.539	0.490 0.000	-0.236 0.053	0.441 0.000	0.332 0.006		
Silt	-0.376 0.002	-0.080 0.515	-0.504 0.000	0.237 0.051	-0.454 0.000	-0.344 0.004	-0.996 0.000	
Clay	0.429 0.000	0.094 0.446	0.518 0.000	-0.224 0.066	0.467 0.000	0.362 0.002	0.891 0.000	-0.927 0.000

Contents: Pearson correlation (r value) *n* = 68
P-Value

Table 5.14. Pearson correlation matrix of the Viðarhólmi Vid-03 magnetic data. Dec = declination, inc = inclination, int = intensity, MAD = Maximum angular deviation, K = magnetic susceptibility, OrgC = organic carbon %.

Viðarhólmi data analysis: summary and evaluation. A tangible NRM is detected in all samples, and directional vectors could be determined with the PCA MAD values of $< 8^\circ$. Magnetic susceptibility (*K*) is high in the upper section of the sequence, and is shown to have a very significant correlation, and a strong predictive power, regarding intensity. Also showing significance as predictors of intensity are the clay and organic carbon contents. The data analysis indicates that there is a link between the preservation of robust NRM vectors, measurable NRM intensity and the ability, or susceptibility, of the sediments to be magnetised (the *K* value).

In a significant number of samples the mean vector values are close to, or within, the expected SV range for a late Holocene site in Iceland. This sample group consists exclusively of samples with higher intensity and *K* values. The measured declination record appears to agree with the expected declination mean, but there is some disagreement when the inclination record was examined. The mean measured inclination value is depressed when compared to the estimated mean inclination expected for an Icelandic site during the last 2000 yr. However, the structure, and the constrained range of a significant proportion of the declination data suggest that this sequence may have potential to be dated using the NRM data. This will be explored in the next section.

5.4. Palaeomagnetic chronologies

5.4.1. Master curves. The Taf and Arne sites are within a region for which the Turner and Thompson (1981) UK master curve is applicable. Despite the comments in Section 5.1 on the lack of good age control in some sections of this curve, this master record is the most appropriate to the Taf site because of its geographical origins and chronological range. The Arne site, because of its comparative young sediments, would be best matched to the UK archaeomagnetic reference curves of Clarke *et al.*, (1988). In the discussion below, estimated uncertainties for the Turner and Thompson (1981) chronology have been interpolated from the Cal BP dates produced by the re-calibration of the published ^{14}C ages shown in Table 5.2.

Iceland does not have its own palaeomagnetic master curve, nor does it lie in the zone covered reliably by the established North American or European archaeomagnetic reference curves. It is 1000 km northwest of the UK, and is located close to the latitude of Sweden and Finland, so it can be expected to have experienced a history of palaeomagnetic SV that will be somewhat compatible to the approximate timing of the major features in these countries (See Section 5.1.5). Therefore, the UK master curve (Turner and Thompson, 1981) and the Scandinavian lake records (Saarinen 1999; Ojala and Saarinen, 2002; Snowball and Sandgren, 2002) were all potential calibration tools for the last 3000 yr. for the Icelandic data.

To produce calibration curves for the Viðarhólmi site the UK master curve (Turner and Thompson, 1981) was rotated so that the declination data agreed with the values for the Viðarhólmi site from the Geological Survey (BGS) geomagnetic models for 1600 to 1890 (Figure 5.3e). These data were then amalgamated with the GEMAG models produced for Iceland using the International Geomagnetic Reference Field (IGRF) and the Definitive Geomagnetic Reference Field (DGRF) (USGS, 2006).

5.4.2. The Taf palaeomagnetic chronology. The magnetic analysis of the Taf-02 and Taf-03 monoliths show that there is non-random structure apparent below 20 cm in the declination data. The inclination data are somewhat chaotic and lack sufficient structure, but have some potential as a chronological tool. In the first instance, the screened declination data used for the correlation analysis (Table 5.6) between the two sequences is plotted (Figure 5.17) alongside the standard declination curve for the UK (Turner and Thompson, 1981).

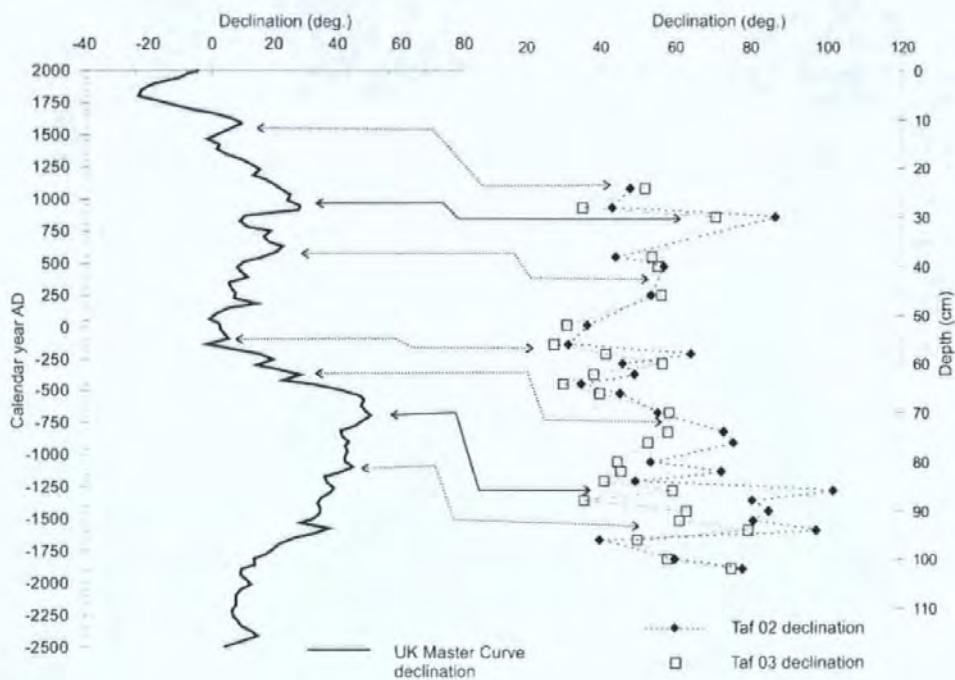


Figure 5.17. The Taf declination data plotted with the UK master curve of Turner and Thompson (1981). Substantive tie-lines in solid lines, probable tie-lines shown broken.

Depth (cm)	Age (AD)	Master curve age uncertainty (yr)
2	2003	0
24	1585	±66
30	905	±84
46	625	±96
56	-135	±128
74	-375	±132
84	-695	±143
94	-1095	±157

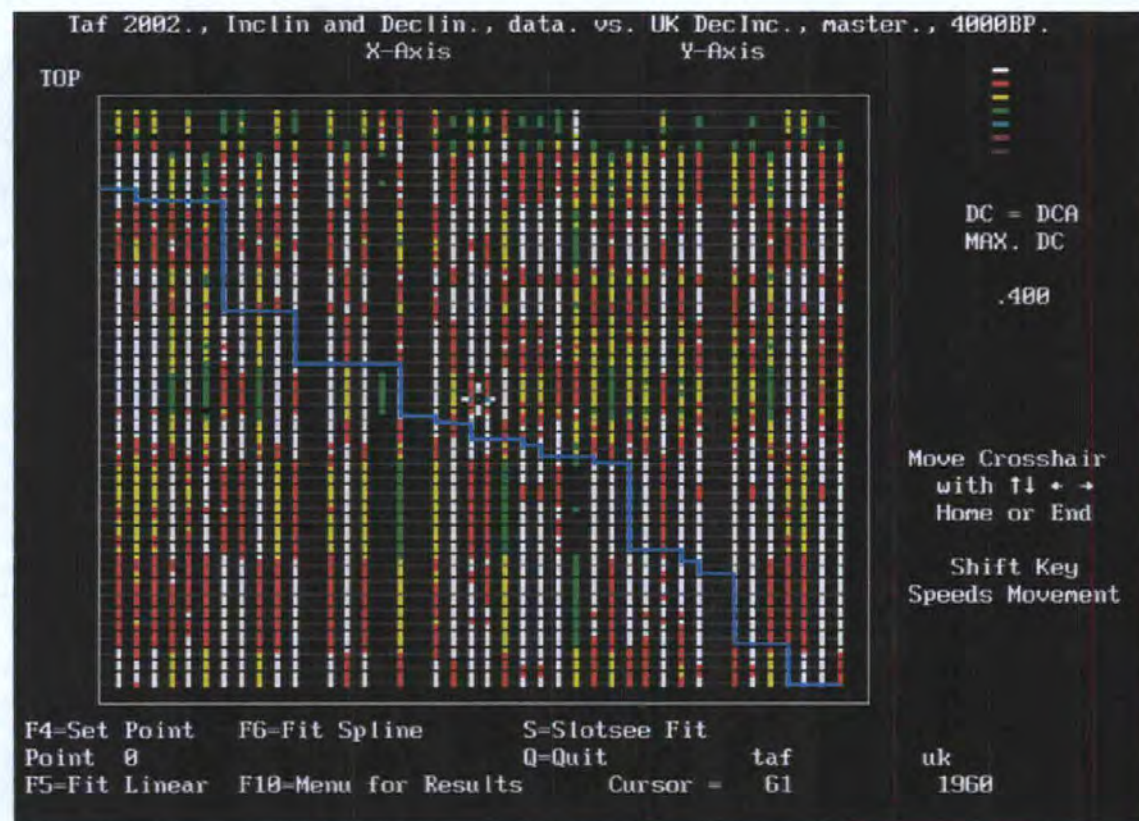
Table 5.15. Sediment ages determined from Taf declination data. Master curve uncertainty is estimated as outlined in section 5.1.5 (See Table 5.2).

Some features in the master curve could be recognised in the Taf record. Notably the eastward declination maxima around 575 BC, 900 AD and 1585 AD, and the westward declination minimum around 15 BC. Chronological ages could be assigned to eight of the Taf horizons (Table 5.15).

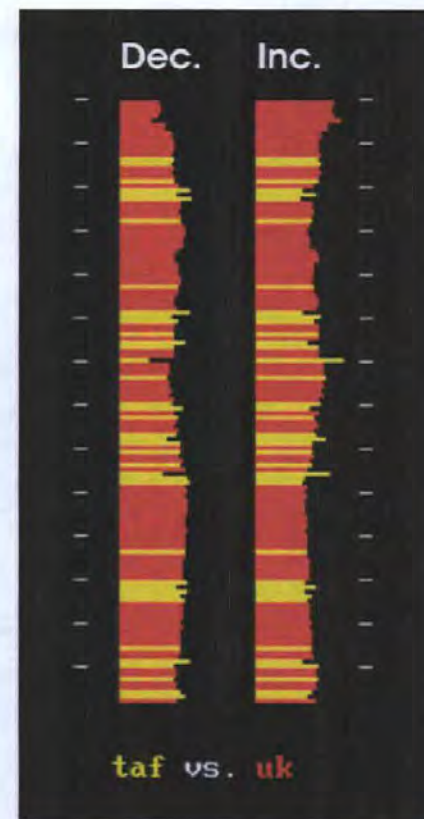
Visual alignment of curves is a straightforward means of obtaining common tie-points between two sets of data. This simple 'wiggle matching' approach is commonly used to compare time series of palaeoenvironmental records, like stable isotope data, and in some cases it is used to calibrate ^{14}C data (See Chapter 3). However, manual wiggle matching does involve a certain amount of subjectivity. In an attempt to reduce this during the calibration of the Taf palaeomagnetic data the sequence slotting software SLOTDEEP (Maher, 1998) was tried (Figure 5.18).

This software was originally designed for correlating two pollen records so that a robust chronology from a primary dated 'master' sediment sequence could be transferred to a similar, but undated, secondary sequence from the same region. It uses the Manhattan Metric dissimilarity coefficient of the pollen data to slot horizons from the secondary sequence into the primary sequence. In common with commercial versions of sequence slotting software, used for correlating well geological logs, SLOTDEEP requires high resolution data strings from a group of common variables for each sequence. In its original application six or more individual pollen species would have been used, and it was not known if the program could work reliably with just two variables.

The SLOTDEEP software creates a matrix of the two data sets (Figure 5.18A) that displays the dissimilarity coefficient of the data as coloured pixels. This highlights the sections of the matrix where the values of the variables are most similar. The operator can choose to exclude data above a preselected maximum dissimilarity. The program suggests a path through the matrix that follows a line of low dissimilarity points. The operator can accept this as a valid solution, or they can plot manually using the suggested pathway as a guide. Once the primary points are selected, ages for depths in the secondary sequence are then interpolated by the software using the line-of-best-fit through the selected points. It is found that if the operator entered the correct approximate ages for the top and bottom of the master sequence, a realistic chronology is suggested by SLOTDEEP. In the case of the Taf scenario shown in Figure 5.18, the bottom of the primary master data set is given the age of 4000 yr cal BP. By comparison, if the same secondary data set is run with a longer master sequence (present day to 6000 yr cal BP), SLOTDEEP would stretch the Taf data to fit, and suggests an age of around 5600 yr cal BP for the bottom of the Taf sequence.



(a)



(b)

Figure 5.18. Screen-shots of the SLOTDEEP (Maher, 1998) alignment of the Taf NRM data with the UK master curve (Thompson and Turner, 1981).
(a) Maximum dissimilarity co-efficient in the matrix is 0.4. Co-efficient scale - white = 0 - 0.1; red = 0.1 - 0.2; yellow = 0.2 - 0.3; green = 0.3 - 0.4.
Chosen pathway of lowest dissimilarity co-efficient highlighted in blue. (b) The graphical representation of the SLOTDEEP slotting of the solution in (a).

It is apparent that SLOTDEEP can not reliably recognise a hiatus in the sequence, or deal with a 'floating sequence' that is not anchored to the top and bottom of the master curve. It will not work at all with only one line of data, and with two variables it defaults to a straight line of best fit that simply joins the top and bottom of the two sequences. It is likely that with only the information contained in two variables the program can only interpolate along a linear pathway. The chronology resulting from the alignment in Figure 5.18 is shown in Figure 5.19. It shows some agreement with the ages obtained by the visual 'wobble matching' shown in Figure 5.17. Both results indicate acceleration in marsh accretion around 500-400 BC that lasted for 200-300 yr. As the wobble matched chronology was only derived from the declination data this suggest that the inclination variability must be in phase with the declination variability, or it is not 'powerful' enough to influence the SLOTDEEP result.

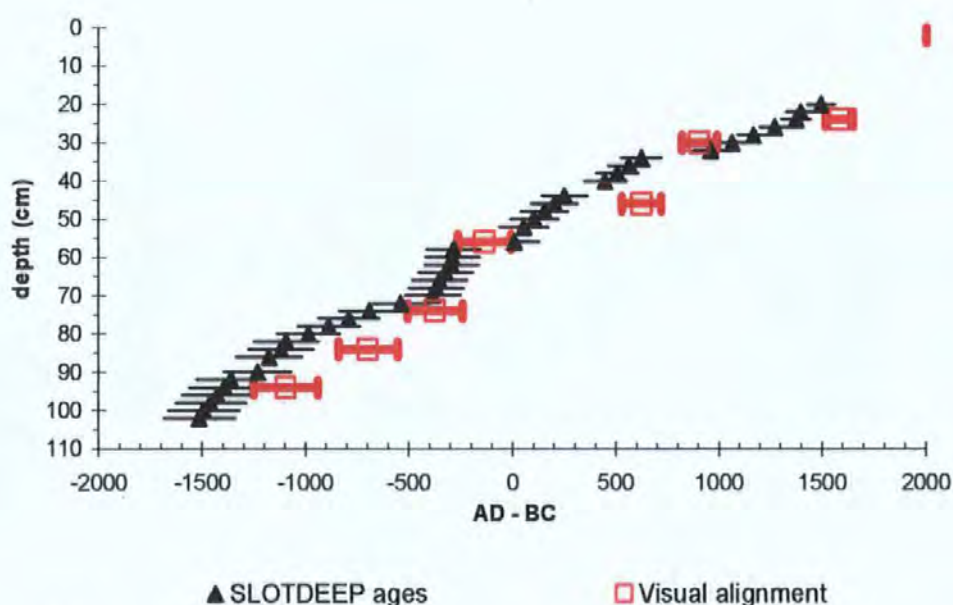


Figure 5.19. Age-depth model for the Taf using the palaeomagnetic ages. Age uncertainties are interpolated from the Cal BP dates shown in Table 5.2.

5.4.3. The Viðarhólmi palaeomagnetic chronology. The Viðarhólmi sequences demonstrates a lack of structure below 60 cm, and no agreement can be seen between changes in the data from this section and the UK master curve (Turner and Thompson, 1981). The Icelandic data from the upper section above the pumice layer at 60 cm, (AD 1226-1227, see Chapter 6) have structure in both the NRM declination and inclination curves, so it was decided to attempt to wobble match these data to the composite Icelandic calibration curve described in Section 5.4.1 (Figure 5.3e).

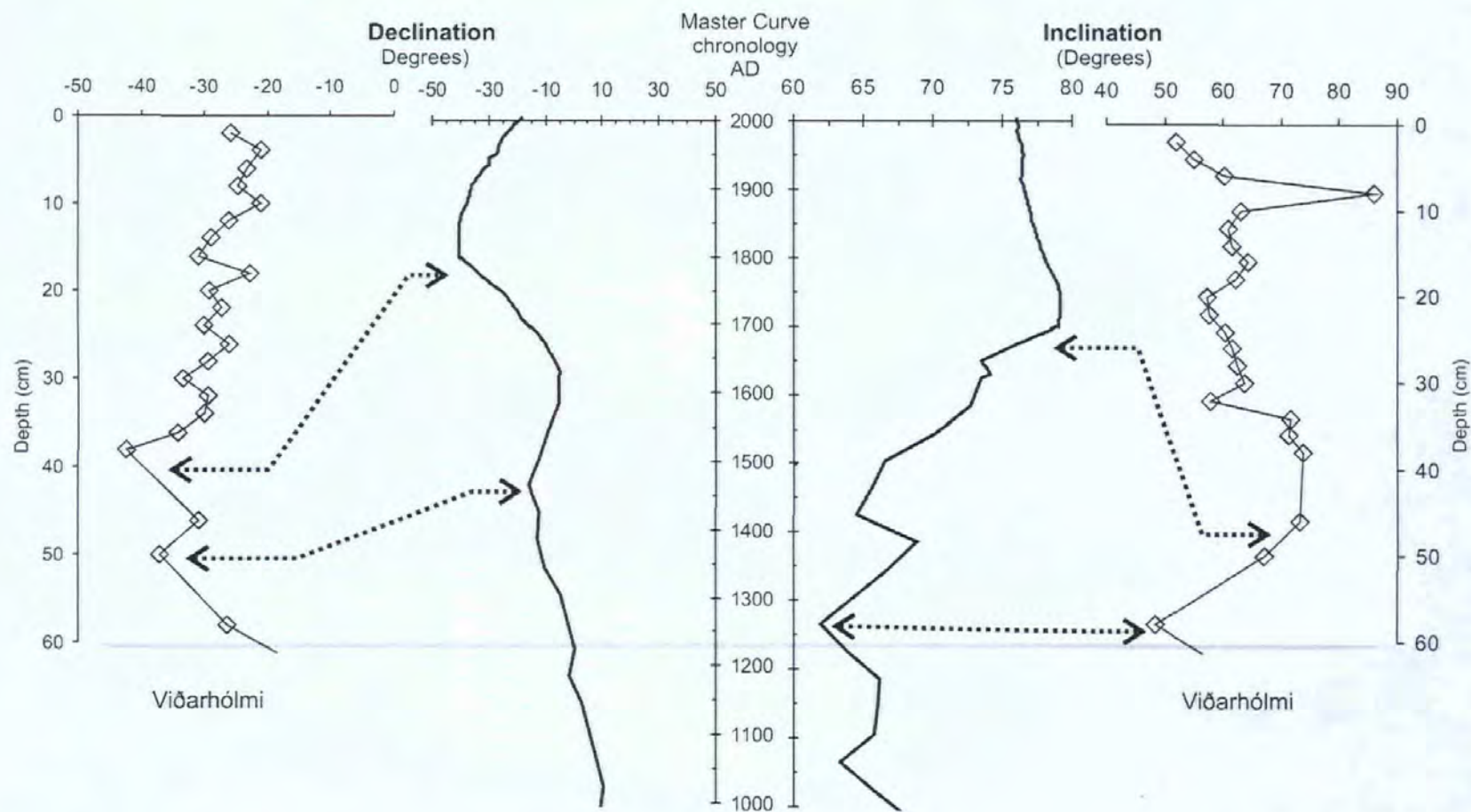


Figure 5.20. Declination and inclination features in the Vid-03 data aligned with a chronology derived from the GEOMag (USGS, 2006) models and the upper section of the UK master curve of Turner and Thompson (1981).

Two points of agreement are proposed in both the declination and the inclination data (Figure 5.20). The inclination values were somewhat displaced from the calibration data but the absolute declination vectors were in some agreement with the modelled data. The last extreme eastward declination minimum dated to 1780-1840 (See Figure 5.3) in many Northern European SV records (Barracough; 1974, 1978; Malin and Bullard, 1981; Thompson and Oldfield, 1986; Alexandrescu *et al.*, 1996) is apparent at 38 cm. This point is awarded the age of AD 1820 $\pm$ 20 (See Gehrels *et al.*, 2006). At 50 cm there is some evidence of the end of the extended eastward declination trend of the 400 yr preceding 1450. Between these horizons the data from 46 cm is in agreement with the end of the upward trend in regional inclination that is dated in the composite calibration curve to 1700-1720. Immediately above the pumice layer at 58 cm the inclination data is also trending in agreement with the calibration curve, but this tie-point would not be conclusive in isolation. The four ages are plotted in Figure 5.20, with the AD 1226-1227 pumice layer.

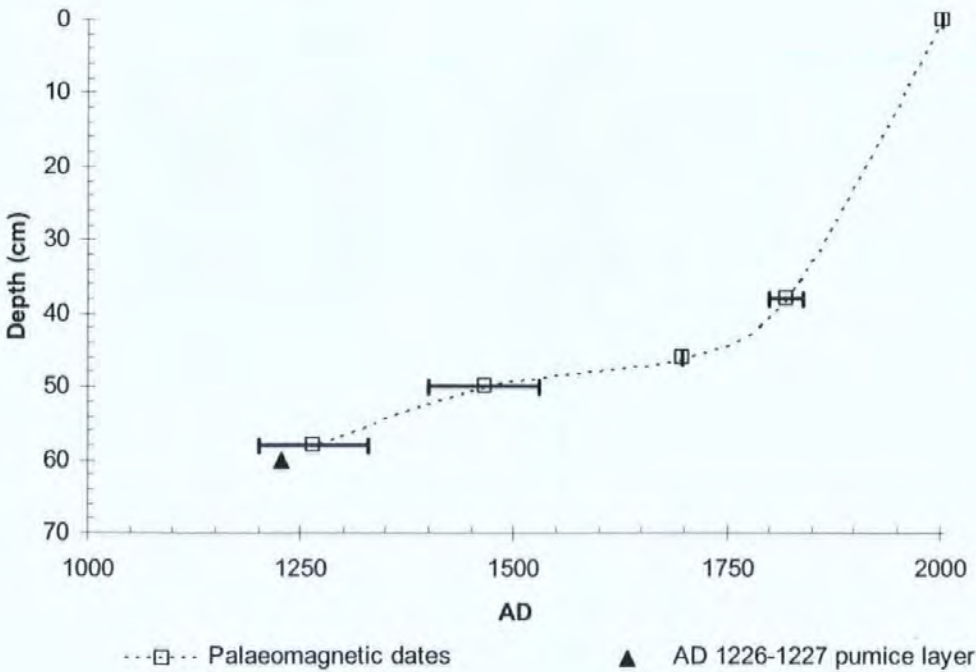


Figure 5.21. The Viðarhólmi palaeomagnetic chronology. Age uncertainties for the pre 1600 dates are interpolated from the Cal BP dates shown in Table 5.2. No uncertainty is shown for the dates derived from the GEMag (USGS, 2006) models.

5.5. Discussion and Synopsis

5.5.1. Grain alignment, flows and physical issues. Magnetic dating relies totally on the alignment of sediment grains by the Earth's geomagnetic field, and the subsequent embedding of a coherent NRM signal within the sediments. The alignment can be by re-magnetisation within the fabric of the grains after heating, or a mechanical rotation of the grains while in suspension or within wet sediments. In a salt marsh, the grains will normally be mechanically aligned, and this will only be possible in zero, or very low energy environments. During deposition, and until the grains are locked in place by de-watering and compaction, any linear water, gravitational or wind flow that is capable of disturbing the sediments will influence the final alignment of the surface sediment grains (Snowball and Sandgren 2002). In addition to the criticality of these factors contemporaneous with deposition, post-deposition re-liquefaction of the sediments by changes in water content of the deposits or bioturbation can 're-set' the magnetic record to the alignment of the magnetic field contemporary to the disturbance of the grains.

This study has achieved some mixed success in producing NRM data from salt-marsh sediments. At two sites the results have revealed some clear trends and dependencies in the data. Clay content was found to have some positive relationship with the K values, thus suggesting a positive relationship between the amount of magnetic minerals in the sediment, as defined by K , and the determination of coherent NRM vectors. This was very apparent when the results of the three sites are compared with each other, but especially when the Arne results are considered alongside the data from Viðarhólmi. The most striking effect of the higher K found in the Icelandic sediments is stronger intensity values and well defined NRM vectors. The robustness of these NRM values is quantified by the low MAD values attached to the PCA on these data. This situation is found throughout the Icelandic sequence, but is more apparent in the upper section, and is attributable to the Viðarhólmi lithology being dominated by volcanic material rich in magnetic minerals.

In contrast to the Icelandic site, the Arne sediments have low K values, correspondingly low NRM intensity levels and chaotic NRM vectors. This reflected the very low occurrence of magnetic materials in the local carbonate dominated

geology (See Chapter 2), but the correlation trend between K , NRM intensity and MAD values found in the other sites is still apparent. Interestingly, the only sediment horizons in the Arne sequence with K and intensity values of any substance are between 40 cm and 50 cm. This section is found to be enriched in industrial fly-ash particles (See Chapter 6).

The Taf K values and NRM intensity levels are also low compared to the Icelandic data, but tangible NRM vectors are present in many of the samples below 20 cm. However, when examined in detail it is apparent that the inclination vectors are depressed below the expected angle for the site, and the horizontal declination vectors appear to have been influenced by alignment processes other than those exclusive to the geomagnetic field. It is proposed that many of the declination vectors from the Taf sediments are the result of both geomagnetic alignment and tidal flow alignment. The low K values for these sediments coinciding with an east-west deflection to the declination vectors suggest that the traction the geomagnetic field could exert on the grains may have been proportionally reduced. This has then resulted in a declination vector that is the resultant of two alignment processes.

Katari *et al.* (2000) showed that sediment grains do not all instantly rotate into a uniform magnetic alignment. There will be a lag, and the time needed for a significant number of grains to be aligned is influenced by the sediment K , the intensity of the prevailing magnetic field and the friction coefficients of the individual grains. If the sediment K value is low it will have the same effect as lowering the magnetic intensity; i.e. it will reduce the effective strength of the prevailing magnetic field to act on the grains, and extend the time needed for the alignment of a significant proportion of the grains. Therefore, the resulting mean horizontal grain alignment would be more susceptible to being influenced and overprinted by over-marsh water flows. Ebbing spring tides at the site could easily introduce an east-west bias to the grain alignment if the water velocity is high enough and the sediments still unconsolidated. If the marsh surface accretion rate, its altitude above sea level, the tidal prism and the sediment lithology stay relatively constant through time then the tidal component of the horizontal vector will remain relatively the same. In this situation the variability in the data can be attributed to the SV in the geomagnetic component, but the mean horizontal alignment will be the product of two different forces.

5.5.2. Data calibration and master curves. The Taf data is used to produce a chronology spanning the period 3500 – 500 yr BP initially by using a manual wiggle-

matching approach with the two Taf declination data sets (Figure 5.16). The Taf-02 declination and inclination data are calibrated using the sequence slotting software SLODEEP (Maher, 1998). Both methods produce a chronology but SLODEEP was originally designed to work with pollen species data and multiple variables. When working with only the declination and inclination data strings SLODEEP is not reliable, especially with floating chronologies. Some pre-existing chronological knowledge is needed to 'tie' the primary and secondary sequences together before SLODEEP can be asked to align the intervening data points. In this Taf calibration the ^{14}C dates (See Chapter 3) have not been used, but the manual calibration of the declination features was felt robust enough in this instance to constrain the unknown chronology to the period between 4000 yr BP and 500 yr BP. The two calibration methods produce similar results, but it is suggested here that a manual calibration is the most reliable method to use initially 'blind' on an unknown sequence of NRM data.

The wiggle-matching method is used to calibrate the Viðarhólmi data, and because there is some structure apparent in the inclination data these are considered in conjunction to the declination data. The short chronology for the Icelandic site is constrained at its base by the tephra layer that bisects this sequence around 60 cm. It provides a splendid chronological marker and is dated to AD 1226/7 (See Chapter 6), but it also marks an apparent subtle change in the salt-marsh environment (See Chapter 2). The horizons above 58 cm and toward the surface are characterised by a decrease in the variability in the NRM vector data, an increase in the NRM intensity, a similar increase in the K values and a decline in the MAD values associated with the PCA. The NRM in these upper sediments supports the trends suggested by the Taf sequence, and confirms the need for a substantial K value in sediments for there to be any potential of obtaining reliable results using palaeomagnetic dating. The chronologies produced by palaeomagnetic method will be compared with the other chronologies available for the Taf and Viðarhólmi sites in Chapter 8.

The resolution and precision possible with the palaeomagnetic dating method is dependent on the availability of a robust calibration data set to produce a high-quality master curve. Batt (1997) points out that the largest proportion of uncertainty in a magnetic date, including analytical errors and any stratigraphic displacement associated with the sampling, will normally be in the chronology of the master curve used to calibrate it. The large uncertainties attached to the UK palaeomagnetic master curve (Turner and Thompson, 1981) have been highlighted and discussed in

some depth, and this situation demonstrates the need for more high quality calibration data sets with good age control to be produced. The UK archaeomagnetic master curve data set (Clark *et al.*, 1988; Batt, 1997, 1998) is being expanded as new dates are produced, and this may offer a more reliable reference data set than one obtained from sediments (English Heritage, 2006). The availability of geomagnetic predictions for any location using the GEOMag (USGS, 2006) models means that for dates during the last four centuries there is a usable calibration curve available, but it is not clear as to the uncertainty that should be attached to the chronology. The raw data used in the models is an amalgamation of various observations from a number of European observatories, including London (Barracough; 1974, 1978; Malin and Bullard, 1981), and US government records (USGS, 2006), and though the age uncertainties are not stated they are likely to be less than those attached to calibration curves constructed from the best archaeomagnetic and palaeomagnetic data sets.

5.5.3. Synopsis. A number of key points have been highlighted by this investigation into palaeomagnetic dating. Notably for this dating method to work in a salt-marsh environment certain geological and environmental conditions must be met and maintained. This chapter has presented the successful use of palaeomagnetic dating at Taf and Viðarhólmi sites, and describes the failure of this method at the Arne site. It is proposed that the lack of success at the Arne site was due to primarily to the low magnetic susceptibility of the sediments, but other factors, e.g. grain size, contributed to the weak and chaotic NRM signal preserved in the sediments. In addition, changes in the local environment, caused by strong tidal flows or storms, are proposed to be detrimental to the preservation of a robust NRM signal.

Chapter 5 has highlighted that difficulties that can arise during the calibration of the NRM data into dates. The data needs to be correlated with a well dated master sequence, or the output of a suitable geomagnetic model, e.g. GEOMag (USGS, 2006). These calibration methods have been explored, and it is concluded that if a well dated archaeomagnetic curve exists for a particular location then this is most likely to offer a better result than sedimentary palaeomagnetic data, but it will not have the versatility of the geomagnetic computer models that can be targeted on a particular geographical location and chronological period.

Chapter 6

Stable particle fallout events 1: Tephra, pollen and spheroidal carbonaceous particles

Chapter 6 and Chapter 7 will examine dating methods that use the deposition history of non-radioactive particles to date sediment horizons. Investigated in this chapter are the products of volcanic eruptions, pollen grains from flowering plants and black carbon particles produced by the high-temperature burning of fossil-fuels

6.1. Tephra based chronologies

6.1.1. Tephra deposits. Tephra can be defined as the air-fall component of the magma ejected during a volcanic eruption. If this material is found in a sedimentary sequence, and the date of eruption known, it can be used as a time marker or isochrone (Edwards *et al.*, 1994; Pilcher, 2002). During an eruption vast volumes of volcanic material are propelled high into the atmosphere. The larger material will rapidly fall back to earth and will form a deposit proximal to the eruption site but the smaller shards of volcanic glass, crystallized magma and ash may be transported great distances by the wind (Legros, 2000; Pilcher, 2002; Rhoades, 2002).

The thickness of the resulting deposit and the grain size of the tephra decrease with the distance from the source (Bonadonna *et al.*, 1998; Koyaguchi and Ohno, 2001). Typical tephra deposits contain glassy and crystalline materials formed from new magma, pumice, and fragments of ancient volcanic rock displaced from the magma pipe and cone during the eruption. The glassy component is liquid magma that has been cooled rapidly as it travelled up into the atmosphere. Under these conditions the magma solidifies into volcanic glass without crystallising. The ejected tephra eventually falls back to the ground and may be found as discrete layers in sedimentary sequences (Knox, 1993).

6.1.2. Identifying and describing tephra. Tephra layers can be described using a number of parameters such as particle size, colour and composition. Different volcanic systems will produce different tephra, and different eruptions, or even different phases of the same eruption, from the same volcano can differ in physical characteristics and geochemistry. If these variables can be quantified it is possible to delimit individual tephra layers, map their spatial distribution and identify their probable source (Pilcher, 2002). For example the silica-rich rhyolitic tephra from

the Katla volcano on Iceland have a distinct grey-green appearance (Larsen *et al.*, 2001) when compared to the blacker basaltic tephra from this system (Wastegård *et al.*, 2003). A more quantified approach is the analysis of the tephra geochemistry, and it has proved possible to 'fingerprint' a particular eruption if its geochemical signature is sufficiently unique (Hall and Pilcher, 2002). The most widely used technique for determining tephra geochemistry is electron microprobe analysis (Hunt and Hill, 1996; Hafildason *et al.*, 2000; Hunt and Hill, 2001; Hall and Pilcher, 2002), but X-ray fluorescence spectroscopy (XRF) (Schmid *et al.*, 2000) and internally coupled plasma mass spectroscopy (ICP-MS) (Eastwood *et al.*, 1998) have both been used with some success.

Far-travelled tephra deposit grains are typically less than 100 microns in size, and an individual layer may be less than three millimetres thick. The traditional detection method has required sequential sampling and microscopic examination of the sediments (Pilcher and Hall, 1992; Dugmore *et al.*, 1995). However, recently attempts have been made to develop less time-consuming detection techniques for cryptic tephra (See Gehrels, M. J. *et al.*, 2007), e.g. whole-core magnetic susceptibility measurements, and bulk sediment scanning using optical and XRF methods (Caseldine *et al.* 1999; Schmid *et al.* 2000; Andrews *et al.* 2002; Hall and Pilcher 2002; Xia *et al.*, 2004).

6.1.3. Icelandic tephra. During the Holocene Iceland has experienced, on average, one significant eruption every decade (Hafildason *et al.*, 2000; Larsen, 2002). The majority of these have involved the volcanic vents near the crustal hot-spot in the southern region of the central system with lesser contributions from the other active zones (Figure 6.1). During historic times two of the most tephra-productive Icelandic volcanoes have been Hekla and Katla, both of which are located in central-southern Iceland and both are characterised by an alkali olivine basalt and transitional alkali basalt petrology (Jakobsson, 1979). The Landnám Tephra or Settlement Layer was produced by the apparent simultaneous eruption of Veidivötn and Torfajökull, dated to 870 AD (Larsen *et al.*, 1999), in the southern volcanic zone. This particular tephra fall coincides with the first settlement of the island by the Norse people, has been used by a number of Icelandic studies to date sediment sequences (Hafildason *et al.*, 1992; Wastegård *et al.*, 2003), and over 75 individual tephra layers have now been identified from Icelandic eruptions during the last three thousand years (See Hafildason *et al.*, 2000 and references therein).

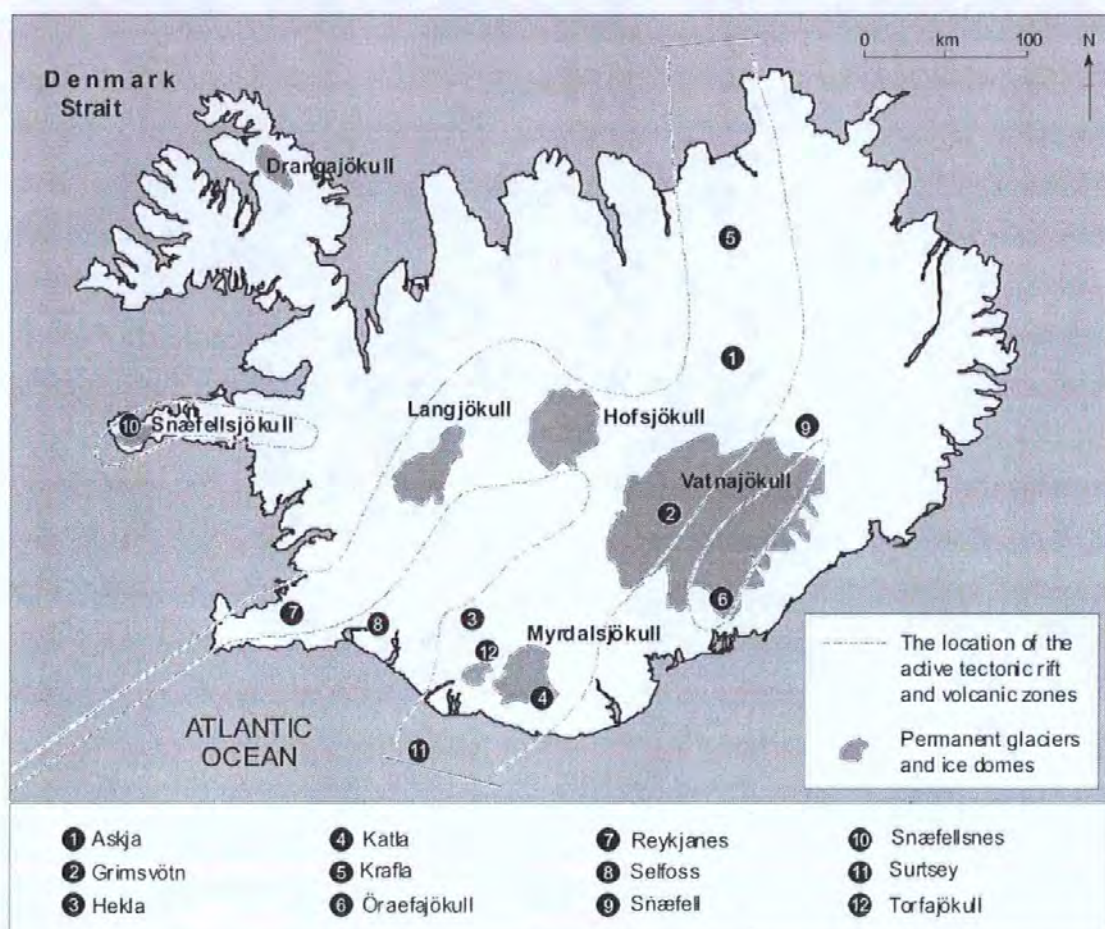


Figure 6.1. The major centres of Icelandic volcanic activity in the Holocene (Numbered black circles).

Numerous eruptions have occurred after the permanent occupation of Iceland by the Vikings in the ninth century AD, and during the next millennium some events were of sufficient magnitude to have dire consequence for the resident population (See Edwards *et al.*, 1994 and references therein). Human tragedies and social responses associated with historic eruptions ensured that some of these volcanic events became embedded in local folklore and later integrated into the romanticised Icelandic Sagas of the twelve and thirteenth centuries (See Kristinsson, 2003 and similar papers). These early written records, although of varying reliability, can provide some confirmation of the deposition date of some Icelandic tephra. Larsen (2002) points out that after the fourteenth century formal records of Icelandic cultural history and documented eyewitness reports give more reliable accounts of past eruptions and tephra falls. A good example is the 1783-1784 fissure eruption of Laki. This event resulted in the loss of around seventy percent of the Icelandic grazing stock due to fluorosis and the subsequent demise of nearly a quarter of the human

inhabitants (Edwards *et al.*, 1994; Thordarson and Self, 2003). There is also evidence that the impact of this event was not confined to Iceland. In addition to contemporary reports of the social and environmental impact surviving on Iceland, the Laki 1783-1784 eruption, the resulting tephra fall and its effect on the weather, were documented in several Northern European countries and reported in the English popular press of the time (Grattan and Brayshay, 1995; Stothers, 1996).

An Icelandic tephra-fall may be widespread in distribution, but a signature may not be preserved in the sediments after the event. If the eruption is small, or occurs sub-glacially, it may not produce any measurable tephra fall (Larsen *et al.* 2001). A further potential complication at an intertidal site will be the tidal state and sea conditions during the height of the tephra fall. A deposit may be spatially discontinuous even at sites proximal to an eruption source. Jóhannesson *et al.* (1981) proposed that the timing of the eruption with regard to local weather conditions, e. g. wind or snow cover (Bergman *et al.*, 2004), is an important factor in tephra preservation. The relationship between prevailing winds, weather patterns and Icelandic tephra dispersion in the North Atlantic is explored by Zielinski *et al.* (1995) and Lacasse (2001).

6.2. The Viðarhólmi tephra analysis

A visual inspection of the exposed Viðarhólmi sediments in the field revealed a layer of reddish pumice, some 6-4 cm thick, about 58-60 cm below the modern marsh surface, and a number of thin laminations in other parts of the sequence. Subsequent examination of the cleaned sediment surface in the laboratory confirmed the presence of a visible white tephra layer, 2-3 mm thick and 81.5 cm down from the surface. Given the presence of these two deposits, and the documented history of tephra fall events in this region, it was decided to attempt to try and locate other layers that may have been preserved in the sequence.

6.2.1. Magnetic susceptibility. Sometimes tephra deposits can be detected using magnetic susceptibility measurements. Although not always conclusive, tephras with a suitable mineralogy can produce a sudden excursion in an otherwise monotonous

series of sequential magnetic susceptibility measurements (Turney and Lowe, 2001; Xia *et al.*, 2004). Many tephras contain significant amounts of Fe and Mn, and both of these are magnetically susceptible and an abrupt increase in their concentration can signal a tephra-rich horizon. In contrast, if the host sediments contain a significant background of magnetic minerals, and if the tephra layer is rich in silicates and present in a high concentration, then a negative excursion can occur (Andrews *et al.*, 2002).

As part of other work attached to this thesis a magnetic susceptibility analysis had been carried out on the Viðarhólmi sediments (See Chapter 5). However, no conclusive result was obtained using this approach to detect possible cryptic tephras. Although some small peaks and excursions were apparent, even the visible tephra layer at 81.5 cm produced no tangible signal (Figure 6.2), so this method was disregarded as being not appropriate for the mineralogy of the Viðarhólmi sediments and Icelandic tephras.

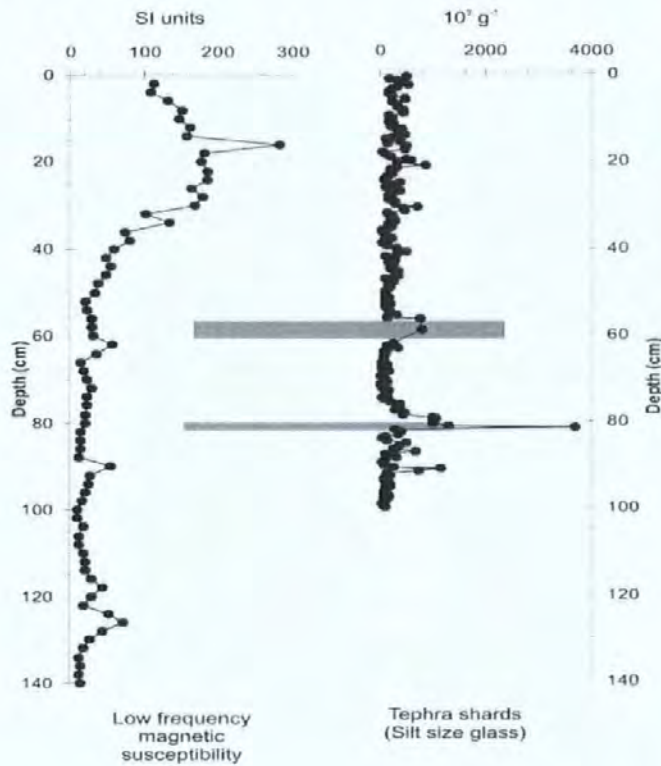


Figure 6.2. Viðarhólmi magnetic susceptibility and glass shard counts. Grey lines (Not to scale) show locations of sea-rafted pumice and the visible tephra layer.

6.2.2 Tephra shard count. The results of a tephra shard count (See Gehrels *et al.*, 2006) carried out by Maria J. Gehrels, University of Plymouth, on the Viðarhólmi sediments have been made available to this study.

Method. The three overlapping Vid-03 monoliths were contiguously sampled every 0.5 cm over the top 100 cm. Difficulty was experienced delimiting the samples in the vicinity of the pumice layer between 59 cm and 61 cm. The samples were ashed at 500°C in nickel crucibles to remove the organic material, and then dispersed in warm hydrochloric acid (10 % v/v). Standardised concentration tablets of *Lycopodium clavatum* spores, commonly used for pollen analysis, were added, and then the samples were dried on a hot plate, before being re-suspended in 500 ml of glycerol. Sub-samples of this suspension were mounted on glass slides, and the tephra shards identified using a polarizing microscope at 400 X magnification and counted in tandem with *Lycopodium* spores. These raw counts were then transformed in to 'shards per gram of dry sediment' values. Three separate glass categories were recorded, brown, pink and clear, but these segregated data did not produce any more tangible information than the total shard numbers per gram.

Results. The total shard data produce an excellent signal that corresponded to the visible tephra layer at 81.5 cm (Figure 6.2). There were also lesser peaks in the counts at 21 cm, 31.5 cm and 41 cm but the only conclusive signal of a tephra layer was the one at 81.5 cm.

6.2.4. Microprobe analysis. After consideration of the total shard information, and the XRF results, nine samples were taken from the monoliths for microprobe analysis. The results reported here are also in Gehrels *et al.* (2006).

Method. A hot acid digestion method (Dugmore, 1989; Dugmore *et al.*, 1992) was used to remove the organic component. After drying at 50°C sub-samples were re-suspended in acetone, and representative un-weathered glass shards, of the 50-100 µm fraction, were selected and manually separated under a low power microscope using a very fine paint brush. To minimise the chance of the material having been transported by water, using the Pettijohn (1975) characterisation, only un-corroded shards that were 'very angular' or 'angular' and exhibiting 'low sphericity' were selected. These were concentrated in acetone, and mounted on preground glass slides using EPO-TEH 301 (Epoxy Technology Inc.) epoxy resin. Once hardened, the resin was ground flat and polished with Kemet® diamond paste (1 µm) to expose the glass shards. A quantified geochemical analysis using an ARL-SEM-Q microprobe was carried out by Gudrun Larsen at the Geological Institute, University of Bergen, Norway. Natural and synthetic glasses and minerals of known composition were used as analytical standards. The standard wavelength dispersal technique was used, with an accelerating voltage of 15 kV, a beam current of 10 nA and a defocused beam diameter of 6-12 µm.

Results. The microprobe analysis indicated that the visible tephra layer at 81.5 cm in the Viðarhólmi section was the Landnám, or Settlement layer, dated to AD 875 ±6 yr (Grönvold *et al.*, 1995; Wastegård *et al.*, 2003). The analysis also confirmed that the geochemistry of the sea-rafterd pumice layer below 58 cm corresponds to the well-documented 'Mediaeval Layer' of AD 1226/27 that was produced by underwater eruptions off the Reykjanes peninsula (Sigurgeirsson, 1992; Haflidason *et al.*, 1992). Of the other samples sent for microprobe analysis many of the shards could not be separated from the geochemical signature of the Snæfellsnes volcanic system, or the identity of the volcanic system could not be reliably established. The sample from the lowest horizon sampled was tentatively identified as coming from the Hekla system, but this information was produced by the analysis of a single shard. However, the sample from 87 cm contained three shards that were identified as originating from the Veidivötn volcanic system (Table 6.1).

Sample depth (cm)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Sum	Interpreted origin of material
9	64.66	0.9	16.28	4.99	0.19	0.64	2.98	4.64	4.51	99.84	Local
	60.78	1.63	15.68	7.01	0.19	1.97	4.24	5.11	2.97	99.62	Local
	60.37	1.57	15.39	8.04	0.27	1.97	4.27	4.42	2.2	98.53	Local
	58.03	1.42	16.06	7.09	0.23	1.84	4.45	4.68	3.34	97.19	Local
	49.64	1.87	14.95	10.16	0.19	6.27	11.75	1.95	0.98	97.79	Local
	49.18	1.63	14.82	10.44	0.2	6.89	12.04	2.37	0.66	98.28	Local
	49.18	1.55	15.18	10.14	0.2	6.72	11.98	2.29	0.94	98.22	Local
	48.84	1.92	15.98	10.61	0.16	6.64	10.74	2.51	1.1	98.55	Local
	48.58	1.66	15.69	9.9	0.16	7.04	11.79	2.35	0.96	98.18	Local
	48.07	2.16	15.76	11.18	0.23	6.89	11.16	2.59	0.99	99.07	Local
	47.9	2	15.81	11.12	0.21	6.76	10.86	2.45	1	98.15	Local
	50.24	1.89	13.69	13.49	0.23	6.78	11.08	2.46	0.22	100.12	VSOS
	48.47	1.85	14.08	11.97	0.15	7.39	12.36	2.01	0.24	98.57	VSOS
Sample of indefinable origin. Mixed glass from catchment											
14	63.5	0.97	16.43	5.88	0.29	0.91	3.56	4.71	3.37	99.66	Local
	59.04	1.49	16.17	7.19	0.15	1.65	4.01	4.62	3.13	97.49	Local
	49.52	1.77	13.65	13.15	0.24	6.7	10.73	1.95	0.21	97.95	VSOS
	49.23	1.72	15.72	10.15	0.21	6.72	11.47	2.25	0.99	98.48	Local
	48.71	2	15.55	10.99	0.13	7.26	11.27	2.52	1.06	99.52	Local
	48.06	1.82	15.5	10.35	0.2	7.56	12.25	2.3	0.54	98.62	Local
	48.04	1.49	15.4	8.94	0.18	9.22	13.26	1.87	0.66	99.11	Local
17.5	47.58	2.25	14.3	12.14	0.25	6.06	11.63	2.43	1.11	97.8	Local
	Sample of indefinable origin. Mixed glass from catchment										
	63.71	0.66	16.2	5.17	0.25	0.53	2.46	5.06	3.83	97.89	Local
	51.01	2.99	14.94	10.8	0.31	3.97	7.89	3.76	1.9	97.61	Local
	47.26	2.86	13.75	12.68	0.29	6.35	12.12	3.79	0.94	100.07	Local
	47.94	1.77	15.87	10.28	0.18	7.34	11.77	2.42	0.5	98.1	Local
	47.86	1.51	15.7	9.12	0.16	8.44	12.93	1.95	0.6	98.31	Local
	48.12	1.4	15.55	9.24	0.18	8.99	13.4	1.9	0.54	99.37	Local
	47.82	1.4	15.47	9.07	0.17	8.49	13.62	1.83	0.51	98.42	Local
	47.86	1.37	15.38	9.35	0.11	8.81	13.29	1.82	0.58	98.6	Local
	47.43	1.37	15.32	9.03	0.12	8.98	12.89	1.69	0.58	97.45	Local
	47.4	1.12	15.95	9.23	0.17	8.52	13.03	2.08	0.22	97.77	Local
	70.2	0.26	14.68	2.19	0.02	0.21	0.84	4.49	4.59	97.53	VSOS
21	49.62	2.24	13.47	13.3	0.26	6.33	10.37	2.62	0.33	98.56	VSOS
	49.86	1.58	13.87	12.32	0.21	7.37	11.52	1.95	0.14	98.86	VSOS
	48.57	1.54	14.48	11.57	0.21	7.53	12.28	2.03	0.24	98.48	VSOS
	Sample of indefinable origin. Mixed glass from catchment										
	49.23	1.8	14.9	10.54	0.25	6.74	11.68	2.33	0.97	98.48	Local
	48.99	1.52	15.82	10.14	0.26	7.99	12.4	2.08	0.48	99.71	Local
	48.34	1.67	15.55	10.52	0.23	7.67	12.33	2.32	0.49	99.15	Local
30.5	46.93	3.16	13.54	12.35	0.22	6.1	11.72	2.53	0.85	97.44	Local
	46.61	3.11	12.84	12.52	0.25	6.52	11.9	2.8	0.93	97.5	Local
	46.27	3.13	13.46	12.55	0.15	6.43	11.81	2.66	0.92	97.41	Local
	49.81	1.85	13.18	12.13	0.16	6.81	11.47	2.51	0.27	98.22	VSOS
63	Sample of indefinable origin. Mixed glass from catchment										
	54.21	1.65	12.22	11.43	0.15	5.67	10.53	1.96	0.21	98.07	Local
	49.67	1.76	15.17	10.4	0.19	5.67	10.63	2.1	1.06	96.69	Local
	48.81	1.8	15.4	10.24	0.18	6.49	10.25	2.38	1.11	96.69	Local
	Mixed glass from catchment										
	50.77	1.41	13.71	12.23	0.16	7.1	11.3	2.07	0.11	98.9	Reykjanes
	49.45	1.85	13.54	12.82	0.22	6.43	11.23	2.23	0.27	98.08	Reykjanes
	49.32	1.84	13.8	12.56	0.19	6.48	11.11	2.28	0.26	97.86	Reykjanes
	47.97	1.85	13.33	12.43	0.28	6.34	10.97	2.33	0.24	95.78	Reykjanes
	70.19	0.29	13.49	3.78	0.11	0.13	1.25	5.11	3.35	97.74	VSOS
63	60.82	1.22	16.05	6.48	0.21	1.26	4.38	4.86	2.77	98.09	Local
	46.93	4.29	13.01	14.69	0.23	5.34	9.85	2.76	0.72	97.86	Katla
Sea-transported pumice. From the Reykjanes system, AD 1226-1227.											

Table 6.1. Microprobe analysis of the individual Viðarhólmi tephra shards. Data from Gehrels *et al.* (2006). Interpreted origin is confirmed when the volcanic system is named, e. g. Hekla, or Local = Glass from the Snæfellsnes volcanic system; VSOS = Glass from an undefined volcanic system outside the Snæfellsnes system.

Sample depth (cm)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Sum	Interpreted origin of material
81.5	70.79	0.4	14.58	2.34	0.1	0.18	0.9	4.81	4.81	98.96	Torfajökull
	70.53	0.9	14.19	2.36	0.08	0.16	0.91	5.02	4.93	99.12	Torfajökull
	70.21	0.26	13.85	2.29	0.06	0.15	0.9	4.2	4.47	96.42	Torfajökull
	69.93	0.26	14.45	2.23	0.08	0.2	0.86	4.14	4.54	96.73	Torfajökull
	69.87	0.15	14.36	2.34	0.09	0.14	0.88	4.37	4.58	96.82	Torfajökull
	69.55	0.27	14.39	2.23	0.12	0.15	0.86	4.37	4.57	96.54	Torfajökull
	49.31	1.77	13.43	12.93	0.2	6.8	11.7	2.25	0.23	98.66	Veidivötn
	49.17	1.88	13.52	12.69	0.2	6.26	11.53	2.15	0.23	97.66	Veidivötn
	49.06	1.62	13.35	12.9	0.2	6.65	11.45	2.24	0.2	97.7	Veidivötn
	48.66	1.79	13.61	13.02	0.25	6.46	11.32	2.17	0.26	97.59	Veidivötn
	48.52	1.75	13.89	13.14	0.22	6.66	11.63	2.17	0.27	98.29	Veidivötn
	48.36	1.94	13.93	12.72	0.2	6.76	11.39	2.37	0.23	97.92	Veidivötn
Settlement Tephra Layer. Both components securely identified – AD 875 ±6 yr.											
87	49.25	1.4	13.82	12.84	0.18	6.57	10.88	2.04	0.16	97.18	Veidivötn
	48.51	1.88	14.09	12.15	0.17	7.37	12.53	2.11	0.22	99.07	Veidivötn
	47.91	1.78	14.92	12.23	0.23	7	11.02	2.19	0.21	97.52	Veidivötn
	49.83	1.41	15.89	8.74	0.14	7.19	13.69	2.27	0.39	99.6	VSOS
	48.69	1.83	14.87	10.81	0.16	6.38	11.17	2.64	1.01	97.58	VSOS
	48.04	1.13	15.59	9.64	0.16	8.09	13.57	1.96	0.29	98.51	VSOS
Potential tephra layer from the Veidivötn system. Approximate age of AD 600-400 or older.											
91	54.78	3.99	11.47	13.02	0.25	2.05	9.45	2.79	1.04	98.88	Hekla
Potential tephra layer from the Hekla system. Approximate age of AD 300-500 or older.											

Table 6.1. (Continued) Microprobe analysis of the individual Viðarhólmi tephra shards. Data from Gehrels *et al.* (2006). Interpreted origin is confirmed when the volcanic system is named, e. g. Hekla, or Local = Glass from the Snæfellsnes volcanic system; VSOS = Glass from an undefined volcanic system outside the Snæfellsnes system.

Interpretation. The location of the sample at 87 cm in the stratigraphy suggested this material was deposited some time before AD 870, and if the accumulation rate between the Settlement Layer and the Mediaeval Layer is considered then an age AD 763 to AD 778 is indicated for 87 cm. Using this as the youngest possible date an examination of the literature found two possibilities. Hafliðason *et al.* (2000) documented two tephra layers originating from the Veidivötn system, with similar geochemistry as the shards from 87 cm. These were deposited in northeastern Iceland at Lake Myvatn between AD 100 and AD 600 (Table 6.2).

Tephra layer	Date	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
Viðarhólmi 87 cm	NK	48.56	1.69	14.28	12.41	0.19	6.98	11.48	2.11	0.20
Twilling 'c' layer	~AD 550	49.55	1.78	14.17	13.05	0.22	6.52	11.69	2.45	0.23
V-150	~AD 150	49.91	1.80	13.44	11.53	0.21	6.82	12.39	2.44	0.21

Table 6.2. The two tephra layers that are possible matches for Viðarhólmi 87 cm shards. Note data are the means of the three Viðarhólmi 87 cm results, and the Hafliðason *et al.* (2000) data is the mean of 13 analysis.

Unfortunately, the information on both these Veidivötn tephra is limited, and it is not known how far west they were dispersed. Lake Myvatn is ~ 350 km east of the Viðarhólmi site. The data from the Viðarhólmi 87 cm sample are only produced by three individual microprobe results and no replicate analysis has been performed. This notwithstanding, it is felt that there is a strong possibility that the shards in the Viðarhólmi 87 cm are from the same eruption that produced the Twilling 'c' layer at Lake Myvatn.

6.2.5. Accumulation rates at Viðarhólmi. The analysis of the tephra and pumice layers have produced two very well dated chronological markers, and some encouraging indications of a third. Assuming this lower layer is the AD 550 Twilling layer a rudimentary age-depth model for the last 1500 years can be created and accumulation rates calculated for the Viðarhólmi site (Figure 6.3).

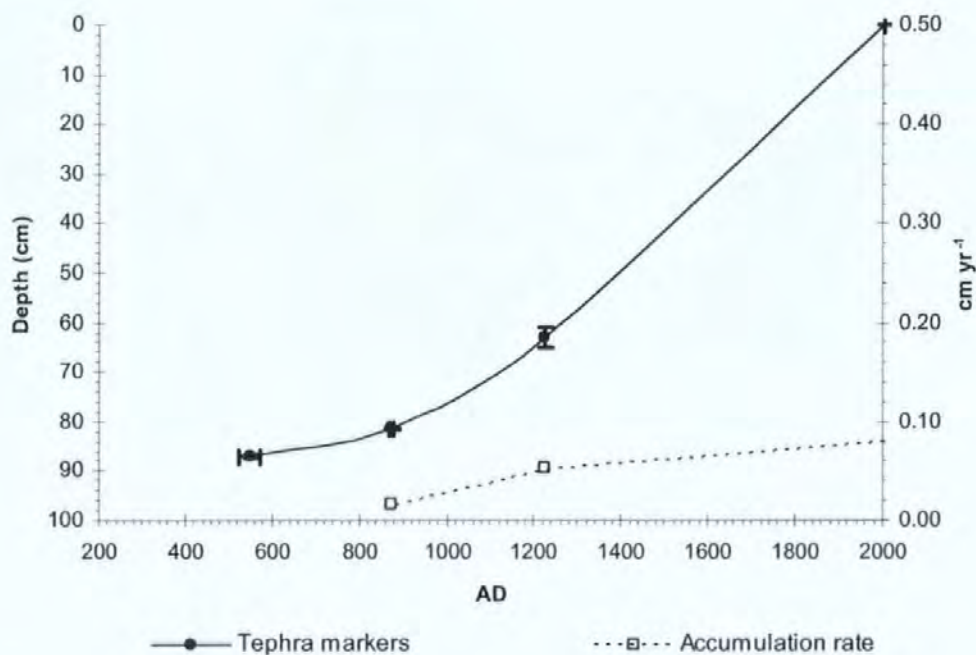


Figure 6.3. Age-depth model and accumulation rates for the Viðarhólmi site using the tephra chronology. The point suggested to be the AD 550 Twilling layer is given an arbitrary ± 25 yr uncertainty. The Mediaeval Layer is given a vertical uncertainty of ± 2 cm.

6.3. Pollen as a chronological marker

Pollen analysis is one of the oldest methods of investigating past changes in vegetation cover and landscape evolution. Its basic principles are covered by a wealth of literature, and for an introduction to this subject the reader is directed to Moore *et al.* (1991) and Faegri and Iversen (1989). In addition to being an important tool in palaeoenvironmental research, under some circumstances pollen can be used as a means to estimate the age of sections of sediment sequences. For example, the widespread and synchronous signal around 5000 Cal BP of the European decline of *Ulmus* (elm) can be used to mark this approximate time in all pollen diagrams that span this event (Parker *et al.*, 2002; Lamb and Thompson, 2005). In the more recent epoch, the rise in *Ambrosia* (ragweed) pollen, marking deforestation following the European settlement of eastern North America in the eighteenth century, has been successfully used in western North Atlantic sea-level studies (Gehrels *et al.*, 2002; Gehrels *et al.*, 2005). In the UK, Long *et al.* (1999) used *Pinus* (Pine) and *Spartina anglica* (Cord Grass) to help constrain the history of sea-level change in Poole Harbour during the 18th and 19th centuries.

This dating method relies on two principles:

1. A historical record must exist that documents and dates an event that is likely to have produced major changes in the local or regional pollen rain.
2. There must be sufficient recognisable pollen preserved in the sediments for the signal to be detected.

The existence of such events can be researched in local historic records, and other archives, before a pollen analysis is attempted. Unfortunately, until the samples are examined under a microscope the preservation level and concentration of the pollen grains in the sediments will remain unknown. The second requirement proved to be a problem with the pollen analysis of the Taf sediments. A reconnaissance analysis showed that there was a lack of recognisable pollen in the Welsh sediments. In the case of the Viðarhólmi sediments, there were some low numbers of pollen grains preserved in the sediments, but a lack of suitable 'pollen-events' in the later record precluded any chronological use of the data. There are no significant changes in the few recent Icelandic pollen diagrams available, and of those that do exist many are fragmentary, or have poor age control. Therefore, the Viðarhólmi and Taf pollen data are not presented here as a dating tool. However, pollen analysis did provide an excellent chronological marker in the Arne sediments.

6.4. The Arne pollen analysis

6.4.1. Site background. Changes in the local percentages of *Pinus* (Pine) and the exotic salt-marsh grass *Spartina anglica* (Cord grass) pollen were used by Long *et al.* (1999) to date recent sediments in Poole Harbour. They attributed a local increase in *Pinus* pollen to the regional expansion of conifer plantations between the mid-1700s and the mid-1800s. This is a signal that has been reported in pollen diagrams for several parts of the UK (Scaife, 1980; Barber, 1981; Waton, 1983). *Spartina anglica* is a hybridization between *S. alterniflora* and *S. maritima* (Ferris *et al.*, 1997) and first appeared in the Solent during the mid-1800s. It spread west arriving in Poole Harbour around 1890 and expanding rapidly during the subsequent decade (Hubbard, 1965; Raybould, 1997).

6.4.2. Method. The Arne sequence was sampled at one centimetre intervals using a 2 cm³ volumetric measure, and the subsequent pollen preparation was the standard procedure of Moore *et al.* (1991). The samples contained a high proportion of fine clay and needed extended microsieving in addition to hot HF (60%) treatment. The samples were mounted in silicone oil and the exotic marker (*Lycopodium clavatum*) method was used to standardise the results to sediment volume (Moore *et al.*, 1991). Counts were made of *Lycopodium clavatum* spores, *Spartina anglica* pollen, *Pinus* pollen and 'other land pollen' using 400 X magnification. In most samples in the upper 50 cm of the section approximately 300 pollen grains were counted. Although not needed for this simple dating exercise, to qualify as 'other land pollen' the grains were identified to family level or better, and they were not recorded if they were damaged or degraded to the extent as to render them unidentifiable.

The pollen grains were identified using standard pollen keys (e.g. Faegri and Iversen, 1989) and type slides prepared for this study and held by the School of Geography at the University of Plymouth. The type slides used to confirm the identification of *Spartina anglica* were prepared from fresh pollen harvested from living plant specimens during 2005. Identifying individual species of Poaceae, the grass family, is not an easy task but it was possible to distinguish the *Spartina anglica* pollen from other grass and cereal pollen grains using two indicative features, grain size and pore morphology (Figure 6.3).

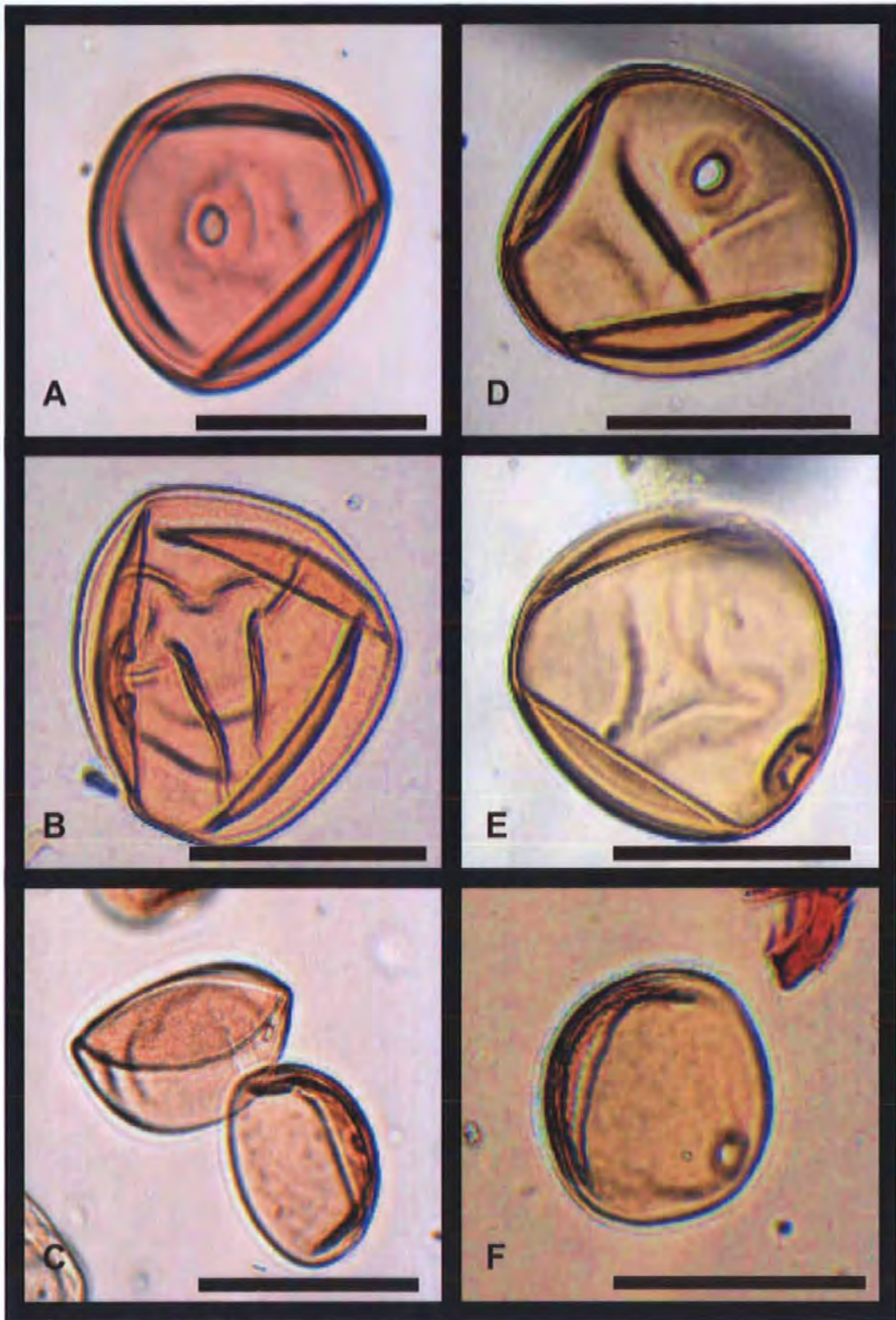


Figure 6.4. The indicative features of size and pore morphology used to identify *Spartina anglica* pollen. *Puccinellia maritima* pollen shown for comparison. Black scale bars are 50 μm . Images: A and B, *Spartina anglica* pollen harvested from fresh plants; C, *Puccinellia maritima* pollen harvested from fresh plants; D and E *Spartina anglica* pollen found in the Arne sediments; F, *Puccinellia maritima* pollen found in the Arne sediments. Images taken at 400 X magnification using a Leica system.

To qualify as *Spartina anglica* the grain had to be larger than 70 μm , and the morphology of the exine in the vicinity of the pore had to conform to that shown in Figure 6.3; i.e. a large, well developed annulus. Of the other large Gramineae pollen found in the Arne sediments none exceeded 65 μm , and none of these grains had the annulus development as shown in Figure 6.4 A, B, D and E

6.4.3 Results. A significant presence of pollen grains was found in all the samples from above 65 cm (Figure 6.5). The total land pollen (TLP) grain count at 64 cm was $21 \times 10^3 \text{ cm}^{-3}$ rising rapidly up profile to 37×10^3 per cm^{-3} at 62 cm, with an average of 38×10^3 per cm^{-3} throughout the sediment section. Below the 65 cm level no identifiable grains were found.

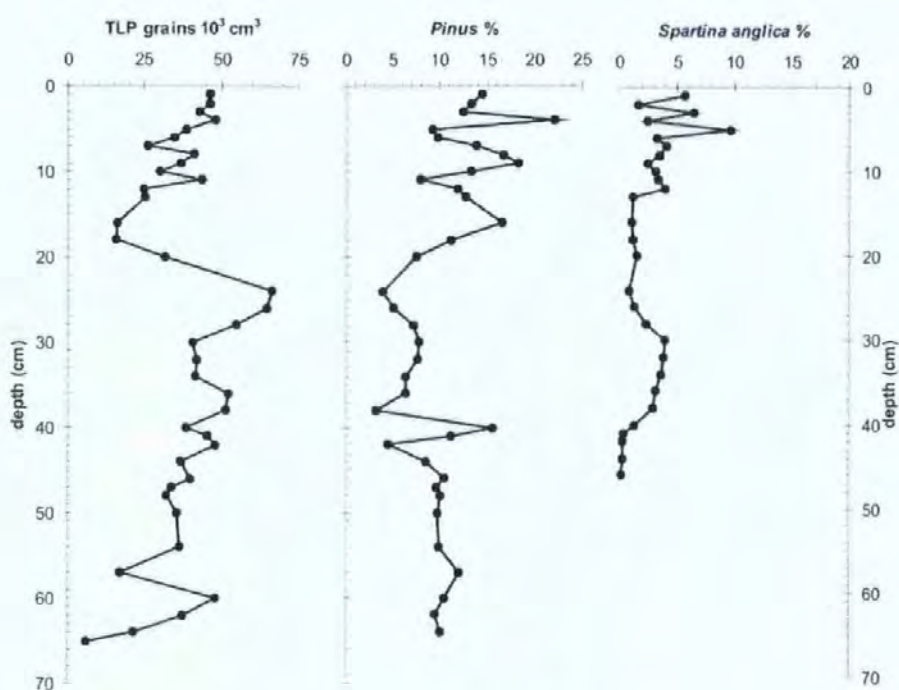


Figure 6.5. Arne *Pinus* sp. and *Spartina anglica* pollen. Total land pollen (TLP) calculated as grains cm^{-3} , and *Pinus* sp. and *Spartina anglica* shown as a percentage of the TLP count.

Above 65 cm the *Pinus* sp. numbers were already established at around 10 % of the pollen count, and no significant change was found in the percentage of this taxon over the time covered by this sequence. Long *et al.* (1999) place the rise in *Pinus* sp. pollen in Poole Harbour around the mid-1700s, so it is likely that the sediments above 65 cm were deposited after AD 1750. The first *Spartina* grains were found at 46 cm, and by 40 cm its presence had rapidly increased to over 1 % of the TLP sum. This signal is interpreted as the documented first establishment, and

subsequent expansion, of *Spartina* in the 1890s as found by Long *et al.* (1999), and therefore a date of AD 1895 $\pm$ 5 yr is assigned to the 40 cm horizon.

6.5. Spheroidal carbonaceous particles

Spheroidal carbonaceous particles (SCPs) are formed from the incomplete combustion of fossil fuels at high-temperature. Along with inorganic ash spheres (IAS), produced by the fusion of minerals present within the fuel, SCPs form fly-ash and can be transported long distances (Jones *et al.*, 1997; Rose *et al.*, 1999; Yang *et al.*, 2001). They have no natural sources, and therefore provide an unambiguous indicator of atmospheric deposition contemporaneous to the activity of the industrial sources (Rose, 2001). Once entombed they are not susceptible to post-depositional alteration, degradation or movement within a sediment column as a result of changing pore-water conditions, e.g. pH or redox (Rose *et al.*, 2003).

Once released into the atmosphere SCPs are rapidly dispersed and can be deposited many hundreds of kilometres from their original source (Rose, 2001). Consequently SCPs have been found in sediments in most areas of the world, both remote and industrialised, e.g., Scandinavia (Larsen, 2003), eastern Europe (Solovieva *et al.*, 2002), North Africa and the Middle East (Rose *et al.*, 2003), China (Wu *et al.*, 2005), North America (Kralovec *et al.*, 2002) and South America (Chirinos *et al.*, 2006). The record of SCP deposition is longest, and most extensive, in northern Europe and the UK, reflecting the long history of heavy industry and the high-temperature burning of fossil fuels in this region (Rose *et al.*, 1999; Tyler *et al.*, 2001; Yang *et al.*, 2001; Rose and Rippey, 2002; Rose *et al.*, 2005).

There is some local variation to the amplitude and precise chronology of the European regional SCP signals, and proximal sources with have a disproportionate influence on local records. The concentration levels found in European lake records for the peak emission period of 1970-1980 are typically around 20-60 $\times 10^3$ SCPs in 1 g dry-mass (DM) of sediment, but this figure will be strongly influenced by geographic location, altitude, proximity to source and local sediment focusing. For

example, Larsen (2003) found $240 \times 10^3 \text{ g DM}^{-1}$ in contemporary sediments at a site close to Bergen in Norway, but in contrast Rose and Rippey (2002) found less than $15 \times 10^3 \text{ g DM}^{-1}$ at a pristine site in north-west Scotland in sediments deposited during the period of the maximum regional deposition in the late 1970s. However, many studies have demonstrated that there is an underlying regional SCP chronology for the UK and north-western Europe, but with local variations in amplitude and short-term timings (Yang *et al.*, 2001; Yang and Rose, 2002; Rose and Appleby, 2005; Muri *et al.*, 2006).

A typical European SCP record will start around 1830-1850, and then SCPs will increase rapidly as the burning of coal by industries involving blast furnaces, and later electrical power generation using both coal and oil, expanded and responded to the social demands of the 19th and 20th centuries. In the post 1945 era most European sediment records show a rapid increase in SCP deposition as post-war rebuilding and industrial expansion drove the industrial use of fossil fuels upward. In response to growing environmental concerns in the 1960s and 1970s, the enactment in a number of countries of various national legislative measures compelled a wide scale reduction in smoke-stack emissions in Europe, (e.g., the UK Clean Air Act of 1968). This resulted in an apparent instantaneous fall to 1945, or lower levels, in many UK SCP records in the late 1970s and early 1980s (Rose, 2001).

Concurrent with the pollen analysis of the Arne and Viðarhólmi, SCPs were counted from the same slides. This avoided the need for extra samples and preparation, and provides a quantified record of SCPs in a known volume of sediment. If, as in the case of the Arne sequence, the bulk density is known of each sample the data can be expressed volumetrically or as SCP numbers per gram (g DM^{-1}). Other preparation and counting methods (e.g. Rose, 1994; Yang, *et al.*, 2001) use similar sequential acid digestion techniques as standard pollen preparations to remove the organic fraction and silicates, but they do not use an exotic marker approach. Instead they rely on counting of all the SCPs present in a standardised sample to enable the results to be expressed as SCPs g DM^{-1} .

6.5.2. The Arne SCP results. The Arne SCP record started at 57 cm, but it was not until 50-48 cm that the count increased to over $1.5 \times 10^3 \text{ cm}^{-3}$ (Figure 6.6). Above this level the particle numbers peaked at 41 cm and then declined, before rising abruptly to the major peak of this record of $12.7 \times 10^3 \text{ cm}^{-3}$ at 5 cm. These data were

converted to SCPs g DM^{-1} using the sediment bulk density measurements calculated for the Arne ^{210}Pb samples. Rose and Appleby (2005) suggest that the late 20th century deposition peak occurred during the late 1970s or early 1980s in this part of southern England, and the records from two of their sites, Abbotsbury on the Dorset coast and Harbour Farm on the Isle of Wight, are shown in Figure 6.6.

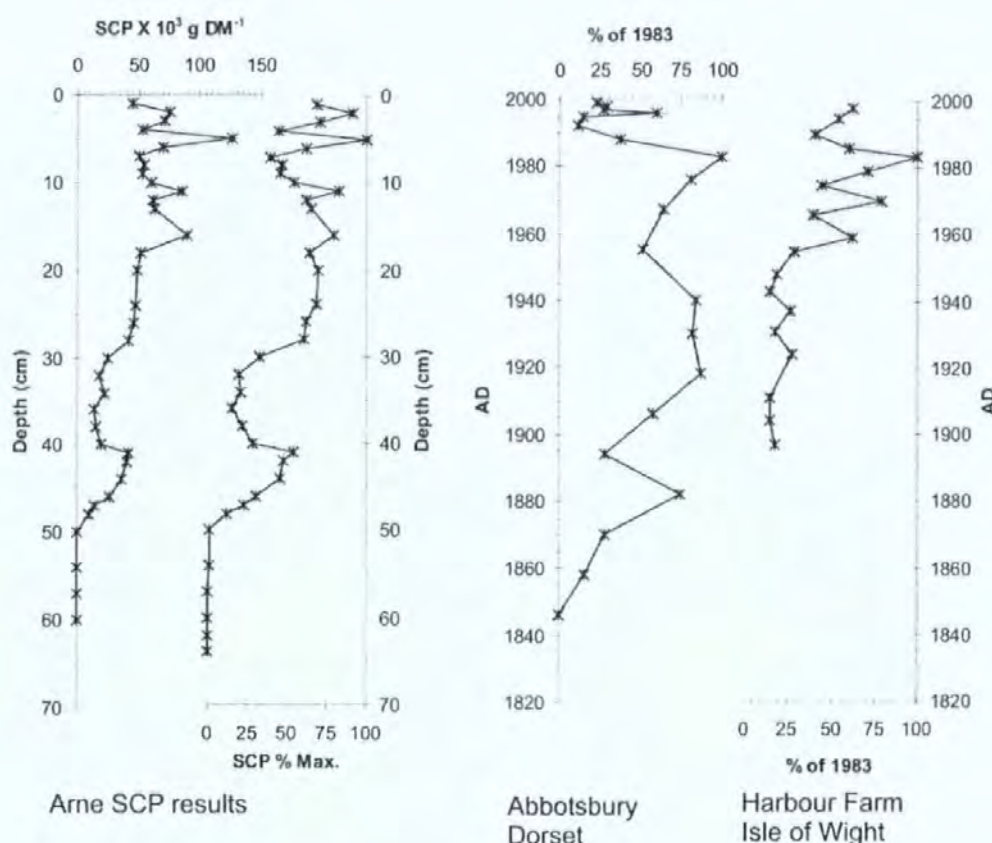


Figure 6.6. The Arne SCP results, presented alongside the ^{210}Pb dated records from the sites of Rose and Appleby (2005) at Abbotsbury, in Dorset, and Harbour Farm, on the Isle of Wight. The Arne data are shown as both SCP numbers in g DM^{-1} and as % of the maximum concentration. The Abbotsbury and Harbour Farm data are shown as a % of the concentration in the sediments dated by Rose and Appleby (2005) to being deposited in 1983. This is the form that these data were supplied in (Neil Rose, personal communication, 2006).

Three SCP age-marker horizons are identified in the Arne sequence (After Rose and Appleby, 2005):

1. 50 cm = 1850 ± 25 yr. The first appearance of SCPs in the sedimentary record.
2. 28 cm = 1950 ± 15 yr. The late 20th century or post WW2 rise.
3. 5 cm = 1983 ± 5 yr. The late 20th century maximum deposition peak.

6.6. The Viðarhólmi SCP record

A reconnaissance examination of the upper 20 cm of the Viðarhólmi found a short SCP record. The count numbers were low when compared to UK and mainland European records, and the curve profile does not fit well with the expected regional model. Unfortunately, there are no published SCP records from Iceland, and the closest well-dated SCP records are from sites in Northern Scotland (e. g. Yang *et al.*, 2001; Rose and Rippey, 2002; Rose *et al.*, 2004) some 1100 km away. If the Scottish records are considered (Figure 6.7) some broad agreement is evident in the lower and middle parts of the Viðarhólmi record, but there is no evidence of the substantial reduction in the numbers near the surface that is a defining feature of the published regional SCP deposition histories. However, if it can be independently dated using the other dating methods investigated in this thesis, the Viðarhólmi record could be used as a rudimentary SCP 'master curve' for other studies in this part of Iceland.

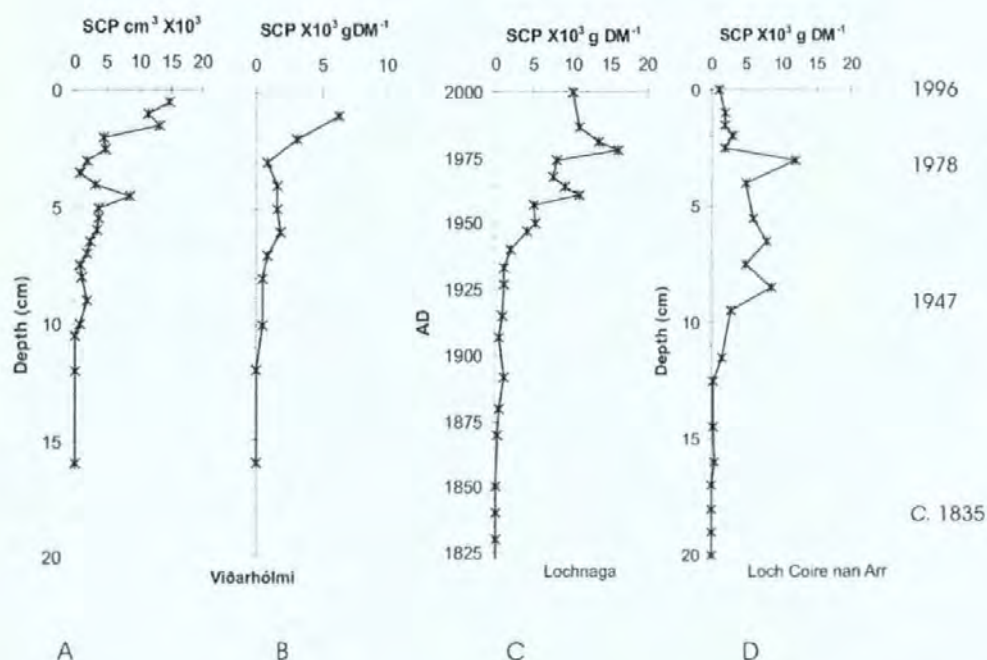


Figure 6.7. The Viðarhólmi SCP record and two SCP records from northern Scotland. Panels A = Viðarhólmi SCPs per cm^3 ; B = Viðarhólmi SCPs as g DM^{-1} ; C = Dated (^{210}Pb) SCP record from Lochnaga (Rose *et al.*, 2004) D = SCP record from Loch Coire nan Arr (Rose and Rippey, 2002). Dates shown here in D are those assigned by Rose and Rippey (2002) to the Loch Coire nan Arr SCP curve from other dated Scottish SCP records.

6.7. Chronologies using pollen analysis and SCPs

The examination of the upper 20 cm of the **Viðarhólmi** could not be corroborated by an independent SCP record. The Arne pollen and SCP analysis produced four chronological markers for the upper section of the sequence. These are shown in Figure 6.8.

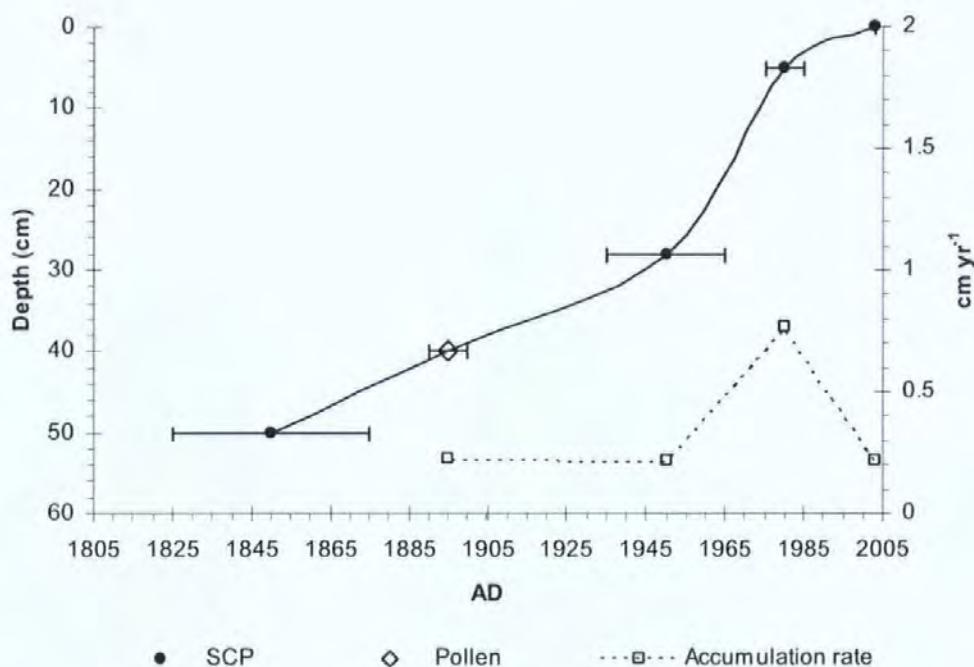


Figure 6.8. The Arne chronological markers derived from the analysis of pollen and SCPs.

6.8. Discussion and synopsis

One well-dated layer of sea-rafterd pumice, one very well defined tephra layer and one tentatively identified tephra layer have been used to construct a chronology for Viðarhólmi sequence. Although this method can not achieve the resolution of other dating methods, e.g. high-resolution ^{14}C dating, the results are subject to less age uncertainty. However, this method does depend on the prior identification, and secure dating, of each individual tephra layer in a 'Master Section' before it can be used to date the sediments in a sequence being investigated, and this original dating may be subject to a chronological uncertainty. This aside, when a well-defined historical tephra layer like the Icelandic Settlement Tephra or Mediaeval Layer can be used, the chronological precision of the date obtained is probably

better than the age-range represented by the vertical uncertainty of the sample in the stratigraphy.

The local lithology at the Viðarhólmi site created a problem associated with isolating discrete tephra layers. In most situations when tephra analysis is being undertaken a key issue is finding the volcanic material amongst a mass of minerogenic and organic sediments (See Caseldine *et al.*, 1999; Blockley *et al.*, 2005; Andrews *et al.*, 2006; Gehrels, M. J. *et al.*, 2007). Even in ombrotrophic bog deposits where the lithology of the host sediment is very different to tephra, many centimetres of peat may have to be examined to find a few elusive glass shards. This process is often likened to the proverbial 'needle in a haystack' task, but in the case of the Viðarhólmi sediments it was more like trying to find one particular needle hidden in a stack of needles.

Volcanic terrains dominate the geology of Iceland, and the Viðarhólmi salt-marsh abuts an early Holocene lava field. The site is within sight of the Snæfellsnes volcano, which last erupted only around 1750 years ago, and much of the coastal area and the inland fluvial catchments contain numerous lesser cones, of which have been active during the Holocene. Consequently the mineralogy of the Viðarhólmi salt-marsh sediments is dominated by volcanic glasses, pumice and igneous rock sands. The challenge here is to find the layers of unweathered air-fall tephra from sources outside the Snæfellsnes system in a ground-mass of texturally mature volcanic sands and eroded glass. The failure of the magnetic susceptibility method to find more tephra layers is most likely not because of the lack of tephra falls at the site. The problem is to distinguish between the high background levels and the subtle signals of microtephra layers.

The manual shard count featured the same problem as the magnetic susceptibility. This method works well with organic rich deposits, for example a peat core. In this case it is a relatively simple matter to isolate volcanic glass from the peat. However, when working with the Viðarhólmi salt-marsh sediments a decision had to be made with every shard beyond just the simple recognition of volcanic glass. Using a subjective selection process, based on the unweathered appearance of the shards, and the Pettijohn (1975) characterisation approach of 'very angular', 'angular' or 'sub-angular', was not a conclusive way of differentiating air-fall shards from

material derived from the erosion of local bedrock. A certain amount of misinterpretation was inevitable, but some notable success was achieved here. This issue of reliably distinguishing the signal of a tephra layer from the background values in volcanic, and other mineral-rich, and magnetically susceptible, terrains is a topic that would benefit from further development and research.

The potential of pollen and SCPs as chronological markers has been explored in this chapter, and it is apparent that both these methods can be used to estimate deposition ages for recent salt-marsh sediments. Unfortunately, it is also evident that the fundamental requirements needed for both these methods are not present at all three sites used in this study, and these issues will limit the areas to which these methods can be applied. Low numbers of preserved pollen, or SCPs, in a sediment sequence will prevent or severely constrain an analysis, and without a means of converting the data into a chronological age the analysis is of little value. The lack of suitable existing well-dated records that can be used for correlation with a working data set is viewed as a fundamental constraint to all unique event dating methods. When tephra analysis is used, the isolating of a discrete layer in the sediments will not produce a deposition age unless one has already been established in a well-dated 'master sequence'.

Although there may be some inherent constraints to the methods, the use of tephra as an event dating tool has been successfully demonstrated at the Viðarhólmi site, and both the other methods produced good results at the Arne site. At the Arne site age estimates are produced for four sediment horizons deposited during the last 175 yr. This demonstrates how these methods can be used to help produce a chronology beyond the normal range of ^{210}Pb dating and other radionuclide based methods, and could be potentially used to 'bridge' some of the problematic sections of the ^{14}C calibration curve. The same is true of the use of the Icelandic tephra chronology. The high precision dates that a tephra analysis can produce make ideal independent chronological markers to cross-check a high-resolution ^{14}C chronology, and this approach will be demonstrated in Chapter 8.

In summary, Chapter 6 has investigated three forms of 'event dating' that, given ideal circumstances, can produce very precise and accurate results. In less than ideal circumstances it is still possible for useful chronological information to be

obtained. In the case of pollen and SCPs, results can be obtained using normal laboratory equipment. All three dating methods are independent of the need for organic carbon, and the stability of a signal in the sediments is, in the main, not influenced by the geochemistry of the sediments. These particles do not become entrained in the pore-water so post-deposition migration is not an issue once the material have been entombed. However, the mechanical degrading of both pollen grains and SCPs is possible if the sediments are very minerogenic, especially if the sedimentation rate is low. In addition, tephra shards can be damaged and fragmented if subjected to re-working by marsh surface water flows.

Chapter 7

Stable particle fallout events 2: stable Pb

Atmospheric dust contains traces of metals derived from both natural and anthropogenic sources. This chapter examines the potential of using the signals of changes in the anthropogenic fraction of atmospheric Pb fallout as age markers in a salt-marsh sediment sequence. As an introduction the first sections present an overview of the history of anthropogenic atmospheric Pb emissions, and the potential use of isotopic Pb analysis for dating purposes. Then the results of the Pb analyses of the sediments from all three of the study sites are presented and evaluated in section 7.4.

7.1. Stable Pb and anthropogenic activity

7.1.1. Salt marshes and metal deposition. Salt-marsh sediments can record past anthropogenic activity associated with heavy metals (Cundy *et al.* 1997; French 1997). Mining and industrial activity have been shown to contribute to the heavy metal load in intertidal sediments (e.g. Vale and Harrison, 1994; Cundy *et al.*, 1997; Pirrie and Camm, 1999; Turner, 1999; Cearreta *et al.*, 2000; Pirrie *et al.*, 2002). The concept of a metal 'pollution-based chronology' has been successfully applied to intertidal sediments in a number of studies, such as those by Varekamp *et al.* (1992) in Connecticut, USA, Berry and Plater (1997) in northeast England and Price *et al.*, (2005) in southwest England. However, these studies involved the analysis of predominantly water-borne metal pollution signals that were confined, in the main, to one catchment and produced by local, relatively short term, anthropogenic industrial activity. We focus here are the signals of more widespread atmospheric Pb fallout histories from dispersed anthropogenic activities. These activities were, to some extent, regionally synchronous (Renberg *et al.*, 2001), and may, in some cases, have continued over decades, or even centuries. These signals chart events that include the emergence of Old World metal working, the expansion of industrial coal burning and the rise, and subsequent decline, in the use of Pb as a vehicle fuel additive (Brännvall *et al.*, 1999; Bindler, *et al.*, 2001; Bollhöfer and Rosman, 2001).

7.1.2. World Pb emissions. The metal Pb has been emitted as an atmospheric pollutant since the dawn of metallurgy (Figure 7.1), but is also produced by other human activities and, in minor concentrations, by some natural sources (Table 7.1). The continuous natural weathering of land surfaces has ensured that there has always been a low-level concentration of atmospheric Pb (Shotyk *et al.*, 1998). The other main natural contributor to atmospheric Pb loading is from volcanic emissions, but this is more episodic (Matsumoto and Hinkl  y, 2001). However, there are indications that signals of specific past eruptions can be detected if the background level is subdued (See Hong *et al.*, 1996; Vallelonga *et al.*, 2003).

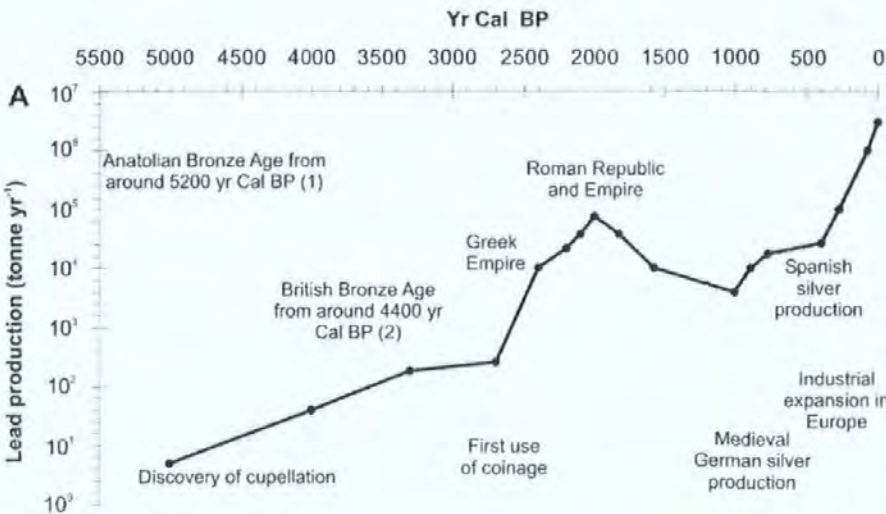


Figure 7.1. World Pb production. After Settle and Patterson (1980), adapted from Reuer and Weiss (2002) with additions (1) Şahoğlu (2005) and (2) Northover (1999).

In antiquity, Pb was extracted and worked as a valuable metal in its own right, and emitted as a by-product of other metal working processes. In its natural state Pb is often found associated with Cu and Sn ores, is difficult to remove and will remain as a contamination in any alloy (e.g., bronze) produced from these base metals. In addition, many Au and Ag deposits are found in quartz sulphide lodes containing Pb. The refining process used to extract the noble metals, cupellation, was discovered around 5000 yr. In this processes the ore is heated to a high temperature and the Pb is oxidised. It is then burnt off, and is released into the atmosphere in particulate form (Weiss *et al.*, 1999). Since the Bronze Age, apart from the late 20th century when fuel additives were the dominant contributor (Table 7.1), non-ferrous metal industries have been the primary anthropogenic source of atmospheric Pb (Reuer and Weiss, 2002).

Natural source	10 ⁶ kg yr ⁻¹	Anthropogenic source	10 ⁶ kg yr ⁻¹
Volcanic emissions	0.5 - 6.0	Vehicle fuel additives	248.0
Windblown soils and rock dust	0.3 - 7.5	Non-ferrous metal industries	30.1 - 69.6
Wild fires	0.1 - 3.8	Coal combustion	1.8 - 14.6
Biogenic particulates	0.0 - 3.3	Steel and iron industries	1.1 - 14.2
Sea-salt spray	0.0 - 2.8	Cement production	<0.1 - 14.2
		Oil combustion	0.9 - 3.9
		Refuse incineration	1.6 - 3.1
		Wood combustion	1.2 - 3.0
		Other miscellaneous	3.9 - 5.4
Total	0.9 - 23.5		288.6 - 352.5
Grand total			288.5 - 376.0

Table 7.1. World Pb emissions in 1983. Data from Reuer and Weiss (2002).

The Greeks, and later the Romans, used large amounts of Pb in their metal industries, and during the height of the Roman Republican Period, around 2000 yr BP, world Pb production is estimated as being around 80,000 ton yr⁻¹ (Weiss *et al.*, 1999). Much of this production was from mines in the Iberian Peninsula (e.g., Rio Tinto ore field; Nriagu, 1983; Leblanc *et al.*, 2000). After the decline of Rome the world Pb production fell until the medieval revival and expansion of the metal working industries in Europe between AD 900 and AD 1200 (Brännvall *et al.*, 1999). After this time there were some temporary reductions in Pb production influenced by the economic declines in Europe associated with the Black Death in the mid 1300s and the Hundred Years War between France and England (1337-1453). However, from around AD 1100 the overall world use of Pb, and the associated atmospheric pollution, continued to increase slowly until the late Middle Ages (Figure 7.1), when a major expansion in metallurgy spread across Europe. This rate of growth remained relatively stable until the rapid development of new metal-based industries during the 19th century, the subsequent increase in the use of coal and the introduction of leaded petrol in the 1930s (Smol, 2002).

A number of sedimentary records of late Holocene Pb deposition have now been published that cover the rise of metallurgy in western Europe (e. g. Shotyk *et al.*, 1998; Brännvall *et al.*, 1999; Dunlap, *et al.*, 1999; Shotyk *et al.*, 2001; Renberg *et al.*, 2002). In the main there is good agreement of these sedimentary records with the estimated chronology of World Pb production history (Figure 7.1), first published by Settle and Patterson (1980), and later adapted by Weiss *et al.* (1999), Reuer and Weiss (2002) and others.

A wide-scale regional development of metallurgy started in Europe during the Late Bronze Age which has resulted in a near-synchronised contemporaneous atmospheric Pb signal in many sedimentary records (Dunlap, *et al.*, 1999; Brännvall

et al., 1999). At some sites the contribution from proximal metal working sources dominates the sedimentary record, but this notwithstanding, the timing of the changes in ancient local Pb deposition are mostly in accord with the wider regional atmospheric signal (e. g. Monna *et al.*, 2004; Le Roux *et al.*, 2004). Likewise, in the later eras, a high level of synchronicity can be found across Europe in the timing, during the late 18th and early 19th century, of increased Pb deposition from metal working and coal combustion, and the more recent signal of the emergence and expansion of the use of Pb additives in vehicle fuels (Figure 7.2) in the 20th century (Rosman *et al.*, 2000; Renberg *et al.*, 2001; Reuer and Weiss, 2002).

Leaded petrol was introduced in the early 1920s (Rosman *et al.*, 2000), and by the early 1970s petrol additives comprised 65-85 % of all anthropogenic atmospheric Pb emissions (Reuer and Weiss, 2002). The maximum world consumption occurred in the late 1960s and early 1970s. During this time over 10⁵ metric tonnes of Pb metal were being processed per year to supply the world-wide demand for leaded petrol, of which 80 % was burned solely in the USA (Nriagu, 1983). Since 1970 the USA and Western Europe have progressively reduced the use of leaded fuel and emissions have consequently fallen significantly (Figure 7.2), but in some less technologically developed areas, e.g., parts of Eastern Europe, the regular use of leaded fuel has persisted into the 21st century (Reuer and Weiss, 2002).

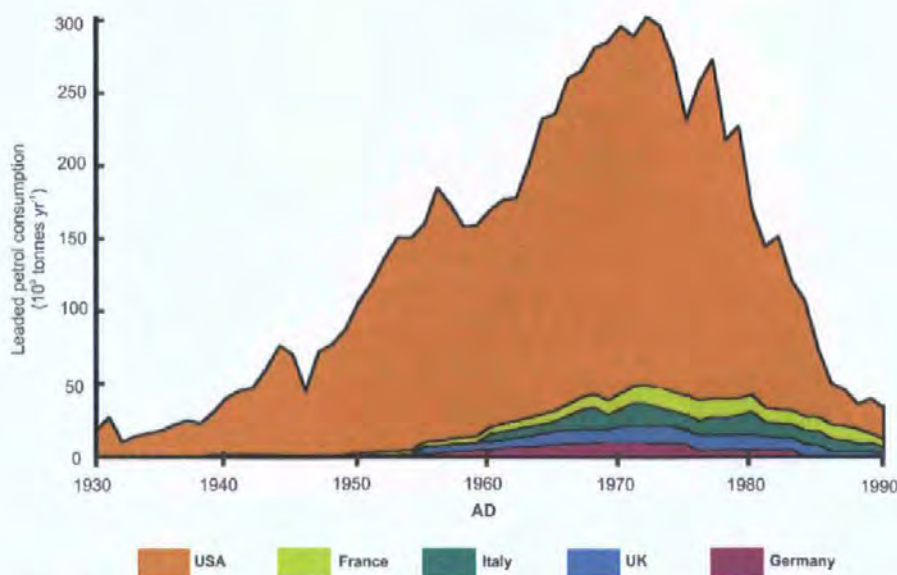


Figure 7.2. Leaded petrol consumption in the USA and the four countries with the highest use in Western Europe, 1930-1990. Adapted from Reuer and Weiss (2002).

7.2. Pb as a chronological marker

7.2.1. Pb deposition histories. Pb has much to recommend it as a 'chemostratigraphic' marker (Renberg *et al.*, 2001). It is freely emitted into the atmosphere by many anthropogenic activities as both fine particles and aerosols, and it is easily scavenged by precipitation. Once deposited and entombed in the sediments it is considered to be immobile (MacKenzie *et al.*, 1998; Shotyk *et al.*, 1998), and, in its stable form, to be relatively inert under normal environmental conditions of pH and redox (Smol, 2002). A number of studies have examined the use of Pb production and fallout histories as a means of dating sediments. The works of Shotyk *et al.* (1998) in the Jura Mountains, and Farmer *et al.* (1999) and Eades *et al.* (2002) in Scotland have shown the potential for this metal as a chronological marker in lake and peat-bog sites. A good example of a lake record is the varve-dated Pb deposition history from Lake Koltjärn, Sweden (Renberg *et al.*, 2002) shown in Figure 7.3. This spans the last 2500 yr, and its profile agrees very well with the Pb production history, first proposed by Settle and Patterson (1980), shown in Figure 7.1. In addition to lakes and peat bogs, and of notable importance to this current study, robust records of past atmospheric Pb deposition have been found in salt-marsh sediments at a number of geographically dispersed sites; e.g., Long Island Sound (Cochran *et al.*, 1998), Gironde Estuary, France (Alfonso *et al.*, 2002), Delaware (Kim *et al.*, 2004), Concepción Bay, Chile (Muñoz *et al.*, 2004), Nova Scotia (Gehrels *et al.*, 2005) and Iceland (Gehrels *et al.*, 2006).

An ideal sedimentary chronostratigraphic marker is not confined to one area, or one time period. If a marker signal is detectable at a number of dispersed sites it facilitates cross-checking of dates, and if a sequence of events is available for correlation this will produce a more robust result than a single point. Atmospheric Pb fallout meets both these criteria. There is evidence for a long history (Figure 7.2) of significant airborne anthropogenic environmental contamination by Pb (Dunlap *et al.*, 1999), and this signal is not just confined to northern Europe or the Northern Hemisphere (Bollhöfer and Rosman, 2000). For example, a wide-spread signal of recent atmospheric Pb fallout is found in both the Americas (e.g., Marcantonio *et al.*, 2002; Reuer and Weiss, 2002; Muñoz *et al.*, 2004), and prolonged Pb fallout sequences have been detected at remote sites in the Antarctic (Boutron *et al.*, 1994; Planchon *et al.*, 2003) and Greenland (Hong *et al.*, 1994; Shotyk *et al.*, 2003).

7.2.3. Stable isotopes and the provenancing of Pb sources. A further advantage of the use of Pb as a chronological marker is the possibility for the metal in a sample to be matched to the likely location of the original ore body, and in some circumstances it can be assigned to an individual pollution source or event (Smol, 2002). Pb provenancing works because, like many elements, natural Pb contains a number of different isotopes, and these ratios can be used to 'finger print' a sample and establish the geological character of the ore body that was used to produce the metal. The original primordial isotope is ^{204}Pb , but the radiometric decay, via intermediate daughters of ^{232}Th , ^{235}U and ^{238}U has created the three radiogenic stable Pb isotopes, ^{206}Pb , ^{207}Pb and ^{208}Pb . Once radiometric stability is achieved the isotopic ratio is fixed in the ore, and under normal circumstance no fractionation occurs when the metal is extracted and processed (Rohl, 1995).

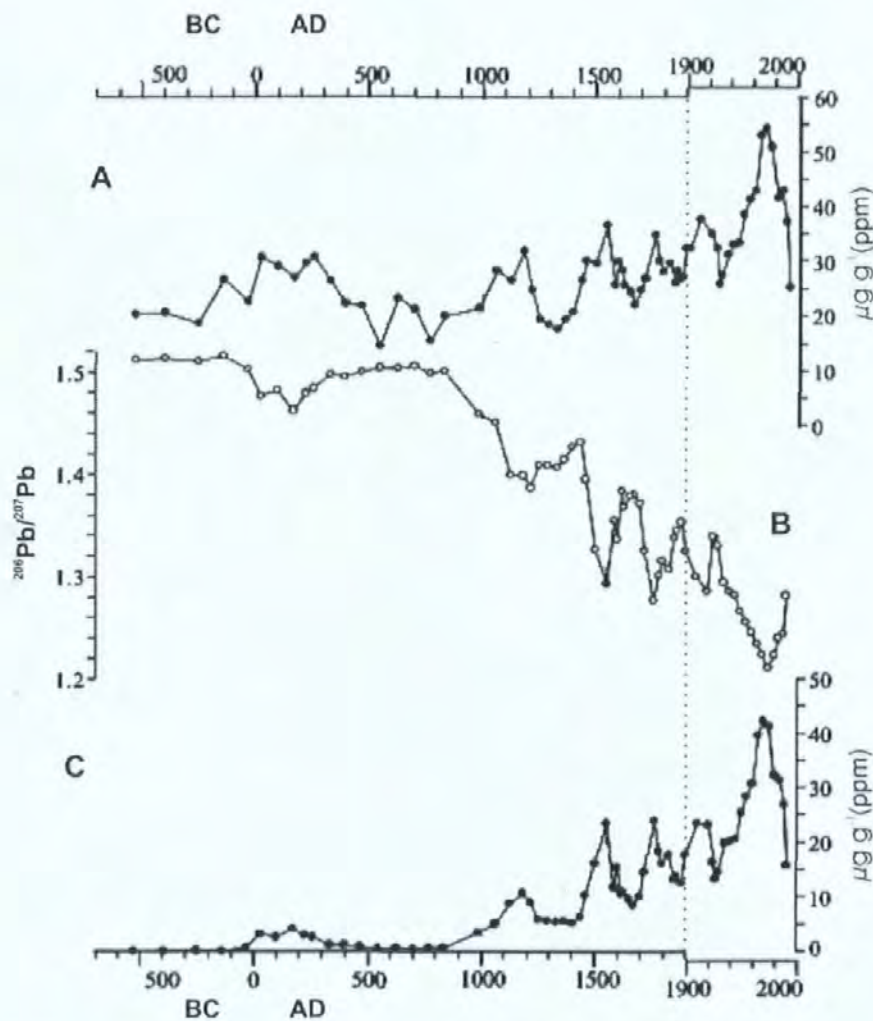


Figure 7.3. Varve dated Pb deposition since 500 BC in Lake Koltjärn, Sweden. Adapted from Renberg *et al.* (2002). Panels: A; Total Pb. B; $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. C; Pollution or anthropogenic Pb. Note change in X axis scale after AD 1900.

The analyses of long-term deposition records from lakes (Brännvall *et al.*, 1999; Renberg *et al.*, 2002), peat bogs (Shotyk *et al.*, 1998) and ice cores (Hong *et al.*, 1994) have shown that there has been a natural presence of atmospheric Pb for all of the Holocene. During this time Pb-lead-enriched minerogenic dust, produced by the normal erosion of soils and rocks (See Table 7.1), would have been the main contributor (Shotyk *et al.*, 1998). These atmospheric dusts would have originated in the world's arid zones like the Saharan region (Weiss *et al.*, 1999). Until around 3000 cal BP it is estimated that the atmospheric $^{206}\text{Pb}/^{207}\text{Pb}$ ratio over Europe would have been relatively radiogenic with values of 1.19 to 1.21 (Shotyk *et al.*, 1998; Weiss *et al.*, 1999).

After 3000 cal BP the consensus of sedimentary records indicate the atmospheric $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has maintained a long-term decreasing trend; e. g. the Lake Koltjärn (Sweden) record shown in Figure 7.3, B (Renberg *et al.*, 2002). This decreasing trend in $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values is interpreted as being the result of the anthropogenic release of Pb depleted in heavy radiogenic isotopes. The trend, profile and event chronology of Lake Koltjärn record is in overall agreement with long-term Pb isotope records from other Scandinavian sites (e.g., Brännvall *et al.*, 2001) and those from other areas of Europe (e.g., Jura Mountains, Switzerland, Shotyk *et al.*, 1998; Basque Country, southern France, Monna *et al.*, 2004; Aran Islands, western Ireland, Schettler and Romer, 2006; Lindow bog, northern England, Le Roux *et al.*, 2004).

Isotopic data can be used to calculate the different relative fractions contributing to the total Pb present in sediments. Often there will be contributions from two or more Pb sources and isotopic analysis may give some means of differentiating between proximal minerogenic Pb and more distal regional atmospheric anthropogenic Pb sources. The Lake Koltjärn record in Figure 7.3 illustrates how this can work. If the absolute $^{206}\text{Pb}/^{207}\text{Pb}$ ratios reported by Renberg *et al.* (2002) for the ancient Lake Koltjärn sediments are examined the values appear to be somewhat high when compared to other studies (e.g., Shotyk *et al.*, 1998). There is also some disagreement here with the absolute $^{206}\text{Pb}/^{207}\text{Pb}$ ratio reported for the modern period by other studies (i.e. Rosman *et al.*, 2000) (See Figure 7.3). To better elucidate the Lake Koltjärn Pb isotope record, Renberg *et al.* (2002) used a simple mixing model described by the following expression:

7.1

$$(C_{\text{sample}} \times R_{\text{sample}}) = (C_{\text{natural}} \times R_{\text{natural}}) + (C_{\text{pollution}} \times R_{\text{pollution}})$$

where C = Pb concentration and R = $^{206}\text{Pb}/^{207}\text{Pb}$ ratio.

Renberg *et al.* (2002) concluded that their simple binary model indicated that there had been some significant contribution from a local radiogenic Pb source to the Lake Koltjärn sediments, possibly from the bedrock. The calibrated anthropogenic atmospheric fallout curve in Figure 7.3C shows an increase in atmospheric Pb deposition dated by varve chronology to between BC 50 and AD 200. Renberg *et al.* (2002) used the isotope ratios to interpret this excursion as the influence of Pb depleted in radiogenic isotopes of the type mined in Spain and used extensively by the Romans (Klein *et al.*, 2004) during the height of the Empire in Europe.

The ore fields in the Iberian Peninsula have isotopic signatures that are subtly different to the ore fields located in the Americas and Australia (Table 7.2), exploited in later eras. This type of knowledge has facilitated the use of isotopic Pb analysis to help establish provenance for archaeological artefacts that contain traces of Pb (Rohl, 1995; Scaife, 1998; Begemann *et al.*, 1999 Klein *et al.*, 2004). To further this work, an extensive Pb isotope data set has been produced by the Isotrace Laboratory at Oxford for the European and the Mediterranean ore fields used by ancient metal workers (e.g., Stos-Gale *et al.*, 1995, 1996; Rohl, 1996).

7.2.4. The modern era and identifying petrol Pb. As the industrial use of Pb has increased over the last 2000 yr, the location, and isotopic composition, of the exploited Pb deposits in the world have changed from being mainly European (Reuer and Weiss, 2002; Smol, 2002) to those located in the Americas and the Australian deposits in the Broken Hill mining district (Table 7.2).

Country	Tonnage produced in 1972	Main mining district	Host rock age	$^{206}\text{Pb}/$ ^{204}Pb	$^{206}\text{Pb}/$ ^{207}Pb	$^{208}\text{Pb}/$ ^{206}Pb
USA	619,000	Missouri & Mississippi	Pennsylvanian	21.78	1.385	1.872
		Idaho	Precambrian	16.45	1.052	2.21
Australia	451,000	Mount Isa	Precambrian	16.08	1.037	2.236
		Broken Hill				
Canada	419,000	British Columbia	Precambrian	16.68	1.064	2.194
		New Brunswick	Ordovician	18.39	1.160	2.096
Peru	208,000	Cerro de Pasco	Miocene	18.86	1.200	2.076

Table 7.2. Isotopic values of the major world Pb ore bodies exploited in the late twentieth century. From Chow *et al.* (1975).

Consequently, the isotopic signature of the signal in the sedimentary record has shifted accordingly. In the last 200 yr the isotopic signature of atmospheric Pb became progressively more radiogenic (Figure 7.3B) until federal controls on Pb

emissions were implemented in both the USA and Europe during the 1970s and 1980s (Smol, 2002). These controls produced an abrupt shift to less radiogenic values (Reuer and Weiss, 2002), but it must be noted here that the peak deposition of petrol Pb occurs in most European records some 10-20 years after the absolute maximum of total Pb deposition from the atmosphere. This can be seen in the long-term Lake Koltjärn record (Figure 7.3), but it is more apparent in higher resolution records (e.g., the 200 yr deposition record of Pb in Alpine snow shown in Figure 7.4; Rosman *et al.*, 2000).

The first leaded petrol was sold in the USA in February 1923 (Nriagu, 1990), and introduced in the UK during January 1928, but not marketed by British Petroleum (BP) until 15 April 1931 (Bamberg, 1994). The extent of the pollution from vehicle fuel emissions, and the subsequent phasing out of leaded petrol, has been successfully monitored using Pb isotopes (Hurst 1996; Wu and Boyle 1997). Blais (1996) showed that the USA was the main source of atmospheric Pb over eastern Canada, and Véron *et al.* (1994) mapped the contamination of the North Atlantic using isotopic fingerprinting, and it is possible to apportion Pb pollution to different sources. For example, in Europe the petrol additives used were derived mainly from Australian ore which has a lower $^{206}\text{Pb}/^{207}\text{Pb}$ than the Mississippi Valley ores, commonly used for fuel additives in the USA (Weiss *et al.*, 1999; Reuer and Weiss, 2002).

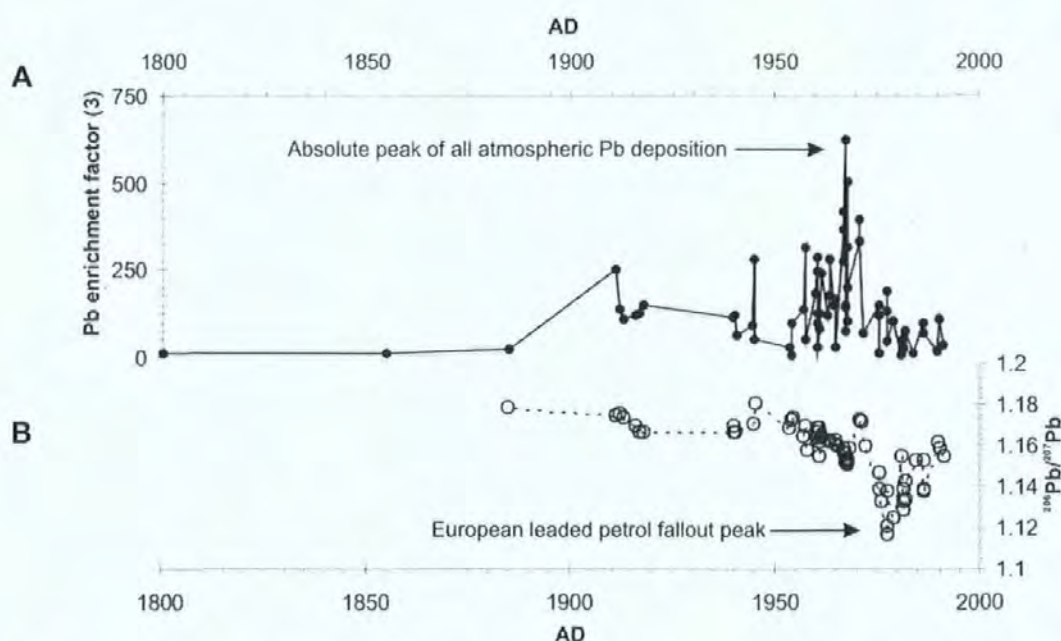


Figure 7.4. Pb contamination of Alpine snow (Mont Blanc) during the last 200 years. Panel A, Pb enrichment; Panel B, $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. From Rosman *et al.* (2000).

The signal of the maximum European petrol Pb emissions in the mid 1970s is dated to around 1977 in the Alpine snow record of Rosman *et al.* (2000) from Mont Blanc. Values for $^{206}\text{Pb}/^{207}\text{Pb} < 1.12$ are interpreted by Rosman *et al.* (2000) as the signal of isotopically depleted radiogenic Australian Pb fuel additives. Unlike the Lake Koltjärn record (Figure 7.3) there appears to be no significant local minerogenic contribution to the Mont Blanc Pb. Flament *et al.* (2002) determined the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the modern European atmosphere to be between 1.106 and 1.124 over the UK, and 1.134 to 1.172 over the more continental regions of the mainland. It can be seen in Figure 7.4 that these values corresponded to the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio measured in the upper snow layers of the Mont Blanc sequence.

7.2.5. Isolating atmospheric Pb enrichment. There are a number of alternative methods that can be used to quantify the amount of Pb that is in excess of the concentration expected to be supported by the local geology. This excess fraction is assumed to have been transported into the sediments by water, deposited directly from the atmosphere or a combination of both. In some situations, changes in the contributions from local geological sources to the total Pb in the sediment may overshadow the fallout signal. If the available dating information is associated with the regional atmospheric fallout history then this signal must be isolated from any proximal contributions, and this usually means some form of calibration may need to be used. If a simple binary model is assumed, and isotopic values can be assigned to the two fractions available, then $^{206}\text{Pb}/^{207}\text{Pb}$ ratios can be used to evaluate the relative contributions from each source. This works well if there is sufficient difference between the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the individual fractions, as with the Lake Koltjärn record (Renberg *et al.*, 2002) shown in Figure 7.3.

If the isotopic method of evaluating the relative contributions is precluded, or there is a desire for an independent calibration, there are other geochemical approaches to this problem. Rosman *et al.* (2000) quantified the atmospheric Pb contribution in their Mount Blanc sequence by calibrating the sample data using an estimate of the natural background crustal ratio of Pb to Ba: $\text{Pb}/\text{Ba}_{\text{sample}}$ divided by $\text{Pb}/\text{Ba}_{\text{crustal}}$ where the $\text{Pb}/\text{Ba}_{\text{crustal}}$ is taken as 0.0294. These data were used to calculate the enrichment factors shown in Figure 7.4. Unfortunately, this method uses published (e.g., Wedepohl, 1995), generalised mean values of the continental crust elemental ratios, and under many circumstances this approach will not detect subtle changes in the distal fraction, and, in addition, it does not respond well to variations, or extremes, in local geochemistry (Weiss *et al.*, 1997).

One of the simplest methods of quantifying the excess Pb in sediments is the traditional normalising approach of relating the concentration of the element of interest to a physical property like grain size, or the concentration, in the sample, of a conservative element that can be used as a proxy for changes in the local minerogenic contribution (Loring, 1991). In its simplest form this is applied as a simple ratio (e.g., pollution metal/standard) but if the local natural background, i.e. the pre-anthropogenic ratio, can be established using samples from the lower sections of a sequence then more sophisticated methods can be used; e. g. $(\text{Metal/standard})_{\text{sample}}$ divided by $(\text{Metal/standard})_{\text{background}}$ (Shotyk *et al.*, 1998). Aluminium has commonly been used to normalise metal concentrations, e. g. Weiss *et al.* (1999) and Schettler and Romer (2005), but other elements have been shown to more applicable in some circumstances (Loring, 1991). Some examples are; lithium, Aloupi and Angelidis (2001), scandium, Shotyk *et al.* (1998) and Monna *et al.* (2004), titanium, Görres and Frenzel (1997) and Shotyk (2002), and zirconium, Shotyk *et al.* (2000).

7.3. The stable lead analysis: Methodology

7.3.1. Sampling and digestions. The monoliths from the Arne and Viðarhólmi sites were sequentially sampled for geochemical analysis every 1 cm, but, because of its apparent slower accumulation rate, the upper 15 cm of the Taf section was sampled at 0.5 cm intervals samples to improve the resolution. Only plastic or surgical grade stainless steel tools were used to cut the sediments, and great care was taken to avoid airborne contaminations at all stages. All reagents used in the analysis were of Aristar® quality and the Pb concentration in all the de-ionised water used, and acid-water process blanks, was typically less than 1 ppb. All the glassware and Teflon® vessels used were double acid washed in 3 % HNO₃ prior to use.

The sediments were oven dried at 50°C for 5 days, disaggregated, homogenised and then stored in screw topped tubes. Subsequently 0.3 g of the dried sediment was weighed into a 30 ml Teflon® screw-topped digestion vessels, 4 ml of concentrated HNO₃ added and the vessels sealed. The tubes were left for 24 hours, before being vented and re-sealed, and then heated to 75 °C on a hotplate for 24 hours. After cooling to room temperature the digestions were transferred to new 30 ml polystyrene tubes using 4 x 5 ml measured flushes of de-ionised water. Acid-water process blanks were inserted at intervals of 15-20 samples, and each batch began and finished with a blank. After standing for 24 hours the samples were centrifuged and the liquid was decanted off. This was then divided into two portions; one of 10 ml, for total concentration analysis, and the remainder for the stable lead isotope analysis.

7.3.2. Total concentration analysis. Total Pb and eleven other elemental concentrations were determined using an ICP-MS Plasma Quad PQ2+ Turbo and an ICP-AES Liberty 200 (Varian, Surrey, UK). The operating conditions are given in Table 7.3.

ICP-MS PlasmaQuad PQ2+ Turbo		
Gas Flows -	Coolant / l min ⁻¹	13.5
	Auxiliary / l min ⁻¹	1.0
	Nebuliser / l min ⁻¹	0.75
Forward power / kW		1.35
Spray Chamber type		Single pass with Impact Bead
Nebuliser type		Burgener
Sample uptake / mL min ⁻¹		1.0
Dwell Time / ms		40 for analytes 10 for internal standards
Internal Standards		100 ng mL ⁻¹ In and 200 ng mL ⁻¹ Tl
Elements determined		Pb, Cd, Cu, Zn, Ag
ICP-AES Liberty 200		
Gas flows	Plasma / L min ⁻¹	15.0
	Auxiliary / L min ⁻¹	1.50
	Nebuliser Pressure / kPa	150
Photomultiplier voltage / V		650
Viewing Height / mm above load coil		7
Spray chamber type		Sturman-Masters
Nebuliser type		Cross-flow
Elements determined		Al, Sr, K, Li, Mn, Sc, Ti, Zn

Table 7.3. Instrumental setup and operating conditions for the ICP-MS and ICP-AES instruments.

To minimise instrumental drift, two internal standards, indium (In) and thallium (Tl), were used. Both 100 ng mL⁻¹ In and 200 ng mL⁻¹ Tl were added to all samples, blanks and standards. These internal standards were chosen because they covered the mass range of the analytes and, from previous semi-quantitative reconnaissance analyses, they were found not to be naturally present in the sample digests at a significant concentration. Calibration standards were prepared by serial dilution of stock standards (10,000 mg L⁻¹, Aristar, BDH, Poole, UK) using 2 % HNO₃. Check standards were run every 15 samples to monitor instrumental drift, which was < 5 % for the ICP-MS instrument and < 10% for the ICP-AES instrument.

If any check standard was found to drift above these values, re-calibration was performed and the previous 15 samples analysed again. To check the recovery of lead during the digest, 16 full process replicate samples of the certified river sediment BCR-320 were inserted at random into the sample batches. The certified concentration for Pb in BCR-320, as soluble in Aqua regia, is 30 mg kg⁻¹. The analysis of the check samples gave a mean concentration for Pb of 25.7675 mg kg⁻¹ confirming that the less aggressive hot HNO₃ digest used here was achieving around 86 % Pb recovery of the certified concentration. Of those 16 BCR-320 samples the maximum deviation from the mean was 2.56 %, and one standard deviation from the mean was 0.83. Zn was very problematic on the ICP-MS because of a polyatomic interference from ³²S¹⁶O₂⁺ on ⁶⁴Zn⁺. This effect was worst in the Icelandic samples, and was thought to be caused by the high levels of volcanic products in this environment. This interference was not as apparent for the Taf and the Arne samples. As a precaution, it was decided to use the Zn data from the ICP-AES for all three sites.

7.3.3. Stable lead isotope analysis. The relative ratios of ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were determined using a sector field VG Axiom Multicollector (MC) ICP-MS (Thermo Elemental, Winsford, UK). Initial experiments determined that all the solutions from the Icelandic samples, and those from a significant number of the other samples, were below the ideal minimum working concentration of Pb for this instrument, i.e., 200-300 ppb. In addition, the variability of the sample matrix created analytical problems. Therefore, chromatography was used to clean and pre-concentrate (6:1) the solutions using Eichrom Technologies 2 ml pre-packed columns containing di-*t*-butylcyclohexano 18-crown-6 in isodecanol supported on a substrate of inert polymeric beads (Horwitz *et al.*, 1994). A vacuum box was used to assist the flow through the columns and ammonium oxalate (0.1 M) was used as a complexing agent to elute the Pb. Higher concentration samples from the Taf and Arne sequences were diluted using ammonium oxalate (0.1 M) where necessary to standardise all solutions to 400-1000 ppb after processing.

The operating conditions for the MC-ICP-MS are shown in Table 7.4. The instrument was initially tuned before each batch using a multielement solution (1 ng g⁻¹) of Mg, Co, In, Pb and U for optimal sensitivity, stability and peak shape, and then the Faraday cup array was aligned using a solution of 300 ng g⁻¹ of Hg, Tl and Pb. Once operational, the accuracy and precision were checked by the replicate analysis of a

known certified standard (e.g., National Institute of Standards and Technology (NIST) 981 Pb Standard Reference Material (SRM)).

RF Forward power (W)	1300	Plasma gas (l min ⁻¹)	14
Reflected power (W)	≤ 10	Auxiliary gas (l min ⁻¹)	0.85
Spray chamber	Coupled cyclonic and bead impact, cooled to -5 °C	Nebuliser gas (l min ⁻¹)	0.83
Torch	Fassel quartz	Sampler and skimmer cones	Ni
Dwell time	On peak 10s, Off peak 5s	Cycles	25
Nebuliser	Glass Expansion 0.2 ml min ⁻¹ Micromist, natural aspiration		
Isotopes monitored	202Hg, 203Tl, 204Hg, 205Tl, 206Pb, 207Pb, 208Pb		

Table 7.4. The operating conditions for the VG Axiom MC-ICP-MS instrument.

During the analysis NIST 981 SRM, diluted to 500 ng g⁻¹ using 0.1 M ammonium oxalate was run periodically, i.e. every eight samples or fewer. To facilitate mass bias correction all samples and standards were spiked with 0.5 ml NIST 997 Tl SRM at 250 ng g⁻¹, and the ²⁰⁵Tl/²⁰³Tl ratio measured for each sample and standard concurrently with the determination of the lead isotopes. The dedicated Axiom software was used to calculate the internal correction for the baseline Pb and Tl isotopes, and then, to correct for mass bias, the data were entered into the Russell correction equation:

7.2

$$^{208}\text{Pb}/^{206}\text{Pb}_{\text{Cor}} = \frac{^{208}\text{Pb}/^{206}\text{Pb}_{\text{Meas}}}{\left(\frac{^{205}\text{Tl}/^{203}\text{Tl}_{\text{Meas}}}{^{205}\text{Tl}/^{203}\text{Tl}_{\text{Cert}}}\right)^{\left(\frac{1\text{n}(\text{RAM}^{208}\text{Pb}/\text{RAM}^{206}\text{Pb})}{1\text{n}(\text{RAM}^{205}\text{Tl}/\text{RAM}^{203}\text{Tl})}\right)}}$$

where *Cor* is the corrected isotope ratio, *Meas* is the measured isotope ratio, *Cert* is the certified isotope ratio and *RAM* is the relative atomic mass. For an explanation of this approach, and the use of the Russell correction equation, see Yang and Sturgeon (2003) and Clough *et al.* (2006). The stable isotopes are presented in this thesis as ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb, with the full tabulated data appearing in Appendix 2. Other combinations of the three isotopes are possible (e.g., ²⁰⁸Pb/²⁰⁷Pb) but the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb configuration was chosen to facilitate comparisons with the published literature (e.g., Stos-Gale *et al.*, 1995; Rohl, 1996;, Renberg *et al.*, 2002;, Shotyk *et al.*, 2005).

7.4. The Taf stable lead analysis

7.4.1. Results: elemental concentrations. K and Al were the most abundant elements observed in the sediments (Figure 7.5). However, the K levels remained relatively constant, but Al showed a marked decrease in concentration from 30 cm depth toward the surface. The Cu and Zn concentrations were in the 10-80 mg kg⁻¹ range, with an abrupt peak of 175 mg kg⁻¹ around 24-26 cm. Cu and Zn concentrations were similar to those of Pb. Cu, Zn and Pb all had similar curves in depth profiles suggesting common deposition histories (Figure 7.5). Li, Al and Sc also had similar curves with a steady decline in concentrations from 30 cm to the surface.

To further elucidate the deposition histories, and to help select the best elements to normalize the Pb concentration against, a Pearson correlation matrix was constructed (Table 7.5). This confirmed the close relationship between the variability in Li and Al, and the validity of grouping Pb with Zn and Cu. It also showed that a significant negative correlation existed between Cd and Li, ($r = -0.77$, $p = 0$), and to a lesser extent with Ag and Li ($r = -0.43$, $p = 0$). Both Li and Al were positively correlated with K. In the heavy metal group, Cu and Pb had a very significant positive correlation ($r = 0.94$, $p = 0$), and both Cu and Pb were significantly correlated ($r = 0.52$, $p = 0$ and $r = 0.59$, $p = 0$) with Zn. There was an insignificant correlation between Pb and Li, ($r = -0.154$, $p = 0.156$) and no correlation between Sc and Pb ($r = -0.091$, $p = 0.4$). This suggests that the variance in the Pb concentrations, and to a lesser extent, Cu and Zn, is somewhat decoupled from the Li, Al and K group.

The concentrations of the elements in the Li, Al, K and Sc group are assumed to be responding primarily to changes in the flux of water-borne minerogenic materials, and therefore offer the potential (See section 7.2) of being used to normalize the Pb concentration values, and thus remove changes in these data associated with local sediment fluxes. Loring (1991) cautions against the use of Sc in estuarine sediments because of its close association with hydrous Fe oxides and the difficulty of obtaining precise and accurate Sc concentration data, and K is not used because of its strong primary association with feldspars. Therefore, Al and Li were chosen to normalize the Pb values.

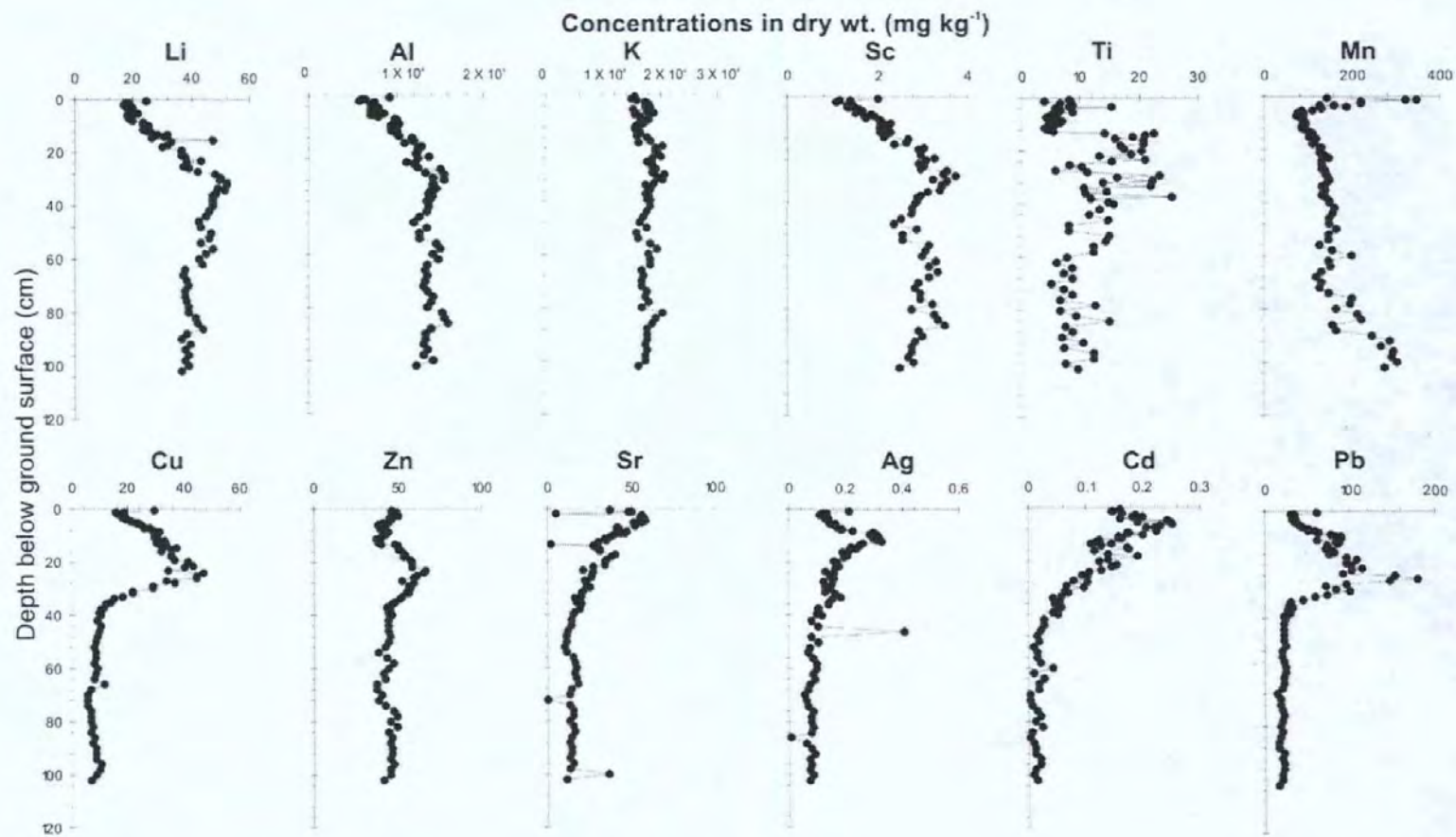


Figure 7.5. Elemental concentrations for the Taf sediments

Al	0.917 0										
K	0.491 0	0.587 0									
Sc	0.235 0.029	0.322 0.003	0.346 0.001								
Ti	0.477 0	0.352 0.001	0.353 0.001	0.041 0.707							
Mn	0.125 0.251	0.17 0.118	0.009 0.938	0.121 0.267	-0.071 0.517						
Cu	-0.324 0.002	-0.391 0	0.059 0.592	-0.152 0.162	0.213 0.049	-0.498 0					
Zn	0.331 0.002	0.246 0.022	0.565 0	0.104 0.34	0.557 0	0.093 0.394	0.522 0				
Sr	-0.751 0	-0.74 0	-0.116 0.287	-0.215 0.046	-0.241 0.025	-0.23 0.033	0.495 0	-0.021 0.845			
Ag	-0.428 0	-0.458 0	-0.246 0.023	-0.164 0.132	-0.026 0.815	-0.529 0	0.632 0	-0.051 0.639	0.451 0		
Cd	-0.773 0	-0.826 0	-0.207 0.056	-0.24 0.026	-0.128 0.239	-0.447 0	0.69 0	0.045 0.682	0.847 0	0.612 0	
Pb	-0.154 0.156	-0.208 0.055	0.159 0.144	-0.091 0.406	0.215 0.047	-0.443 0	0.937 0	0.594 0	0.336 0.002	0.541 0	0.503 0
	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd

Table 7.5. Pearson correlation of the Taf geochemical data. $n = 85$. The 0.01 significance level (two tailed) is $r = 0.284$. Cell Contents: Pearson correlation
P-Value

The Pb/Al ratio data show a good similarity to the total Pb curve (Figure 7.6). The major peak in both curves was at 25 cm, and the Pb concentrations and Pb/Al ratio values decrease toward the surface. However the Pb/Li data show elevated values around 8-14 cm, with a secondary peak defined around 10 cm, indicating a change in the relative contributions from two or more Pb sources, each with a subtly different relationship with Li and Al, in the upper section of the sequence.

In contrast, the curves below 40 cm show constant values, indicating a constant supply of Pb to a stable sedimentary environment. The data show that there has been no significant change occurring during this time in the relative Pb contributions to the sediment fraction that is described by the Li and Al concentrations (e.g., clay sized minerogenic material).

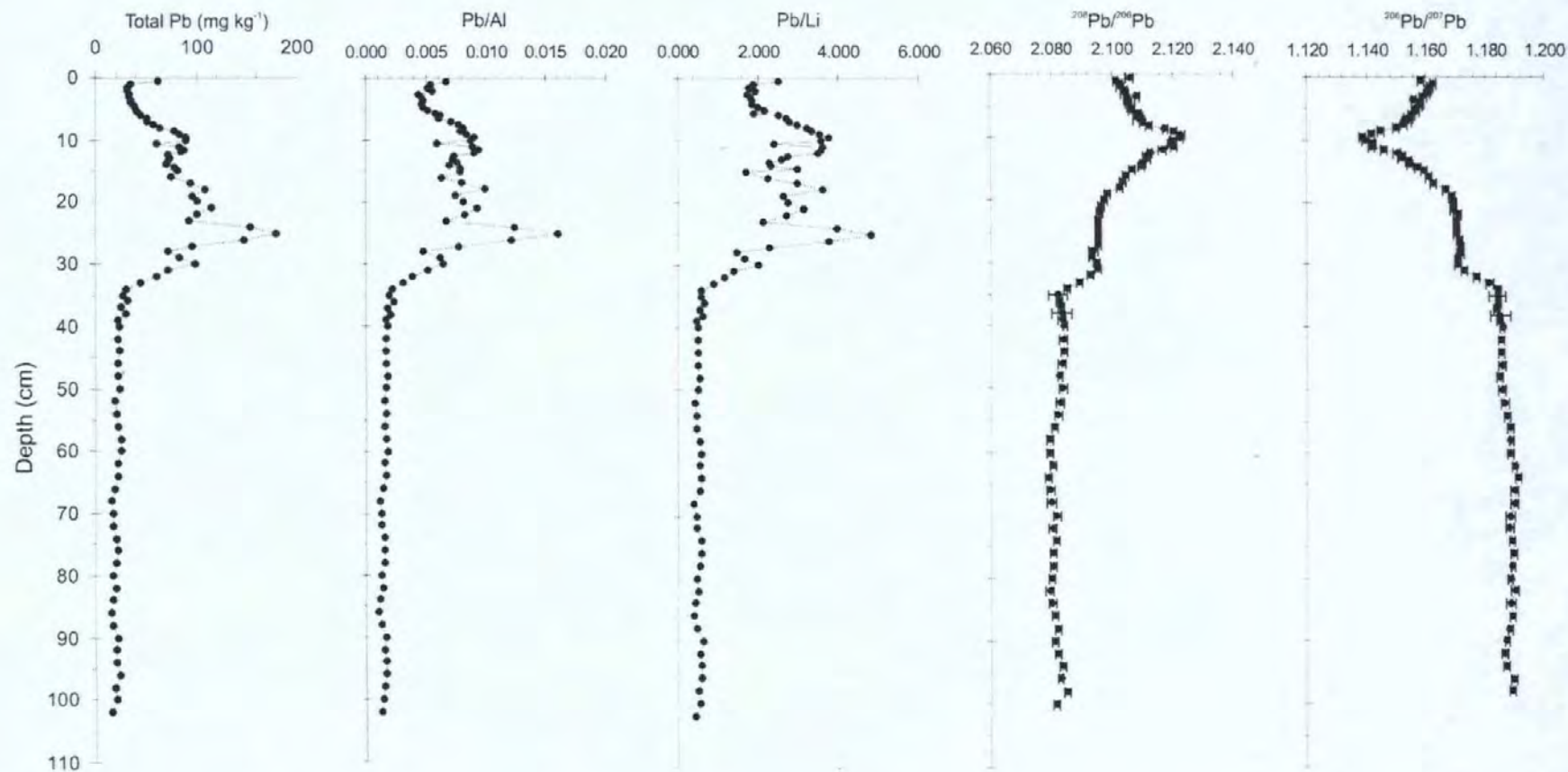


Figure 7.6. The Taf: Total Pb, ratios and stable isotopes. Uncertainties attached to the total Pb analysis (2.5%) are smaller than symbols; stable isotope uncertainties are propagated as per Clough *et al.* (2006) and shown in Appendix 2.

7.4.2. Results: stable isotopes. There was little change in the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values below 40 cm, with the mean values of respectively 1.188 and 2.082. Above this level, at 34 cm, both ratios move abruptly to less radiogenic values of 1.170 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.095 ($^{208}\text{Pb}/^{206}\text{Pb}$), and then remain stable up to around 20 cm (Figure 7.6). At this level the ratio values start to move progressively toward less radiogenic values; at 10 cm they are 1.140 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.123 ($^{208}\text{Pb}/^{206}\text{Pb}$). From here to the surface the trend is reversed, and the surface sample had values of 1.158 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.106 ($^{208}\text{Pb}/^{206}\text{Pb}$).

7.4.3. Interpretation and source apportioning. The results from the elemental analyses, the elemental ratios and the stable isotope ratios all indicate a constant rate of low Pb contributions to the sediments below 40 cm. Above this level the Taf Pb concentration increase concurrently to a two-stage shift in the stable isotopes to less radiogenic values. To examine this further, and using the change points in the elemental ratios curves as a guide, the isotope data were sub-divided at 40 cm, 25 cm and 10 cm and the four groups of $^{206}\text{Pb}/^{207}\text{Pb}$ values plotted versus $^{208}\text{Pb}/^{206}\text{Pb}$ values (Figure 7.7 (A)). These data have a well-defined linear trend ($r^2 = 0.996$) and form a 'mixing line' with the least radiogenic samples plotting in the top-left sector and the most radiogenic samples plotting in the right-lower sector. An inspection of the plot also indicates that there are several clusters in the isotope data that in some instances appear to be simply related to Pb concentrations. However, when these clusters are compared to the enrichment factors (Figure 7.7 (B)) calculated using the $^{206}\text{Pb}/^{207}\text{Pb}$ values and the Pb concentration it is apparent that the location of each sample on the mixing line is not a simple relationship with the Pb concentration or age.

To explore the past sources for the Pb present in the Taf sediments the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values for the regional Pb bearing geologies were plotted. The Pb signatures from below 40 cm could all be attributed to local geological sources as they were approximately equidistant isotopically from the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values (Table 7.6) of the south Wales Taff Merthyr, Cwm and Deep Navigation coal seams, and the mean of the Pb isotope values for material weathered from Upper Continental Crust (UCC) published by Millot *et al.* (2004) from the analysis of bulk sediments from the Earth's major river basins, i.e. 1.208 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.067 ($^{208}\text{Pb}/^{206}\text{Pb}$). The UCC data are used here only as a 'broad brush' approximation,

but this notwithstanding, the isotopic character of the lowest sample group can all be confidently attributed to the Pb sources in the local geology.

Coal*		$^{206}\text{Pb}/^{207}\text{Pb}$	1 s.d.	$^{208}\text{Pb}/^{206}\text{Pb}$	1 s.d.
Regional coal production mean values	England and Wales	1.184	0.006	2.076	0.004
	Scotland	1.181	0.011	2.098	0.006
	Ireland	1.178	0.012	2.045	0.007
Foreign imported coal mean values	S. Africa, Poland, Colombia & Germany	1.194	0.022	2.086	0.006
South Wales coal sources :-					
	Cynheidre	1.172	0.002	2.082	0.003
	Taff Merthyr	1.176	0.003	2.097	0.004
	Cwm	1.190	0.004	2.065	0.006
	Deep Navigation	1.186	0.005	2.065	0.006
	Cwmbargoed	1.180	0.002	2.077	0.002
Regional metal ores**					
NW Wales - lead ore (Bala)		1.162	ns	2.098	ns
NE Wales lead and copper (Great Orme)		1.171	ns	2.095	ns
Mid Wales copper and lead ores (Copa Hill)		1.161	ns	2.106	ns
Bristol and Mendips lead, Cheddar (Blackdown)		1.182	ns	2.078	ns
N Cornwall polymetallic ores (Red Hills/Greystone, Launceston)		1.171	ns	2.093	ns
Mid Cornwall polymetallic ores (1971 workings)		1.176	ns	2.088	ns
Wheal Jane, Carnon Valley; Truro					
Ireland, Bronze Age copper, (Ross Island, Co. Kerry)		1.166	ns	2.096	ns

Table 7.6. Potential geological sources of atmospheric Pb to the Taf sediments. Coal isotope data from Farmer *et al.* (1999)*, metal ore isotope data from Rohl (1996)**.

Apportioning the source of the Pb in the sample group from 26-40 cm is not as simple. These samples form the rising limb of the initial significant rise in Pb concentrations, and this section contains the abrupt shift to less radiogenic values. The isotope plot (Figure 7.7) shows how the isotopic ratios in these samples extend to, and slightly beyond, the isotopic limits of the local geology in this part of South Wales. However, there are a number of regional copper and lead ores that were traditionally mined from the Welsh Bronze Age (See Rosen and Dumayne-Peaty, 2001 and Mighall *et al.*, 2002) that have sufficiently radiometric characteristics to produce the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios found in this section of the sequence. In addition metals derived from polymetallic ores in other metalliferous regions of the UK, i.e. Sn and Cu from Cornwall, have been imported to Wales from around 2000 BC (Rohl, 1995; O'Brien, 1999). If processed on arrival these imports would have had the potential to move the local atmospheric $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios to less radiometric values (Table 7.6).

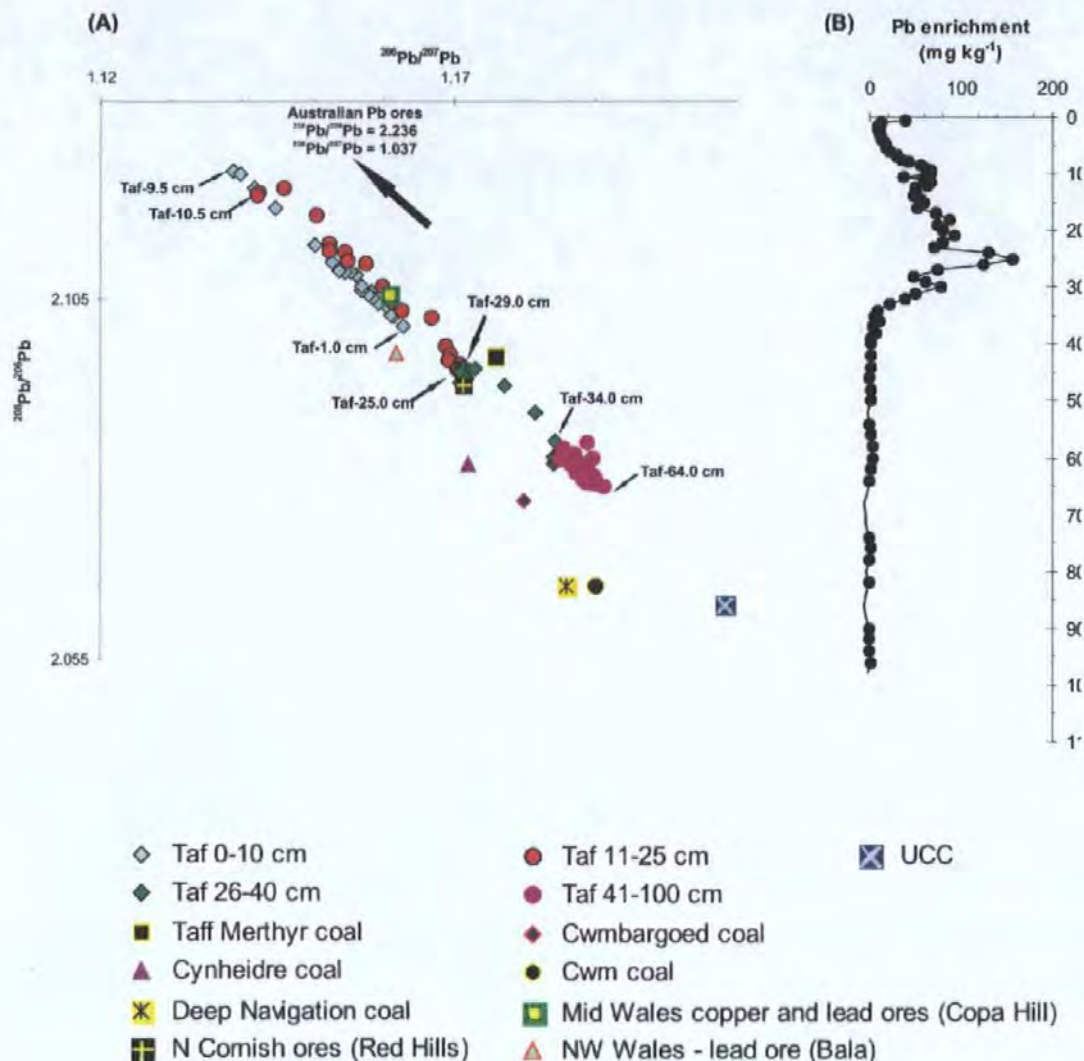


Figure 7.7. (A) Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{208}\text{Pb}$ for the Taf salt-marsh samples and most likely sources. (B) Taf Pb anthropogenic enrichment factor. Calculated using the method described by Renberg *et al.* (2002) (See equation 7.1), with the 'natural background' being derived from the mean values of the lowest five Taf samples. Australian Pb data from Chow *et al.* (1975), Welsh coal data from Farmer *et al.* (1999), and Welsh and Cornish Cu and Pb data from Rohl (1996). Upper Continental Crust (UCC) mean Pb isotope ratios from Millot *et al.* (2004).

The provenance of the Pb in the upper 25 cm is more complex. Many of the younger samples have radiometric isotopic ratios that range beyond most of the geological Pb sources in Wales and other parts of the British Isles (Table 7.6). The sample from 25 cm is relatively enriched in radiometric Pb isotopes. Moving stratigraphically upward, the sediments become progressively less radiometric, concurrent with a drop in Pb enrichment values until a small recovery around 11 cm (Figure 7.7 (B)).

The secondary peak in enrichment values is at 10.5 cm, but the extreme radiogenic end member of the sequence is the sample from 9.5 cm. The isotopic ratios in the sediments above 9.5 cm move steadily away from the isotopically depleted, or less radiometric, extreme of the plot, and by 1 cm the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios have returned to values that are once again within the range produced by the regional geology. Toward the surface the shift to more radiometric values in isotopic ratios is mirrored by a steady decline in enrichment levels until around 1 cm where pre-34 cm values are reached (Figure 7.7 (B)).

To explain the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios values measured in the younger Taf sediments some atmospheric contribution from a source depleted in radiometric Pb is required. None of the major Welsh or English ore fields have sufficiently depleted values, but if the isotopic data on all past UK Pb mining sites are examined there are some obscure Scottish galenas from the southern Grampians that have $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.143 and 2.129 respectively (Rohl, 1996). These ores were mined and smelted at Tyndrum in central Scotland between 1741 and 1862, and this operation has been shown to be the source of significant particulate Pb pollution in the fluvial sediments found in the local catchment (MacKenzie and Pulford, 2002). This notwithstanding, the Tyndrum Pb mining operation is too distant to be a likely source of long-distance atmospheric Pb contributions to the Taf sediments.

A far more likely source of depleted atmospheric Pb to the Taf sediments is the industrial use of metal from radiometric Australian and Canadian ores (See Section 7.2.4) that started in the first half of the 19th century. Farmer *et al.* (1999) points out that although England 'was the centre of world smelter production of lead' during the early 1800s, imported Australian ores became increasingly significant as a source of Pb metal in the UK in the later years of that century. As described in Section 7.2.4, this situation continued into the 20th century as both the industrial use of Pb, and its later use as a petrol additive, increased rapidly.

7.4.4. The Taf stable lead chronology. To construct a chronology using the Taf Pb data it is necessary to interpret the data as a time-series; i.e. in terms of past changes in both atmospheric deposition and $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. The older sections will be considered first, but below 40 cm there are no tangible signals of change in the concentration data, and the isotopic character is consistent with the local geology. Some indications of anthropogenic activity may be apparent in the lower horizons at 76 cm, and 56-60 cm and 40-46 cm (Figure 7.7), but it is not possible to assign an age to these samples other than that they are most likely Bronze Age or younger. This situation changes above 40 cm where the Pb enrichment factor increases rapidly toward the surface up to 25 cm. This is concurrent between 40 - 20 cm with a shift in $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios indicating a change in the relative Pb contributions during this time. Between 20 cm and 25 cm the Pb enrichment factor increases to an abrupt maximum (Figure 7.7) before falling, but the isotopic signature remains steady, suggesting an increase followed by a reduction in emission levels but no change in the relative isotopic contributions from different Pb sources.

To interpret the data from 40 – 25 cm further it is necessary to review first what is known about the local history of non-ferrous metallurgy in south Wales, before looking toward the established super-regional chronology of atmospheric Pb pollution. There is no apparent evidence for significant metal working in the immediate vicinity of the Taf Estuary, and the prehistoric and historic metal mining areas of Wales are some distance north of the Taf (Mighall *et al.*, 2002). This stated, the Swansea Valley lies only some 20 km to the east, and this area has a long history of metallurgy. In part this was because of the trading links available via rivers and sea ports, and later the proximity of extensive coal deposits.

The primary metal processed in the Swansea Valley was Cu, but Pb would have been emitted as a by-product during the smelting of other metals. The Cu ore would have initially come from Welsh mines to the north, and then later as trade developed, Cornwall and other more distance metalliferous mining centres. By the early 19th century around 50 % of the world's copper was being produced from ores mined in Devon and Cornwall (Duff, 1992) and much of this was transported to Wales. The first known south Wales smelting works were operational at Aberdulais Falls, near Neath, in 1584, and by the early 1700s several small-scale metal-works were established in the Lower Swansea Valley smelting Pb, Zn and Cu. By the mid-

1700s 50 % of the UK Cu was being smelted in this area, and significant tonnages of both Pb and Zn were also processed here. This activity expanded over the next 100 years and reached maximum levels during the late 1800s, and then continued at much reduced levels into the 20th century. Pb smelting was at its maximum in the Lower Swansea Valley in the last decades of the 19th century (See Rosen and Dumayne-Peaty, 2001 and references therein).

Rosen and Dumayne-Peaty (2001) present a geochemical analysis of a peat sequence from Crymlyn Bog, West Glamorgan, which they conclude records the local atmospheric fallout of Cu, Zn and Pb associated with the historic smelting activities in the Swansea Valley summarised above. Sediment deposition ages from Crymlyn Bog were obtained by ²¹⁰Pb analysis and two ¹⁴C dates, and the timing of the maximum concentration values for Pb, Cu and Zn are in agreement with the local historic record, i.e. around 1890 (Rosen and Dumayne-Peaty, 2001). This has important implications for the Taf chronology. The information reported by Rosen and Dumayne-Peaty (2001) indicates that the maximum Pb deposition in this part of South Wales predates the established super-regional maximum Pb deposition for the rest of the UK and Western Europe by some 60-70 years (See Section 7.2).

When the depth profile for Pb from Crymlyn Bog is considered alongside the Pb enrichment profile from the Taf there is a good level of agreement (Figure 7.8), but with reduced absolute values. Although only the Pb data are discussed here, it is noted that this situation is the same if the Cu and Zn depth profiles reported by Rosen and Dumayne-Peaty (2001) from Crymlyn Bog are compared with those presented in Figure 7.5 from the Taf.

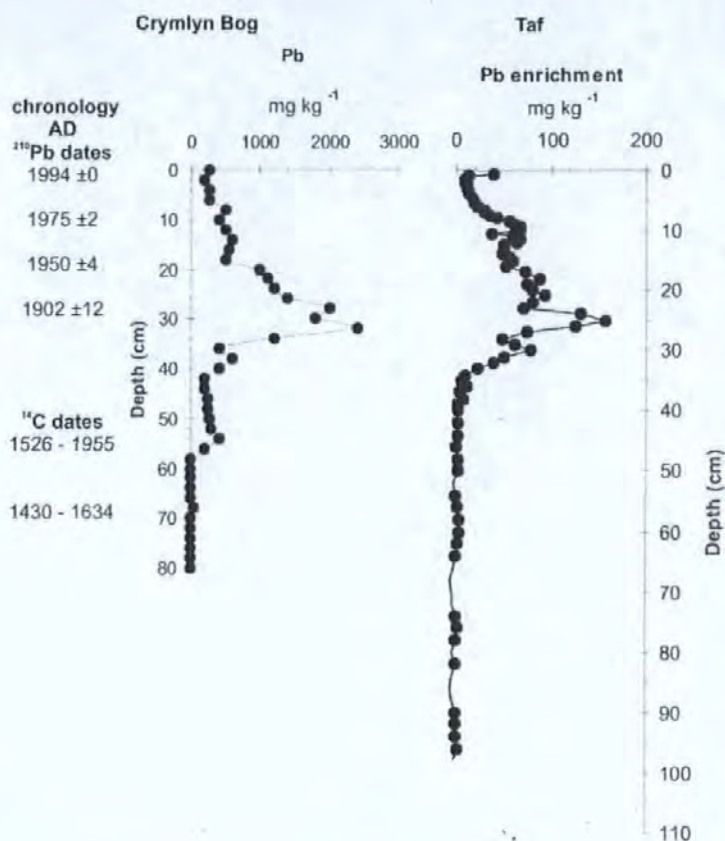


Figure 7.8. The history of Pb deposition at Crymlyn Bog (Rosen and Dumayne-Peaty, 2001) and Pb enrichment factors from the Taf Estuary (This study).

The reduction in absolute concentration values at the Taf when compared to the Crymlyn Bog data may be the result of the physical differences in the sites, e.g. a possible reduced ability of salt-marsh sediments to retain fallout when compared to the peat bog. Alternatively it may be because the Taf site is more distant from the pollution source. Either way, the similarity in the chronology of the depth profiles, i.e. the 'event timing', suggests a common source of atmospheric metal pollution at both sites. The most likely explanation of the significant change in Pb enrichment between 40 cm and 25 cm in the Taf sediments is that this is a signal of the timing of the development, increase and subsequent maximum of Pb emissions during the late 19th century from metallurgy in the Lower Swansea Valley.

The isotopic signatures in the samples below 15 cm can all be explained by a model of local bedrock isotopic values that have become progressively dominated by depleted radiometric values from Welsh, Bristol or Cornish ores. If the likelihood of there being no significant contribution from the Tyndrum ores in the Taf sediments (See 7.4.3) is accepted then above 15 cm the samples are too depleted in radiometric Pb to be simply the product of UK geological sources. Unfortunately, this

information does not yield a precise date because the introduction of depleted foreign Pb spanned a number of decades in the 19th century. These depleted ores were already established as the dominant source of atmospheric Pb in the UK, some time before the introduction of leaded petrol in the 1920s (Farmer *et al.*, 1999). However, the cessation of the use of Pb as a fuel additive produced a discernable shift in European atmospheric Pb to more enriched isotopic values (See Figure 7.4). This shift is suggested by Farmer *et al.* (1999) to have started in the UK around the mid 1970s, and they propose that by 1998 the contribution from leaded petrol was below 50 % of what it had been in 1975.

The most isotopically depleted sample in the Taf sequence is from 9.5 cm (Figure 7.7), and this is taken to mark the maximum deposition of Pb from sources depleted in radiometric isotopes (e.g., Pb fuel additives derived from Australian ores). Above this level, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in the sediments steadily move to more radiometric values toward the surface. This is interpreted as the progressive reduction in the impact of leaded petrol emissions on the isotopic signature of atmospheric Pb over the Taf site. Using these data, and the other information presented above, it is possible to use the Taf Pb data to produce a number of approximate age assumptions; and some relatively robust and precise chronological markers. These can be summarised as:

1. 9.5 cm. The location of the signal of the maximum deposition of atmospheric Pb from leaded petrol in western Europe. Taken here as AD 1977 $\pm$ 2.5 yr (Farmer, *et al.*, 1999; Rosman *et al.*, 2000; Reuer and Weiss, 2002).
2. 12 -11 cm. This secondary maximum is interpreted as the AD 1955-1965 absolute peak in 20th century of regional atmospheric Pb deposition levels (Farmer, *et al.*, 1999).
3. 25 cm. Interpreted as the timing of the maximum deposition of Pb from 19th century smelting activities in the Swansea Valley, and is awarded an age of AD 1890 $\pm$ 5 yr (Rosen and Dumayne-Peaty, 2001).
4. 20 cm - 30 cm. An 'isotopic plateau' between 30 cm and 20 cm is concurrent with steady increase in Pb concentration values is interpreted as the signal of the establishment of significant, and long-term, historic smelting activities in the Swansea Valley in the early-to-mid 1800s using local coal supplies and a mix of Welsh and English ores (Rosen and Dumayne-Peaty, 2001).
5. 35 cm. The deposition age of the sediments below 35 cm is most likely older than AD 1800.

The age-depth curve for the Taf sequence produced from these data is shown in Figure 7. 9.

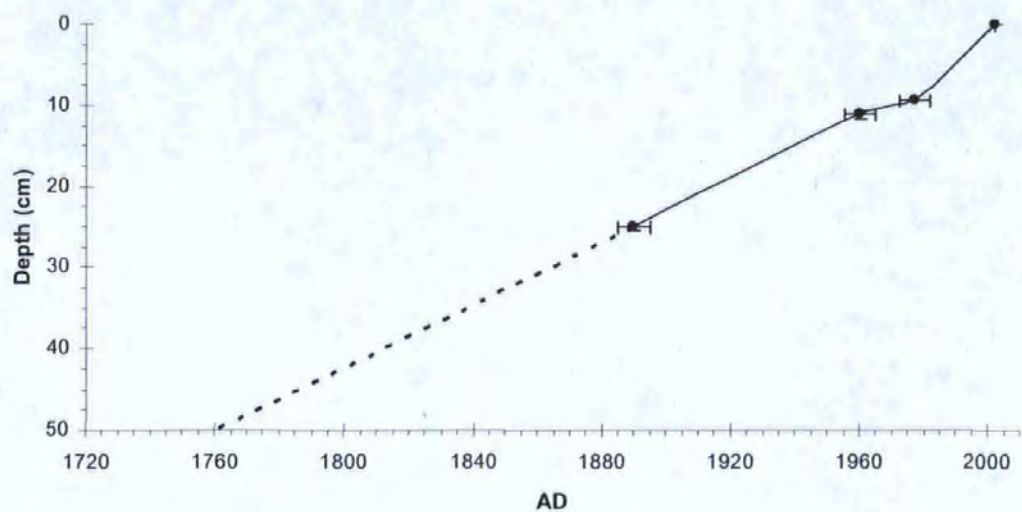


Figure 7.9. Age – depth curve for the Taf derived from the Pb deposition history. The broken line is modelled backward from the slope of the lowest two data points. Overall accumulation rate calculated for this section from these data is 0.21 cm yr^{-1} .

7.5. The Arne stable lead analysis

7.5.1. Results: elemental concentrations. The Arne geochemical concentration results are presented in Figure 7.10. The maximum concentrations for Li, Al, K, Cu, Ag and Pb are found between 24 cm and 26 cm. Ti and Sr also show an increase in concentrations in this zone, but Ti has its maximum at 84 cm. Most of the elements have lower concentrations in the section between 58 cm and 69 cm, and here the values for Li, K, Ti and Mn all drop below the minimum detection level (MDL) of this analysis. The exception is Sc which has its maximum concentration in the sediments at 60 cm and is below the MDL in all of the samples from the upper 20 cm apart from the one from the surface. Mn also has a zone of low concentration, and some samples below MDL in the upper section between 3 cm and 20 cm. It is noted that the zone of extreme variability and very low concentrations between 58 cm and 69 cm coincides with a marked change in the lithology of the sediments. Above 70 cm the sediments change from clays to a more organic lithology, concurrent with an appearance of silty sand in this section of the sequence (See Section 2.3).

K, Sr and Pb appear to have similar depth profiles (Figure 7.10) and the agreement between these curves is confirmed by the Pearson correlation matrix shown in Table 7.7. Correlation between K and Sr ($r = 0.936$, $p = 0$), K and Pb ($r = 0.978$, $p = 0$) and Sr and Pb ($r = 0.932$, $p = 0$), and each individually with Al (e.g., Al and Pb, $r = 0.904$, $p = 0$) is highly significant. Pb and Sc were significantly negatively correlated ($r = -0.365$, $p = 0$). Only Ti was shown to be decoupled from Pb ($r = 0.037$, $p = 0.71$), and not significantly correlated with Al ($r = 0.222$, $p = 0.028$), or K ($r = 0.080$, $p = 0.435$). Ti was significantly correlated with Zn ($r = 0.389$, $p = 0$), Ag ($r = 0.487$, $p = 0$) and Cd ($r = 0.659$, $p = 0$).

These data suggest that the Pb in the Arne samples is strongly associated with the elements representing the minerogenic fraction, Li, Al and K, and that any independent contribution, e.g., from atmosphere, is not great. The very significant correlation between Pb and K is taken here to indicate a strong association of the metal with feldspars in these sediments (See Loring 1991). When candidates are sought against which to normalise the Pb data the use of Li, as used in Section 7.4.1, or Sc, is precluded here because of extreme variability and noise in the concentration data, and the number of values below the MDL (See Figure 7.10). The Ti data have the same issues below 55 cm. Therefore Al and Ti are selected, but due to the noise and low concentration values below 55 cm only the upper section of the data set is used.

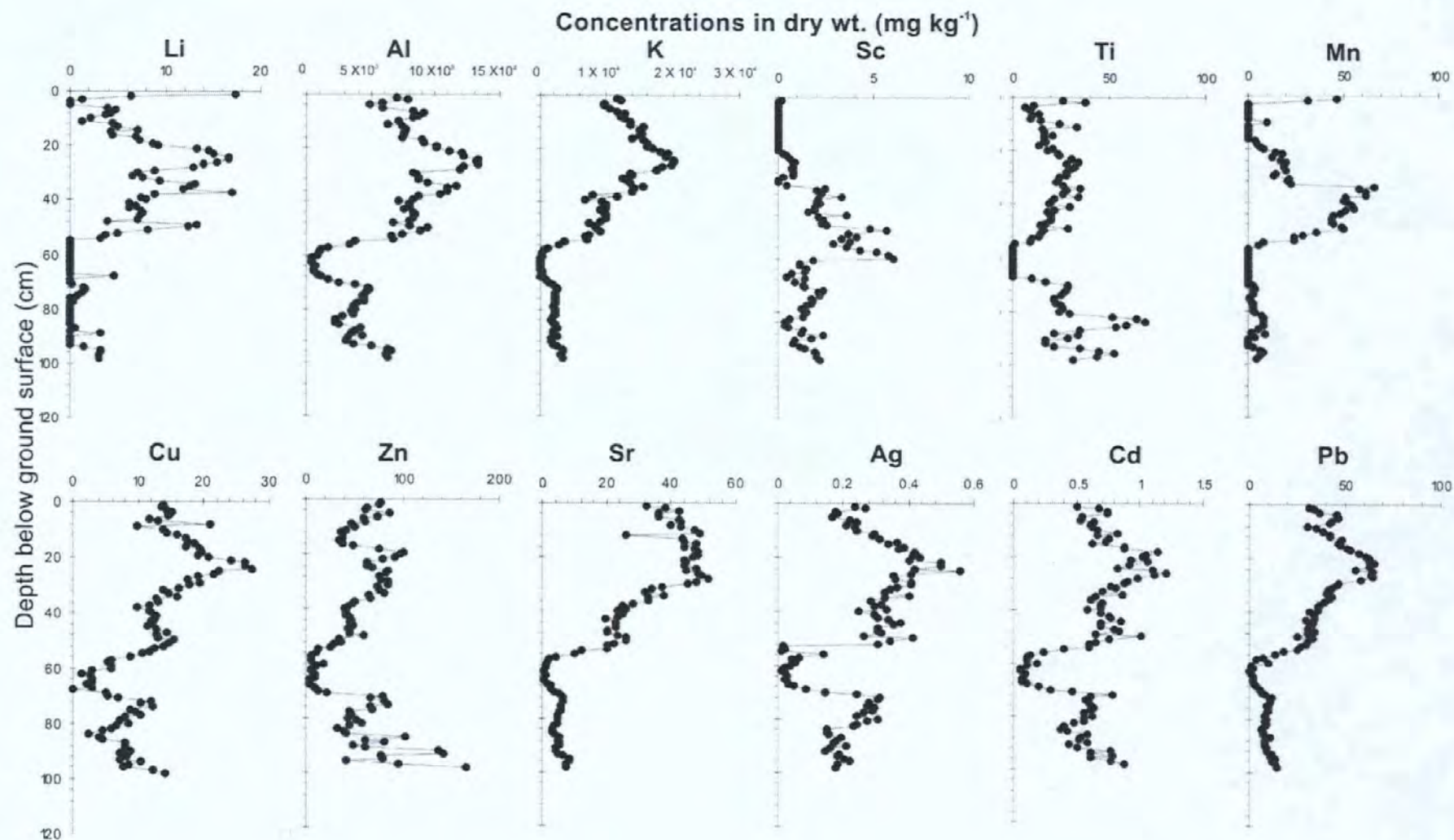


Figure 7.10. Elemental concentrations for the Arne sediments

Al	0.87 0											
K	0.791 0	0.915 0										
Sc	-0.04 0.697	-0.196 0.052	-0.397 0									
Ti	0.168 0.099	0.222 0.028	0.08 0.435	-0.223 0.027								
Mn	0.645 0	0.535 0	0.346 0	0.33 0.001	0.155 0.127							
Cu	0.73 0	0.884 0	0.903 0	-0.272 0.007	0.073 0.474	0.249 0.013						
Zn	0.302 0.003	0.469 0	0.343 0.001	-0.29 0.004	0.389 0	0.063 0.541	0.472 0					
Sr	0.671 0	0.827 0	0.936 0	-0.428 0	0.021 0.838	0.245 0.015	0.841 0	0.317 0.001				
Ag	0.703 0	0.834 0	0.77 0	-0.261 0.009	0.349 0	0.392 0	0.798 0	0.487 0	0.697 0			
Cd	0.647 0	0.861 0	0.769 0	-0.247 0.014	0.354 0	0.344 0.001	0.834 0	0.659 0	0.717 0	0.869 0		
Pb	0.77 0	0.904 0	0.978 0	-0.365 0	0.037 0.717	0.333 0.001	0.909 0	0.365 0	0.932 0	0.769 0	0.797 0	
	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd	

Table 7.7. Pearson correlation of the Arne geochemical data.

$n = 98$. The 0.01 significance level (two tailed) is $r = 0.267$. Cell Contents: Pearson correlation

P-Value

The profile of the Pb/Al and Pb/Ti ratio data show little similarity with the total Pb curve apart from an apparent rise to a peak in the upper 7 cm (Figure 7.11). However, even this small change may simply be an artefact of the decrease in the values of the Al and Ti data in the samples from 3 - 5 cm (Figure 7.10) and not an absolute increase in the Pb flux. The maximum value in the Pb concentrations is found between 22 cm and 27 cm, but in this zone both the Pb/Al and Pb/Ti ratio profiles fall to a minimum. Therefore, these data indicate that the apparent rise in the Pb concentration in the sediments is concurrent with a rise in the concentration of Al, and the other elements associated with the minerogenic fraction. As a result, when the Arne Pb concentration data are evaluated solely with the Pb/Al and Pb/Ti ratio data it is not possible to disentangle proximal Pb enrichment (from local changes in the water-borne minerogenic sediment flux) and anthropogenic atmospheric Pb pollution.

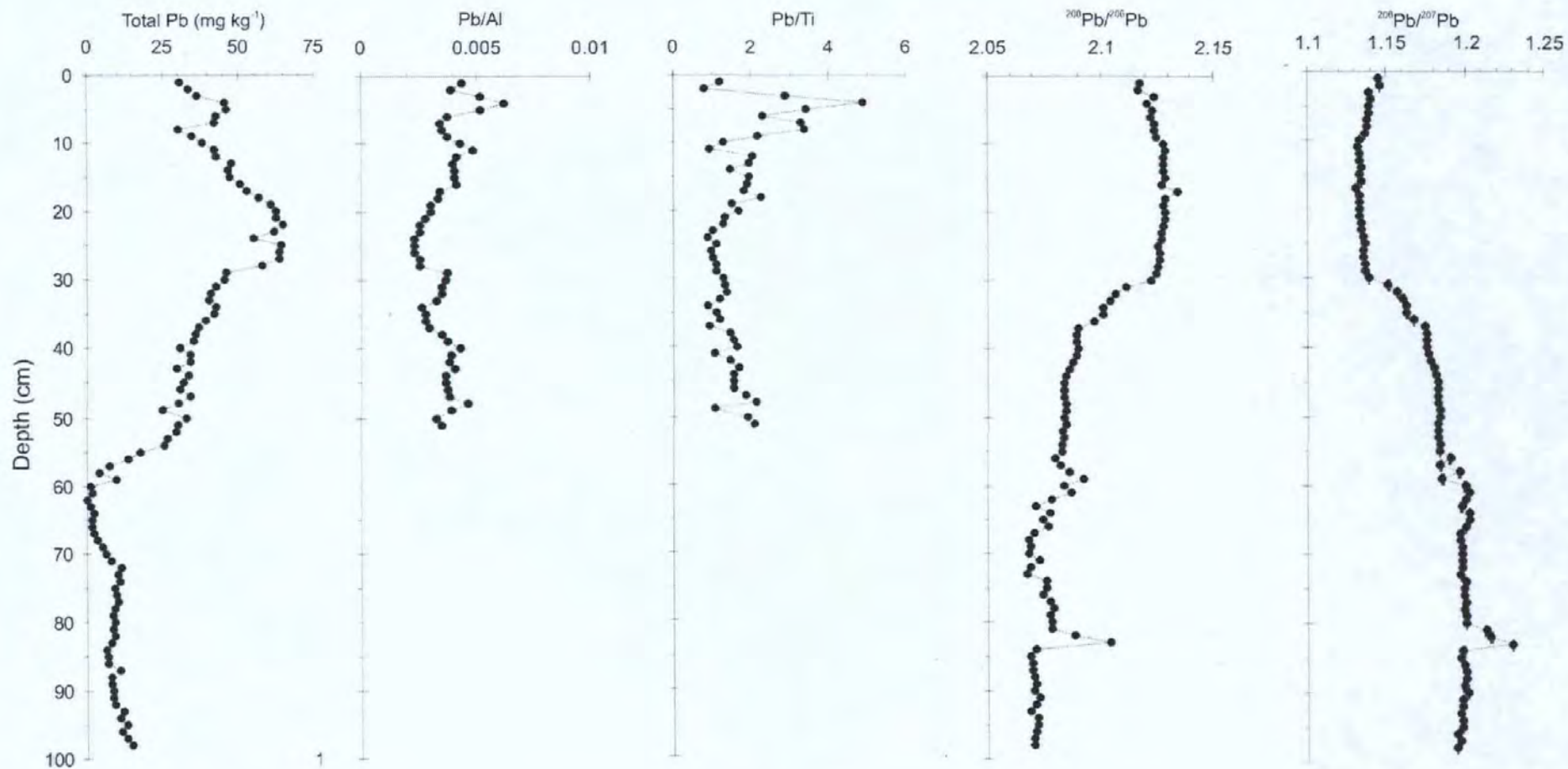


Figure 7.11. The Arne: Total Pb, ratios and stable isotopes. Uncertainties attached to the total Pb analysis (2.5%) are smaller than symbols; stable isotope uncertainties are propagated as per Clough *et al.* (2006), and are shown in Appendix 2.

7.5.2. Results: stable isotopes. Below 60 cm the mean $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values are 1.200 and 2.075 respectively, and there is little change in this lower section apart from an abrupt excursion to less radiometric values between 81 cm and 84 cm (Figure 7.11). Above 60 cm both ratios move gradually to less radiogenic values toward the surface, and at 37 cm they are 1.174 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.090 ($^{208}\text{Pb}/^{206}\text{Pb}$). Between 36 cm and 30 cm the samples are further depleted with values of 1.139 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.122 ($^{208}\text{Pb}/^{206}\text{Pb}$). Above 30 cm, and up to the surface, the values remain relatively stable with means of 1.135 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.125 ($^{208}\text{Pb}/^{206}\text{Pb}$). However, near the surface the sediments start to become more radiometric, and the modern surface sample of the Arne sequence had values of 1.145 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.117 ($^{208}\text{Pb}/^{206}\text{Pb}$).

7.5.3. Interpretation and source apportioning. Using the same approach as that applied in Section 7.4.3 to the Taf data, the Arne Pb isotope data are arbitrary subdivided at 60 cm, 40 cm and 20 cm and the four groups of $^{206}\text{Pb}/^{207}\text{Pb}$ values plotted versus $^{208}\text{Pb}/^{206}\text{Pb}$ values (Figure 7.12 (A)). The result is a well-defined linear array ($r^2 = 0.989$) that form a defined 'mixing line' with the least radiogenic sample, Arne 11 cm, plotting in the top-left sector, and the most radiometric sample, Arne 73 cm, plotting in the right-lower sector. In this sector the older samples are more scattered suggesting that any systematic, long term influence from anthropogenic pollution sources has not been significant, and the isotopic signatures are likely to represent values of, or close to, the natural background $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. All the samples from below 60 cm plot in this sector, which is bounded by the mean $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values for the UCC and the mean $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values published for UK coal deposits. In addition, the more depleted UK Pb ores (e.g., Bristol and Mendips), and the values for foreign coals, also plot in this sector. However, the Pb enrichment factor for these lower levels is calculated as zero (Figure 7.12 (B)), so it is proposed that there has been no significant Pb atmospheric contribution to the sediments below 60 cm.

Upward from 57 cm the situation changes. The samples from 38 cm down to 57 cm all plot with a defined linear trend and move progressively toward less radiometric values. This is concurrent with the start, and the subsequent increase, of measurable Pb enrichment factors in the sediments, suggesting an increasing and systematic influence on the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values, and the development of a significant long-term anthropogenic pollution contribution to the Pb flux. This

cluster is isotopically bounded by a cluster of samples which have $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values slightly more radiometric than the isotopic signatures of metal ores from the North Cornish mining district. The mines in the South West of England all have similar isotopic signatures (Rohl, 1996), and were a significant source of non-ferrous metals during the major periods of industrial expansion in the UK in the 19th century (Duff, 1992). In addition, this group of samples is less depleted than the mean isotopic signatures of Scottish coal deposits, which only started to become a significant source of atmospheric Pb over the regional UK during the early 1900s (Farmer *et al.*, 1999).

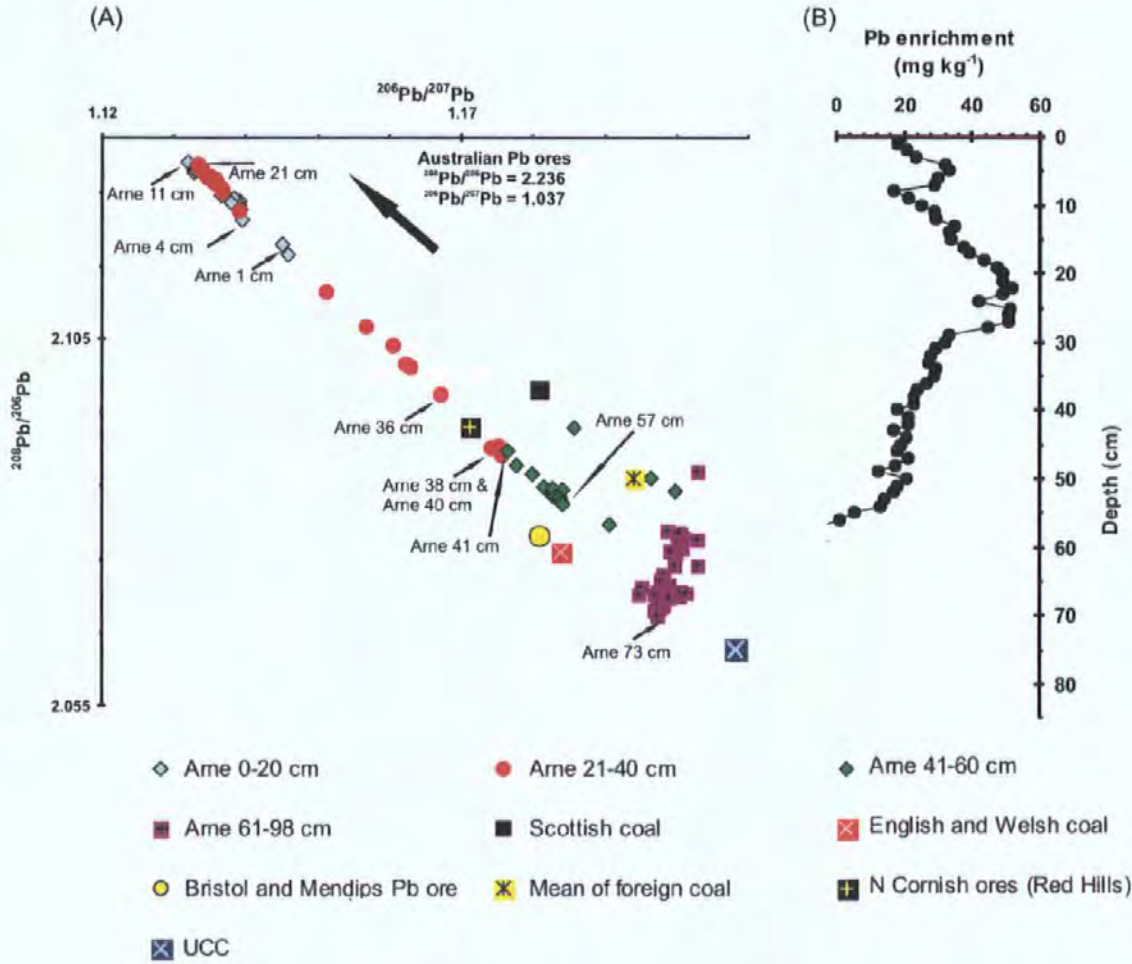


Figure 7.12. (A) Plot of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ for the Arne salt-marsh samples and most likely sources. (B) Arne Pb anthropogenic enrichment factor. Calculated using the method described by Renberg *et al.* (2002) (See equation 7.1), with the 'natural background' being derived from the mean values of the lowest five Arne samples. Australian Pb data from Chow *et al.* (1975), Coal data from Farmer *et al.* (1999), and representative UK Pb ore data from Rohl (1996). Upper Continental Crust (UCC) mean Pb isotope ratios from Millot *et al.* (2004).

Bacon *et al.* (1996) use the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of archived plant material from southern England to show that atmospheric Pb became progressively more isotopically depleted during the late 19th and early 20th centuries. This trend continued, and by 1930 Bacon *et al.* (1996) propose that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in atmospheric Pb over England was 1.145. Therefore, it is logical to conclude that this increasingly enriched atmospheric Pb contribution would have produced a systematic and progressive depletion in the isotopic signature of the Arne sediments. This situation would agree with the data shown in Figure 7.12.

The Arne Pb enrichment factors climb to maximum levels at 27 cm of around 50 mg kg⁻¹, and these levels are maintained up to 21 cm before an overall decreasing trend is established to the surface. This profile is in some agreement with the published records of European Pb deposition discussed in Section 7.1 (e.g., Renberg *et al.*, 2002), and Section 7.2 (e.g., Reuer and Weiss, 2002). When the isotopes are considered, above 38 cm the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are too depleted to be produced without a significant contribution from highly radiometric Pb (e.g., lead metal and petrol additives derived from Australian Broken Hill ores). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the sample from 30 cm is 1.139, and, given the values quoted by Bacon *et al.* (1996) discussed above, this indicates a deposition age some time after 1930. The most depleted $^{206}\text{Pb}/^{207}\text{Pb}$ ratio value in the Arne sequence, 1.132, is from 11 cm and it marks the maximum influence of exotic radiometric Pb, and most likely corresponds to the timing of the peak usage of leaded petrol in this part of England.

It is noted that the Arne most depleted $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.132 is not as low as the most depleted $^{206}\text{Pb}/^{207}\text{Pb}$ ratios measured by Rosman *et al.* (2000) in their Mont Blanc snow sequence. However, the Arne surface $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.145 is significantly less depleted than the values published by Flament *et al.* (2002) of 1.06 to 1.24 for the modern UK atmosphere, indicating that the isotopic signature of the recent sediments has been modulated by an enriched source. This may be evidence of continued contributions from the bedrock geology, but equally may be the result of some contribution from atmospheric Pb pollution derived from coal combustion.

7.5.4. The Arne stable lead chronology. The record of Pb enrichment preserved in the Arne sediments contains a number of features that can be matched to the established chronology of regional atmospheric Pb pollution, as described in Sections 7.1 and 7.2. The early 19th century rise of industrial Pb pollution can be identified in the sediments around 55 cm, and a good estimation can be made of the location of the signal of the start of the use of leaded petrol in the 1920s, and its subsequent rapid increase between 32 cm and 36 cm. The enhanced concentrations measured between 27 cm to 22 cm are taken to mark the late 20th century absolute maximum of Pb deposition from the combined emissions of industry, power generation and petrol emissions in the 1950s and 1960s. However the most robust marker is at 11 cm which is interpreted as the regional maximum deposition of atmospheric Pb produced by leaded petrol in the late 1970s. The markers selected can be summarised as:

1. 11 cm. The location of the signal of the maximum deposition of atmospheric Pb from leaded petrol in western Europe. Taken here as AD 1977 $\pm$ 2.5 yr (Farmer, *et al.*, 1999; Rosman *et al.*, 2000; Reuer and Weiss, 2002).
2. 22 - 27 cm. This is interpreted as the location of the AD 1955-1965 absolute peak in 20th century of regional atmospheric Pb deposition levels (Farmer, *et al.*, 1999).
3. 32 – 36 cm. The introduction and start of the widespread use of leaded petrol in the UK and Europe between AD 1930 and AD 1935 (Nriagu, 1990).
4. 55 cm. The early 19th century increase in industrial Pb emissions (Farmer, *et al.*, 1999).

Using these marker points a simple age-depth curve can be constructed (Figure 7.13).

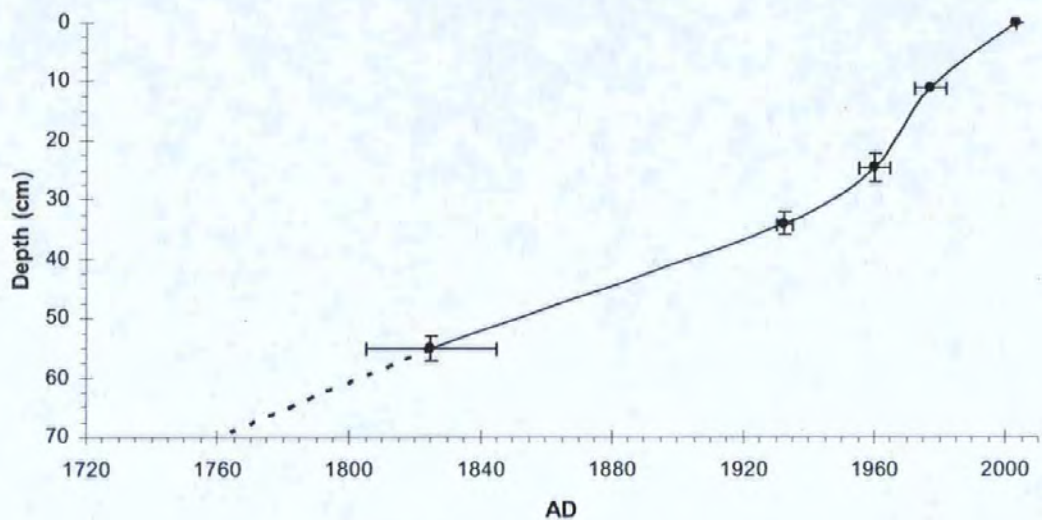


Figure 7.13. Age – depth curve for the Arne derived from the Pb deposition history. The broken line is modelled backward from the slope of the lowest two data points. Overall accumulation rate calculated for this section from these data is 0.31 cm yr^{-1} .

7.6. The Viðarhólmi stable lead analysis

The Pb and Li concentrations, and the Pb/Li, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ data, from the upper 55 cm of the Viðarhólmi sediments that are presented in this chapter are the same as reported in Gehrels *et al.* (2006).

7.6.1. Results: elemental concentrations. A first inspection of the Viðarhólmi data shows that Ti, Mn and Sr are found in significantly higher concentrations in the Icelandic sediments than those determined in the other salt-marsh sequences reported in this thesis. On average the Mn and Sr concentration values are a magnitude higher, and the Ti values are two magnitudes higher. This is attributed to the dominant influence of volcanic geology at the Viðarhólmi site. In addition, the concentrations determined for Pb are much lower than those for the Welsh and English sites. The surface concentration determined for Pb is only 1.65 mg kg^{-1} , which increases rapidly down profile at 9 cm to 4.57 mg kg^{-1} before falling to 0.95 mg kg^{-1} at 40 cm. However, all the elemental concentrations are above the minimum detection levels (MDL).

The concentrations determined for Al, K, Sc, Ti, Mn and Sr all increase down profile from the surface to around 20 cm. The maximum values for these six elements are found in these levels (Figure 7.14). The concentrations for Li also increase down profile, but they are at maximum values significantly below the 20 cm level. The Ag and Cd data show variation, but remained relatively constant around a mean concentration throughout the sequence. Li, Al, Cu and Zn all have minimums around, or just below, 81 cm, and Mn have a well defined peak between 56 cm to 64 cm.

Some similarity can be seen between the Al, K, and Mn profiles. A Pearson correlation analysis (Table 7.8) confirms the relationships between Al and K ($r = 0.758$, $p = 0$) Al and Mn ($r = 0.532$, $p = 0$) and K and Mn ($r = 0.827$, $p = 0$) as being very significant. Al is found to be significantly correlated with Sc ($r = 0.472$, $p = 0$), Zn ($r = 0.528$, $p = 0$), Cd ($r = -0.308$, $p = 0$) and Pb ($r = 0.459$ and $p = 0$). Significant correlation is found between Pb and K ($r = 0.588$, $p = 0$) and Pb and Li ($r = -0.331$, $p = 0$). Ti is significantly correlated with Al ($r = 0.5$, $p = 0$), but it is not significantly correlated with Pb ($r = 0.195$, $p = 0.02$). No correlation ($r = -0.011$, $p = 0.9$) is found between Ti and Li.

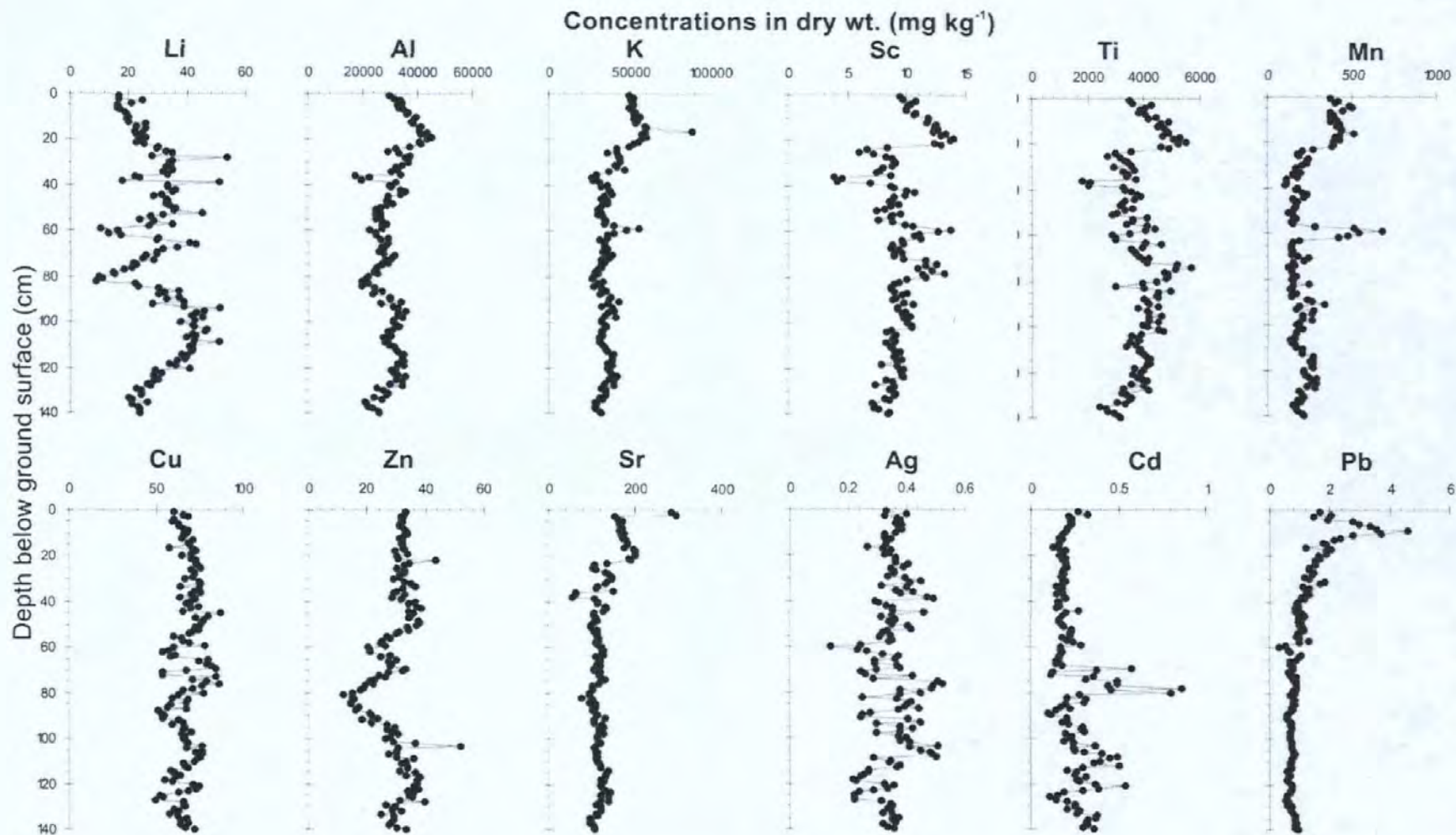


Figure 7.14. Elemental concentrations for the Viðarhólmi sediments.

It has been established that variability in the concentrations of the Li, Al, K, Sc and Ti group are normally associated with changes in the flux of water-borne minerogenic materials (Loring, 1991). However, the dominance of the local geology by volcanic products at the Viðarhólmi site requires consideration. The concentration profiles, and the Pearson correlation analysis, indicate that the Li, Al and Ti concentrations all have the potential to be used to normalise the Viðarhólmi data. As discussed in Section 7.2.5, Li is preferred over Al. Ti is present in significant concentrations, and is found to be significantly correlated with Al. Therefore, variability in the Ti concentrations is, to some extent, concurrent with Al. In addition, Ti is shown by the Pearson correlation analysis to be decoupled from Li, and not significantly correlated with Pb. This element is significant in tephra and other volcanic products, and so it could potentially be used to represent the unweathered background contribution from the local catchment geology. Therefore Ti and Li are chosen to normalise the Viðarhólmi Pb data.

Al	0.203 0.016											
K	-0.243 0.004	0.758 0										
Sc	-0.295 0	0.472 0	0.561 0									
Ti	-0.011 0.901	0.5 0	0.384 0	0.779 0								
Mn	-0.39 0	0.532 0	0.827 0	0.593 0	0.276 0.001							
Cu	0.157 0.064	-0.031 0.714	-0.132 0.121	0.045 0.6	-0.01 0.907	-0.286 0.001						
Zn	0.348 0	0.528 0	0.272 0.001	-0.141 0.096	-0.149 0.079	0.128 0.132	0.237 0.005					
Sr	-0.203 0.016	0.701 0	0.768 0	0.545 0	0.435 0	0.67 0	-0.118 0.166	0.289 0.001				
Ag	0.101 0.233	-0.183 0.031	-0.276 0.001	-0.092 0.282	0.052 0.542	-0.433 0	0.561 0	-0.114 0.178	-0.164 0.053			
Cd	-0.106 0.213	-0.308 0	-0.326 0	0.128 0.132	0.132 0.12	-0.245 0.004	0.325 0	-0.157 0.064	-0.177 0.036	0.4 0		
Pb	-0.331 0	0.459 0	0.588 0	0.254 0.002	0.195 0.021	0.46 0	0.08 0.348	0.212 0.012	0.556 0	0.167 0.049	-0.187 0.027	
	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd	

Tabel 7.8. Pearson correlation of the Viðarhólmi geochemical data.

$n = 142$. The 0.01 significance level (two tailed) is $r = 0.256$. Cell Contents: Pearson correlation
P-Value

There is a marked similarity between the Pb, Pb/Li and Pb/Ti depth profiles (Figure 7.15). The peak at 9 cm is similar in all three profiles. The values in all three profiles decline from 9 cm to the surface where values of 46 %, 41 % and 43 % of the maximum values are respectively recorded for Pb, Pb/Li and Pb/Ti. In the lower sections below 40 cm there is little overall change in the absolute concentration of Pb in the sediments, but all three profiles show a decrease in values of between 140 cm to 125 cm. The data from 140 cm represent 26 %, 16 % and 27 % of each of the respective values recorded for the sample from 9 cm. This strongly suggests that the elevated values found here represent an absolute increase in the Pb concentration in the sediments that is independent of the local sediment flux, i.e. a signal of a changing contribution from atmospheric Pb. However, there are some apparent differences in the lower sections of the depth profiles. The Pb/Li profile shows a lesser peak around 80 cm, and the plotting of the data as Pb/Ti ratios produces a peak between 32 cm and 40 cm. This variability in elemental ratios is interpreted as past changes in the concentrations of Li or Ti, or both, and not as changes in the amount of Pb being added to the sediment.

7.6.2. Results: Stable isotopes. The overall, up-sequence trend of the stable isotope ratios is towards more isotopically depleted values. At 140 cm, the base of the sequence, stable Pb isotope values of 1.204 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.053 ($^{208}\text{Pb}/^{206}\text{Pb}$) are measured. Up sequence, the values move to slightly enriched values around 125 cm of 1.220 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.036 ($^{208}\text{Pb}/^{206}\text{Pb}$). From 125 cm up to 40 cm there is a slight trend toward less radiometric values. The most radiometric samples in this section of the Viðarhólmi sequence are from around 40 cm and 98 cm, where values of 1.210 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.045 ($^{208}\text{Pb}/^{206}\text{Pb}$) and 1.221 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.033 ($^{208}\text{Pb}/^{206}\text{Pb}$) are measured respectively. Up sequence from 40 cm the trend is to isotopically depleted values, and the ratios move steadily to values of 1.161 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.096 ($^{208}\text{Pb}/^{206}\text{Pb}$) at 9 cm. From this level to the surface the trend is reversed, and the modern surface sediments have values of 1.177 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.082 ($^{208}\text{Pb}/^{206}\text{Pb}$).

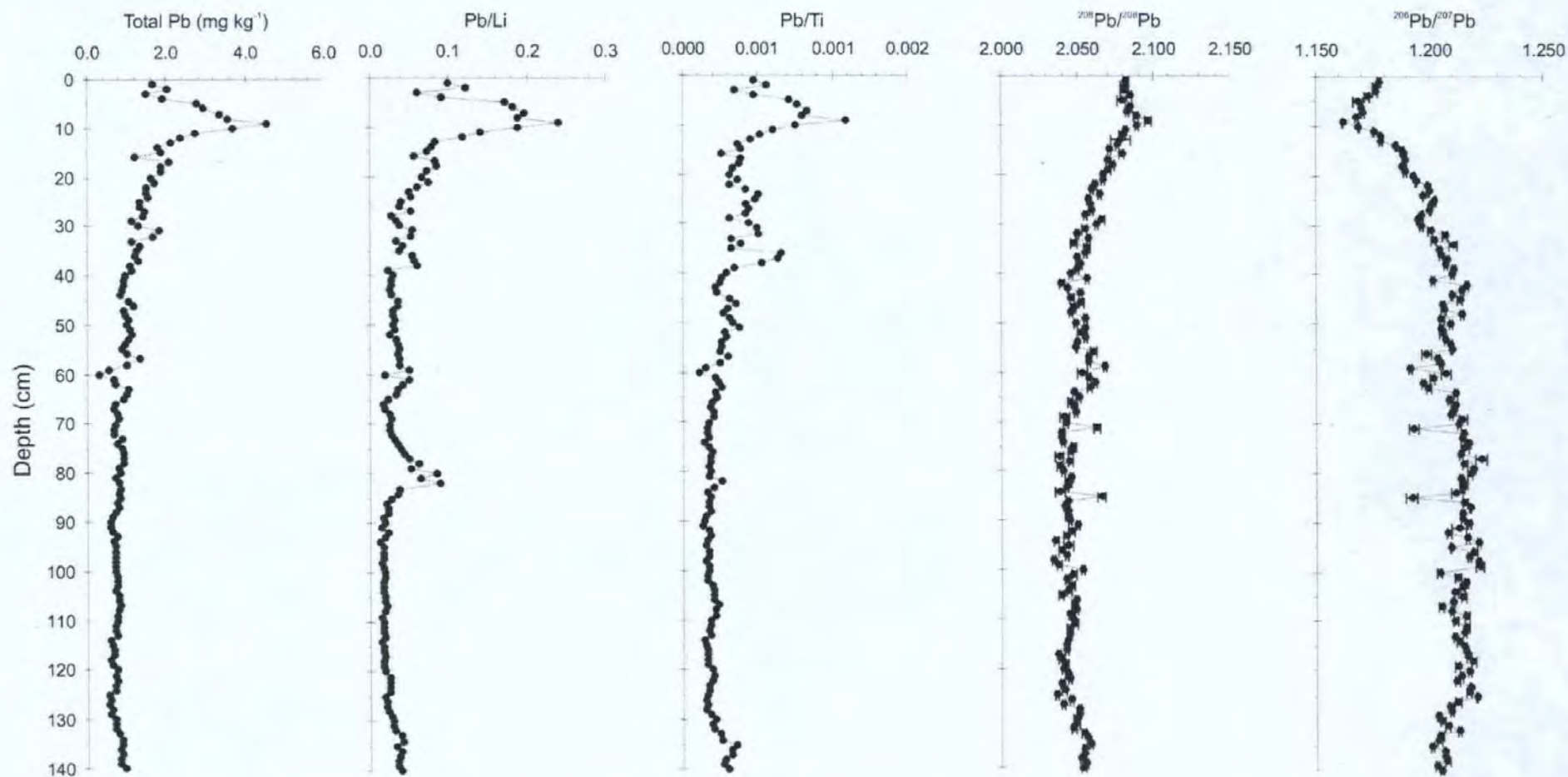


Figure 7.15. Viðarhólmur: Total Pb, ratios and stable isotopes. Uncertainties attached to the total Pb analysis (2.5%) are smaller than symbols; stable isotope uncertainties are propagated as per Clough *et al.* (2006) and shown in Appendix 2.

7.6.3. Interpretation and source apportioning. Using the Pb concentration data as a guide the Viðarhólmi stable isotope data are sub-divided at 90 cm, 40 cm and 15 cm, and the four groups of $^{206}\text{Pb}/^{207}\text{Pb}$ values plotted versus $^{208}\text{Pb}/^{206}\text{Pb}$ values (Figure 7.16 (A)). The values for UCC Pb are shown to aid comparisons with the other sites reported in this thesis.

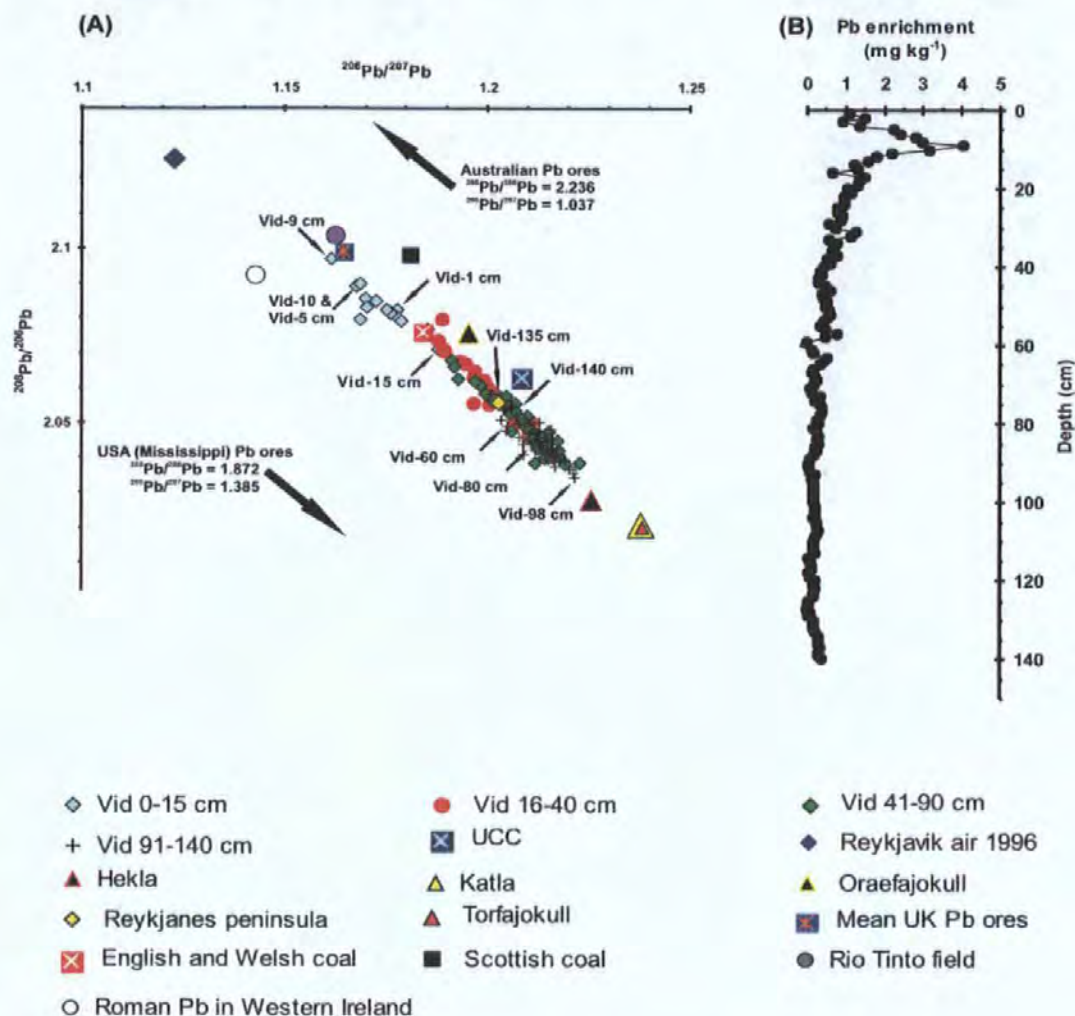


Figure 7. 16. (A) Plot of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ for the Viðarhólmi salt-marsh samples and other relevant values. (B) Viðarhólmi Pb anthropogenic enrichment factor. Calculated using the method described by Renberg *et al.* (2002) (See equation 7.1), with the 'natural background' being estimated from lowest Pb concentration found in the Viðarhólmi samples (Vid-125 cm). Upper Continental Crust (UCC) mean Pb isotope ratios from Millot *et al.* (2004), Australian and USA Pb ore data from Chow *et al.* (1975), UK coal data from Farmer *et al.* (1999), UK Pb ore data from Rohl (1996) and Rio Tinto ore data from Stos-Gale *et al.* (1995). Also shown are the mean Pb isotope ratios for the signal of Roman Pb found in Western Irish lake sediments by Schettler and Romer (2006). The Pb isotope data from Icelandic volcanic sources are: Hekla and Reykjanes, Thirlwall *et al.* (2004), Katla from Park (1990), Öraefajökull, Prestvik *et al.* (2001), Torfajökul, Stecher *et al.* (1999). The Pb isotope ratios for the air over Reykjavik in 1996 are from Bollhöfer and Rosman (2001).

The data produce a well-defined linear array ($r^2 = 0.958$) with the most radiometric samples plotting in the lower right-hand sector. These samples are from the lower sections of the sequence, and all have isotopic signatures that are within the range that can be attributed to the local geology; i.e. they plot on a mixing line between the isotopic end-members of the Icelandic volcanic systems (Prestvik *et al.*, 2001; Thirlwall *et al.*, 2004). However, the most radiometric sample is from 98 cm, and the oldest samples, 135 cm to 140 cm, plot significantly toward the less radiometric section of the mixing line. This indicates some contribution in these lower levels from a Pb source depleted in radiometric isotopes. An explanation for this situation is not straightforward. The Pb in these lower levels could contain a contribution from a less radiometric volcanic source on Iceland, e.g. the Öräfajökull system, but there is no physical evidence in the Viðarhólmi sequence, or published report of an Öräfajökull tephra known to the author, to support this scenario.

With the information available here it is a matter of conjecture as to the magnitude of the Pb contribution required to influence significantly the isotopic signature of the sediments. Unfortunately, the sequence was truncated at 140 cm and does not contain a sample that can provide older background data. A more detailed analysis of the Pb concentrations and isotope ratios in the local bedrock and lava flows would be needed to quantify reliably the level of Pb contribution required to produce a specific isotopic signature. However, it is possible to elucidate this situation further by considering the ancillary information that is known regarding this sequence (Chapter 2). The Viðarhólmi sediment sequence contains a visible tephra layer at 81.5 cm that has been identified (See Section 6.2) as the the Landnám, or Settlement layer, dated to AD 875 $\pm$ 6 yr; (Grönvold *et al.*, 1995; Wastegård *et al.*, 2003). This tephra was produced by an eruption in the Torfajökul volcanic system, and the isotopic signature of this system has been measured by Stecher *et al.* (1999) as 1.239 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.020 ($^{208}\text{Pb}/^{206}\text{Pb}$). There is visible evidence of this tephra fall in the sediments, so it is reasonable to assume that this event around AD 875 would have produced a detectable signal in the Viðarhólmi Pb isotope data. This notwithstanding, when the data for this layer is examined closely (Figure 7.17) then no signal is detected in the isotope data or the enrichment data. This lack of response in the data indicates that one of the largest eruptions in Iceland during historical times, that is known to have produced a visible tephra layer in the Viðarhólmi sequence, did not change the isotopic signature of the contemporary sediments deposited at the site. Therefore, it is unlikely that an unidentified enriched

volcanic source could have contributed sufficient Pb to produce the isotopic values measured in the sediments from the base of the sequence, and not left a visible tephra layer in the sediments.

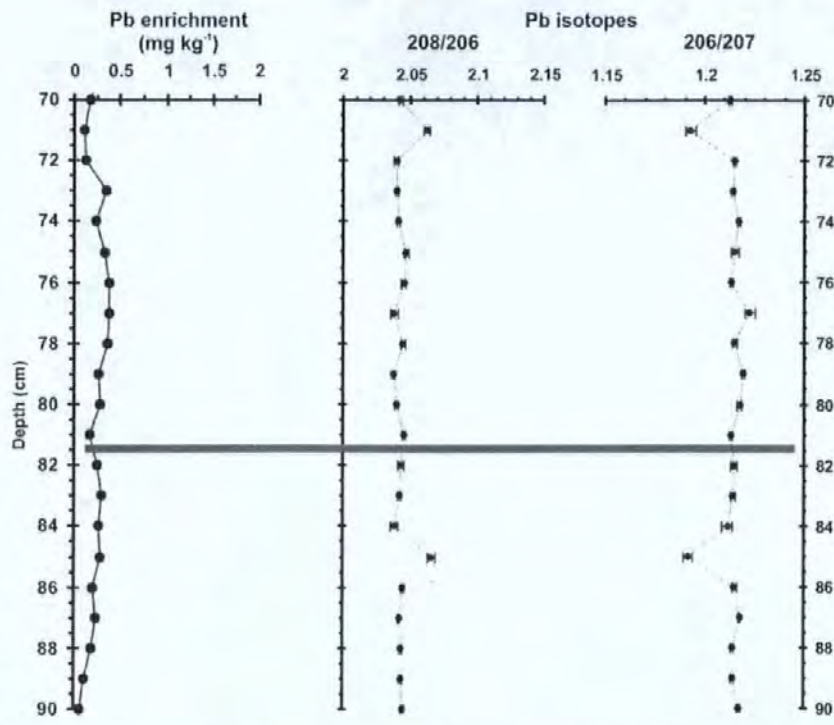


Figure 7. 17. The section of the stable Pb data for the Viðarhólmi sediments containing the visible tephra layer. The location of the Landnám tephra is shown by the grey line. No isotopic signature for the tephra layer is apparent. Uncertainties as per Figure 7.15.

An alternative explanation of the isotopic signature of the oldest Viðarhólmi sediments from 135 cm to 140 cm is that this is the signal of the deposition of depleted Pb from a long-range atmospheric source. Binder *et al.* (2001) show that the atmospheric Pb deposited in Nunatak Lake in South Western Greenland during the last 2200 yr originated in Europe. They prove conclusively that, even during the height of the US petrol Pb emissions in the 20th century, the southern region of Greenland received Pb fallout from Europe, not North America. The established northern European records of Pb deposition (e.g., the Swedish lake record published by Renberg *et al.* (2002) shown in Figure 7.3) are characterised by a shift to more depleted isotope values during the height of the Roman use of Pb, and other metals, between 100 BC and AD 200 (Section 7.2.3).

7.6.4. The Viðarhólmi stable lead chronology. The record of Pb deposition at the Viðarhólmi site is in good agreement with that established for northern Europe during the last 2000 yr (See Section 7.1). The oldest sediments in the Viðarhólmi have an isotopic signature that suggests a contribution from Roman metal working industries. Le Roux *et al.* (2004) found the signal of Roman Pb in a peat core from northern England, and a recent study in western Ireland (Schettler and Romer, 2006) detected low-level Pb enrichment that was attributed to the Roman use of metals from mines in Spain and England around AD 0 to AD 100. These two ore sources are difficult to distinguish in the sedimentary record using stable isotopes (Figure 7.16), but the chronological timing of usage is not significantly different. The Roman occupation of England began in 43 BC, and would have exploited the pre-existing metal industry. Their domination and influence in England peaked around 130 AD, and the local metal ores would have represented a valuable resource to the Empire (Le Roux *et al.*, 2004). This time period coincides with the maximum of the Roman Pb fallout signal found in many other regions of Europe (e.g., by Shotytk *et al.* (2001) in Switzerland, Renberg *et al.* (2002) in Sweden and Kylander *et al.* (2005) in Spain). Given this situation, and the known deposition of Roman Pb in Ireland (Schettler and Romer, 2006) and Greenland (Binder *et al.*, 2001), the samples from 135 cm to 140 cm are interpreted as containing Pb that was emitted during the height of the Roman Empire in Europe, and are therefore dated to AD 50 $\pm$ 50 yr.

There was a decline in the Pb enrichment in the sediments above these lower horizons, and no significant enrichment was detected up profile until around 64 cm. Above this level, a small rise in Pb enrichment values was apparent, concurrent with a shift in isotopic values to less radiometric values. This pattern of reduced Pb concentrations in the record for an extended period after a previous time of enrichment is in agreement with the widespread reduction in European atmospheric Pb emissions that followed the heightened production levels that were a feature of the Roman era (Reuer and Weiss, 2002). Therefore, although not prominent, the small rise in Pb enrichment and isotopic move to less radiometric values upward from 64 cm is likely the signal of the expansion of metallurgy in Europe during the Medieval (See Section 7.1.2), and is awarded the age of AD 1000 $\pm$ 75 yr.

There are increases in the rate of change signalled around 45 cm and 39 cm that suggest two distinct phases of increasing Pb deposition and expanding contributions from Pb sources depleted radiometric isotopes. These are interpreted as the signals of the industrial and social expansion in Europe that started around 500 yr BP, and

the development of new technologies and the expansion of European metallurgy during 19th and 20th centuries (Reuer and Weiss, 2002). These levels are awarded the ages of 1550 ± 75 yr and 1820 ± 20 yr respectively. The marker for AD 1820 from 39 cm is the same as interpreted for this site by Gehrels *et al.* (2006). With the benefit of the extra geochemical information and Pb isotope data presented here it has now been possible to calculate Pb enrichment factors using the method described by Renberg *et al.* (2002) (See equation 7.1). These data, and the refinement of enrichment factors, were not available to Gehrels *et al.* (2006). Therefore, although essentially the same, there are some differences in the interpretation above 39 cm.

The rapidly increasing radiometric signature of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios around 17 cm is now interpreted as the rapid development of new metal-based industries, and the increase in the use of coal containing radiometric Pb. This started during the late 19th century (Smol, 2002), and this signal is assigned the age of 1900 ± 20 yr. The start of the isotopic shift to less radiometric values at 14 cm is interpreted as the timing of the widespread introduction of leaded petrol in Europe during the early 1930s. This isotopic shift terminates at 9 cm. This is also the location of the peak in Pb concentration values. Without the benefit of the newly calculated Pb enrichment values this marker was interpreted by Gehrels *et al.* (2006) as the late 1950s early 1960s peak in total atmospheric Pb depositions, as suggested by the record published by Shotyk *et al.* (2005). However, the sample from 9 cm is the isotopic end member in Figure 7.16, and it plots significantly above the most isotopically depleted UK coal values reported by Farmer *et al.* (1999). Therefore, this signal is interpreted here as the timing of the maximum deposition of Pb from leaded petrol emissions in the UK and Europe during the late 1970s (See Section 7.1.4).

The age markers selected here are summarised as:

1. 9 cm. The location of the signal of the maximum deposition over western Europe of atmospheric Pb isotopically enriched by leaded petrol, AD 1977 $\pm$ 2.5 yr (Farmer, *et al.*, 1999; Rosman *et al.*, 2000; Reuer and Weiss, 2002).
2. 14 cm. The introduction and expansion of the widespread use of leaded petrol in Europe between AD 1930 and AD 1935 (Nriagu, 1990; Reuer and Weiss, 2002).
3. 17 cm. The increase in the use of coal in the UK and northern Europe around 1900, and assigned the age of AD 1900 $\pm$ 20 (Smol, 2002).

4. 39 cm. The early 19th century increase in industrial Pb emissions, AD 1820 $\pm$ 20 (Farmer, *et al.*, 1999).
5. 45 cm. Expansion of European industries during the 16th century, AD 1550 $\pm$ 75 (Reuer and Weiss, 2002).
6. 64 cm. The start of the Medieval post Roman revival of European metal working, assigned the age of AD 1000 $\pm$ 75 (Reuer and Weiss, 2002).
7. 137.5 cm. The signal of Roman Pb emissions, AD 50 $\pm$ 50 (Reuer and Weiss, 2002).

These markers are shown as an age-depth model in Figure 7.18.

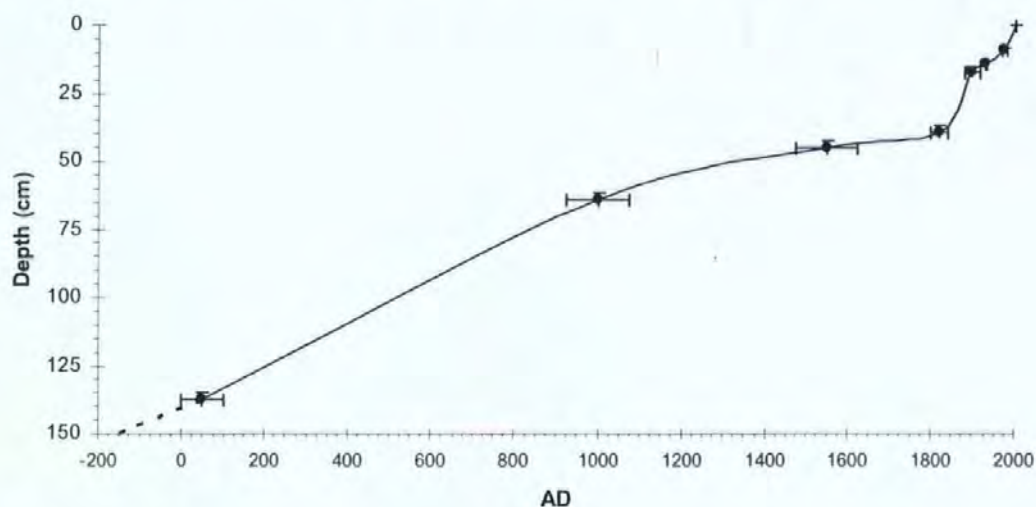


Figure 7.18. Age – depth curve for the Viðarhólmi sediments derived from the Pb deposition history. The broken line is modelled backward from the slope of the lowest two data points. Overall accumulation rate calculated for this section from these data is 0.07 cm yr⁻¹.

7.7. Discussion and synopsis

This section has shown that the use of stable Pb as a chronological marker has a number of advantages. In aerosol form it is easily transported, and disperses freely within an environment subjected to fluid flows and movements. This notwithstanding, once deposited and entombed the metal does not migrate freely within the sediment pore-space, and becomes bound to clay sized particles. Under normal sedimentary geochemical conditions, this metal is not subject to post-burial modification, enrichment or depletion. Its use surmounts the need for organic carbon samples, and therefore this independent dating method can be used to constrain ¹⁴C

dates and thus improve the robustness of a chronology. However, in common with all 'event dating methods', stable Pb data must be calibrated by correlation with a dated master chronology, and so the quality of this initial information will greatly influence the final accuracy, precision and temporal resolution that can be obtained for a sediment sequence.

In the case of the Taf sequence the data could be calibrated using the published UK regional history of Pb emissions and measurements of past deposition, and the documented history of metal working in the Swansea Valley. This additional information for a relatively local, and long-term, significant source of atmospheric Pb pollution enabled the Taf chronology to be established for the 18th and 19th centuries. In addition, because the likely source of the metal ores exploited during different times was known, this information, in conjunction with the published isotopic signatures of the south Wales coal field, could be used to estimate the changing contributions to the sediments from different atmospheric sources through time. The use of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios elegantly described how the influence of petrol additives, derived from isotopically depleted Australian ores, changed through time as the signature of the sediments migrated in 'isotopic space' along the mixing line. All three sites have a clear signal of the timing of the maximum radiometric depletion of atmospheric Pb that is dated to around 1977 in western Europe. These data plot as an extreme end member of the isotopic mixing line for each site, and are in all cases followed chronologically by a rapid return to more radiometric isotopic values, and lower Pb enrichment levels in the overlying sediments.

Using the mixing line approach also highlighted how the continued influence of local geological Pb sources at the Taf and Arne sites has been influenced by fallout Pb from 'exotic' depleted sources. In addition, it is very evident when the Icelandic mixing line is examined that the high volcanic influence at the Viðarhólmi site has ensured that the isotopic signatures of the sediments are significantly enriched when compared to the UCC mean Pb isotope ratios published by Millot *et al.* (2004). However, when the empirical Pb isotope ratio data for the air over Iceland is examined the influence of the local volcanic sources is shown to be much reduced. The 1996 $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios for the air over Reykjavik are not substantially different to those found in other locations in Europe (e.g., Reykjavik 1.123 and 2.126, Avignon 1.124 and 2.126, and Prague, 1.127 and 2.132, respectively $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios; Bollhöfer and Rosman, 2001). This

suggests that any significant contribution to atmospheric Pb from active volcanic systems is spasmodic and short lived.

During an ongoing eruption it is possible that some isotopic enrichment of the atmospheric Pb may be detected over Iceland. The most recent major eruption to 1996 was the one from Hekla in 1991 (Larsen *et al.*, 1992), but data published by Bollhöfer and Rosman (2001) shows that any aerosols produced by this event were dispersed during the subsequent five years. This is in agreement with the proposal presented in Section 6.7.3 that it is possible for substantial eruptions to take place and no corresponding change to be detectable in the record of atmospheric Pb, or that fraction falling to earth (See Figure 7.17). Therefore, the major source of Pb fall-out from atmosphere in Iceland is not on-island volcanic emissions, and the prolonged source of Pb enriched in radiometric isotopes in the Viðarhólmi sediments is from weathered volcanic bedrock or re-worked tephra.

In both the Taf and Arne sediments there is a significant background level of Pb and it is not possible to isolate changes in the atmospheric fraction before the 19th century with any certainty. The sediment flux at these sites contains a significant Pb contribution from local minerogenic sources that obscures any variability in the signals of regional atmospheric Pb fallout. However, the reverse was true for the Icelandic sequence. Here the low levels of Pb contained in the local geology facilitated the detection of atmospheric Pb fallout. In addition, the isotopic signatures of the local volcanic Pb emissions are sufficiently different to allow this information to be used to confirm an off-island source for the majority of the Pb detected in the samples.

In summary, the Pb analysis of each of the three sediment sequences has successfully produced a high resolution sequential record of Pb enrichment for each of the study sites. Elemental and isotopic ratios have been determined using advanced mass spectrometry, and these data have been used to isolate the contribution from atmospheric fallout to the total Pb inventory retained in the sediments. Chronologies have been subsequently produced for each site using Pb data calibrated using the published record of World Pb production, supported by correlations with other sedimentary studies of northern European atmospheric Pb deposition. In the case of the Taf and the Arne the chronology spans the last 200 yr, but at the Icelandic site the chronology extends back for 2000 yr. These chronologies will be evaluated, and combined with the other chronological information from each site, in the next chapter.

Chapter 8

The combined chronologies

Chapters 3 to 7 of this thesis have examined the use of a number of different methodologies for dating salt-marsh sediments at three sites. These results were reported and discussed in each section, but now Chapter 8 will refine the results and present a chronology for each site by combining and interpreting all the information available from the different dating methods. In this way it will be possible to evaluate the apparent level of success achieved at each site for the individual dating techniques. Finally, this chapter will highlight and discuss any specific issues that have emerged while constructing the combined chronologies.

8.1. Approach

8.1.1. Accuracy and precision. To create the best chronology, the most robust age markers must be selected. Therefore, the chronological accuracy and the dating precision (or the uncertainty) need to be evaluated. Consideration needs to be given to the reliability of the raw data used by each dating method, the analysis used to produce it, and the way it has been calibrated into a calendar date. For example, an instrument, like a mass spectrometer, may be said to be both accurate and precise if it can reliably measure an amount, or concentration, correctly each time, and do it with a narrow, or precise, range of uncertainty. If the result can be replicated 'at will' the instrument can be said to be reliable, and the results it produces robust. If data produced by such an instrument are converted into a date using an equally accurate and precise calibration method then a robust age will be obtained, i.e. it will be chronologically both accurate and precise, and could be judged reliable. If a date can be replicated by duplicating the analysis and calibration, this could be judged as robust. This could be from a replicate sample using the same analysis, or, even better, a duplicate section. However, if a dating result is in agreement with one, or more, independent methods, it can be judged as very robust.

Alternatively, if a calibration method used to convert raw data produced by a robust analysis into a calendar date has a large age uncertainty attached to it the final age may be chronologically accurate, but the result will have low dating precision. The resulting date will have a wide age range, and may be only useful as part of a low resolution chronology. For example, an SCP analysis can be analytically very accurate if the counting is carried out carefully, but if it is calibrated using a low

resolution regional master curve, with poor initial age control, it may be reliable and reproducible, and may be accurate within a given age range, but it will have low chronological precision.

8.1.2. The evaluation method. To initially display all the data, and to facilitate the manual selection of the age markers, OXCAL v3.10 (Bronk Ramsey, 2005) was used to calculate the distribution plots of the individual age markers for each site. These were not created for the ^{210}Pb chronologies from the Taf and the Arne. The ages, and the associated error margin, obtained from each method were entered as calendar dates into OXCAL. The program was then used to produce distribution plots for these data, and the pre bomb ^{14}C dates from each site using the Intcal04 calibration curve. Unlike CALIBomb, the version of OXCAL used here (v3.10) does not offer the facility to combine seamlessly calibration curves, nor will it accept post-bomb ^{14}C data in F^{14}C format. Therefore, to simply display the fit of the post-bomb dates into the chronology, probability distribution plots were produced by inputting the Arne CALIBomb calibrated ages as calendar dates.

To evaluate the performance of each of the dating methods, all the viable chronological information, produced for each of the three sediment sections investigated, were plotted together for each research site using age and depth. Using a simple subjective, but systematic, approach robust age markers were selected from each set of chronological data. If the dates were supported by one or more independent age markers they were viewed with more credibility than isolated single markers. The age markers were evaluated as to the level of agreement demonstrated between the marker being considered and one, or more, independent methods. In addition, the markers were selected while maintaining the strict stratigraphic order of the samples. In this way oldest and youngest boundaries can be established that constrain sections of a chronology using the concept of 'prior knowledge'.

8.1.3. Creating the chronologies. The objective was to create a chronological envelope that would encompass the most likely ages for the sediment deposition at each level for each site. Where two, or more, methods agreed as to the deposition age of a level, the marker with the best chronological precision, i.e. the smallest age range, was used to constrain the chronology.

8.2. The Taf chronology. The individual Taf chronological age markers are shown in Figure 8.1. The ^{210}Pb CIC chronology is not included in this diagram but are shown in Figure 8.2B. The 1998 radionuclide data (W. R. Gehrels, unpublished data) used here have been depth corrected to 2003 by adding five years sediment accumulation. This was calculated as 1.8 cm using the ^{137}Cs 1956 marker at 15 cm. An inspection of the data in Figure 8.2A identifies two distinct sections:

1. 0 cm to 25 cm.
2. 25 cm down to 108.5 cm.

The base of the upper section (1) is constrained by the stable Pb marker at 25 cm. This is considered a robust marker because it was produced by a very precise analysis, and has a very secure age calibration. Consequently it has a small age uncertainty associated with it. It is also in agreement with the lowest dates produced by the ^{210}Pb CIC chronology. Higher in the sequence there is disagreement between the ^{210}Pb CIC chronology and the lowest ^{137}Cs marker at 17.5 cm, but there is agreement between the ^{137}Cs marker at 10.3 cm, the stable Pb marker at 11.5 cm and the CIC chronology at these levels. There is good agreement between the CIC chronology and the 1977 leaded petrol marker at 9.5 cm, and the ^{137}Cs marker at 4.3 cm.

When all this information is considered, all the age markers shown in Figure 8.2B are selected between 0 cm and 25 cm as being plausible with the exception of the isolated ^{137}Cs marker from 17.3 cm. This is rejected because the calibration of this point is not as secure as the other markers and it disagrees with the ^{210}Pb CIC chronology (see Chapter 4). To create the combined chronology it is first noted that the ^{210}Pb CIC chronology lies to the right of the other markers. Therefore, this is used as the upper age limit down to 25 cm were it is felt the stable Pb marker is more robust, and so is used to constrain the chronology here as AD 1885 $\pm$ 5 yr. The analytical error attached to the Taf ^{210}Pb analysis is not known but an uncertainty of $\pm$ 10 yr around 1900 would be typical (see Chapter 4) of this type of data, so an arbitrary $\pm$ 5 yr (1.8 cm) to $\pm$ 10 yr (25.3 cm) is used. This produced a line for the older boundary that was within the range of all the stable Pb markers, and impinges the ^{137}Cs marker at 4.3 cm. The ^{137}Cs marker from 10.3 cm has an age of 1960 to 1966 but the CIC chronology age for this depth, with the error estimated as described above, is 1969 to 1982.

Surface Cal. Date 0 cm 2003
 ^{137}Cs - Cal. Date 4.3 cm 1986 $\pm$ 3
 Stable Pb Cal. Date 9.5 cm 1977 $\pm$ 5
 ^{137}Cs Cal. Date 10.3 cm 1963 $\pm$ 3
 Stable Pb Cal. Date 11.5 cm 1960 $\pm$ 5
 ^{137}Cs - Cal. Date 17.3 cm 1956 $\pm$ 5
 Palaeomag Cal. Date 24 cm 1585 $\pm$ 66
 Stable Pb - Cal. Date 25 cm 1890 $\pm$ 5
 Palaeomag Cal. Date 30 cm 905 $\pm$ 84
 ^{14}C 30.5 cm 509 $\pm$ 33BP
 ^{14}C 34.5 cm 746 $\pm$ 37BP
 ^{14}C 39.5 cm 692 $\pm$ 39BP
 ^{14}C 44.5 cm 842 $\pm$ 41BP
 Palaeomag Cal. Date 46 cm 625 $\pm$ 96
 ^{14}C 49.5 cm 982 $\pm$ 36BP
 ^{14}C 54.5 cm 1237 $\pm$ 43BP
 Palaeomag Cal. Date 56 cm -375 $\pm$ 128
 ^{14}C 59.5 cm 1038 $\pm$ 28BP
 ^{14}C 64.5 cm 1637 $\pm$ 28BP
 ^{14}C 69.5 cm 1416 $\pm$ 36BP
 Palaeomag Cal. Date 74 cm -375 $\pm$ 132
 ^{14}C 74.5 cm 1524 $\pm$ 42BP
 ^{14}C 79.5 cm 2070 $\pm$ 39BP
 Palaeomag Cal. Date 84 cm -695 $\pm$ 143
 ^{14}C 84.5 cm 2061 $\pm$ 42BP
 ^{14}C 89.5 cm 2044 $\pm$ 41BP
 Palaeomag Cal. Date 94 cm -1095 $\pm$ 157
 ^{14}C 94.5 cm 4800 $\pm$ 45BP
 ^{14}C 99.5 cm 3047 $\pm$ 33BP
 ^{14}C 106.5 cm 3099 $\pm$ 37BP
 ^{14}C 107.5 cm 3047 $\pm$ 36BP
 ^{14}C 108.5 cm 3456 $\pm$ 36BP

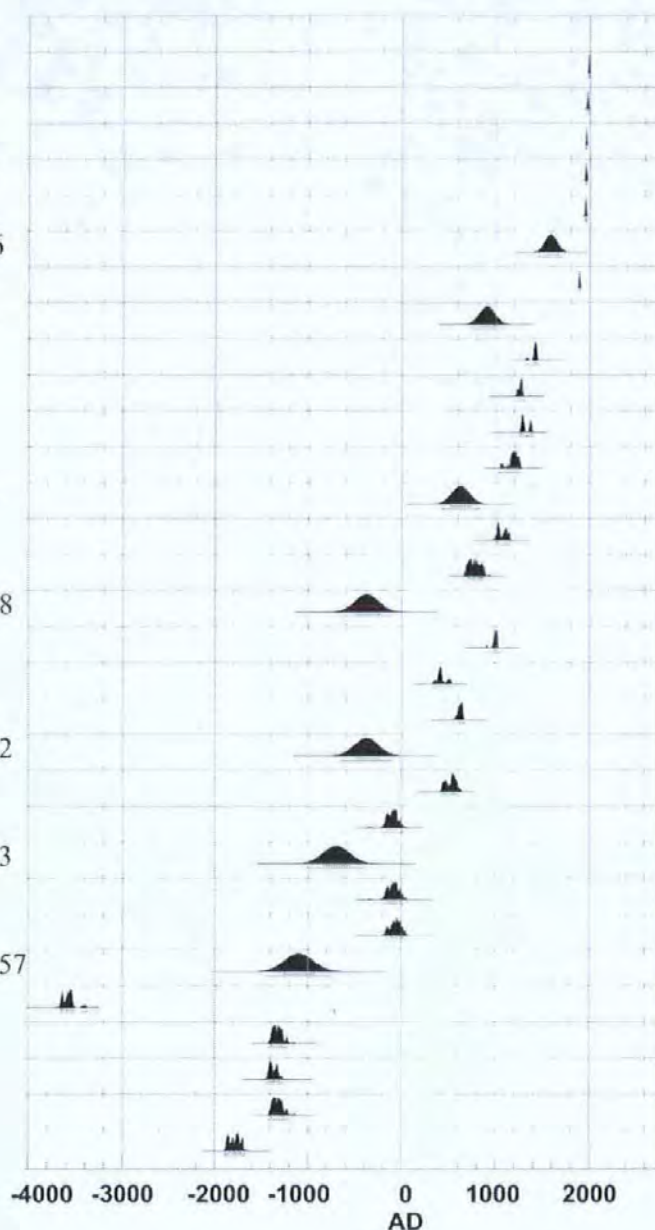


Figure 8.1. The individual Taf age markers, and the distribution plots calculated by OXCAL v3.10 (Bronk Ramsey, 2005). Note: the ages are shown in stratigraphic order, and no vertical age scale is implied. Negative Cal. dates are BC. Note the ^{14}C date from 94.5 cm is regarded as an outlier.

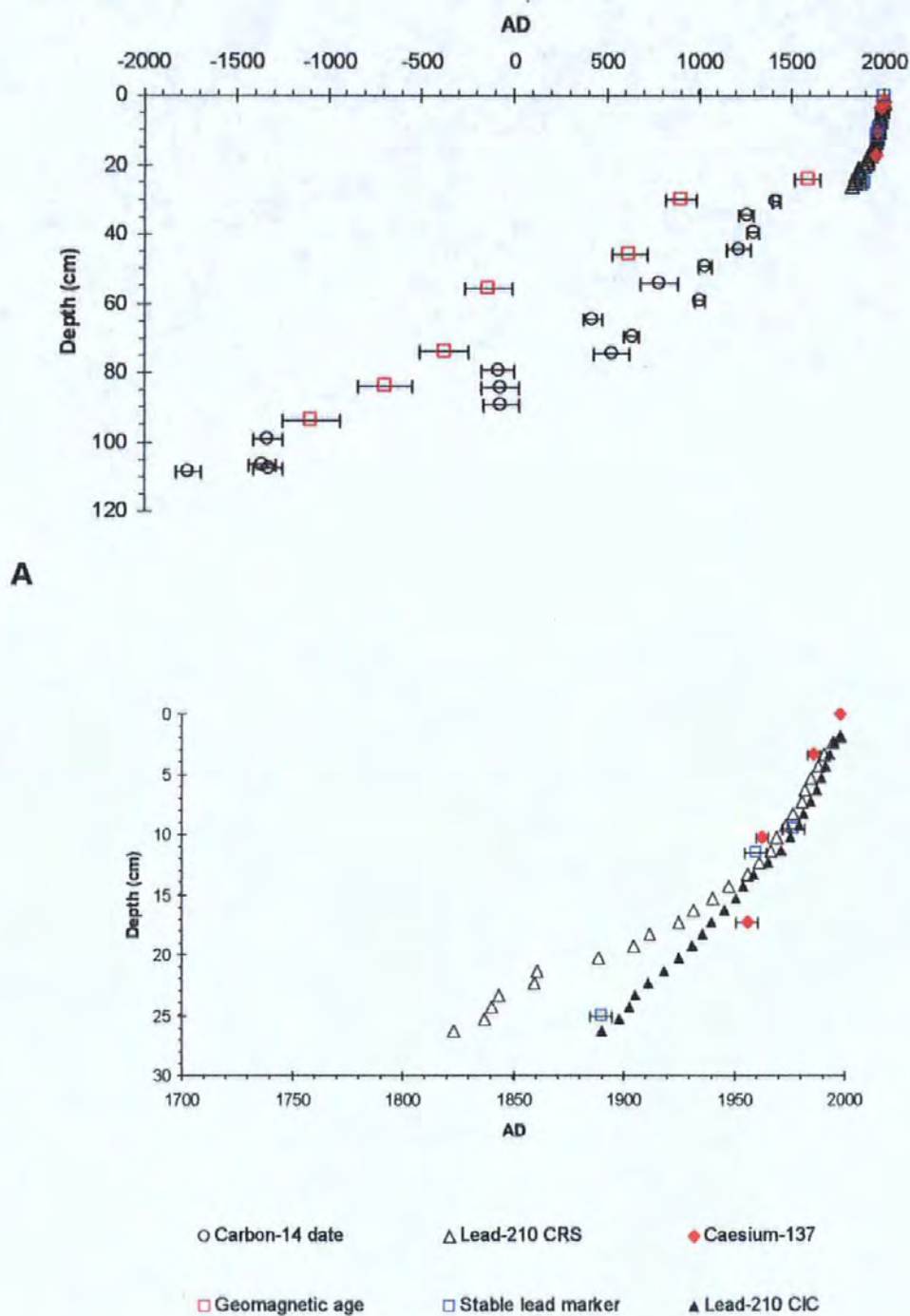


Figure 8.2. All of the viable Taf chronological data. The ^{14}C outlier (4800 ± 45 BP) from 94.5 cm and the ^{210}Pb CIC data are not plotted in panel A.

The lower section (2) contains all the ^{14}C and palaeomagnetic ages and is bounded by the deepest ^{14}C date from 108.5 cm at the base, and the stable Pb marker at the

top. There is a significant amount of scatter in the ^{14}C data with a number of stratigraphic reversals. In addition, there is disagreement between both the stable Pb marker at 25 cm and the ^{14}C ages, and many of the palaeomagnetic ages (Figure 8.2). The stable Pb marker has already been evaluated as robust in section 1, but to decide which of these other markers are robust the palaeomagnetic ages are examined first.

The highest palaeomagnetic marker (24 cm) is in chronological disagreement with the stable Pb marker at 25 cm and is therefore immediately rejected. However, to evaluate the robustness of the other palaeomagnetic markers it is necessary to examine the initial analysis. If the raw palaeomagnetic data are considered, one measure of robustness discussed in Section 5.2.1 is the MAD value. Only samples with MAD values below 3° can be regarded as robust (English Heritage, 2006) and those above this value must be treated with caution. The MAD value is generated during the PCA stage of the data handling, and is detrimentally influenced by weak NRM intensity values, and these are in turn associated with low K values. In summary, the lower the magnetic susceptibility (K value) of the sediments, the less reliable the NRM data. This information can therefore be used to select the palaeomagnetic dates that have been produced by the most robust raw data. Beyond this, it is not possible to assess the precision and accuracy of each individual palaeomagnetic age calibration, but any difference in the master curve accuracy with each sample is assumed to be minimal, and is therefore ignored.

When the MAD values for the Taf palaeomagnetic dates are considered (Table 8.1), only the result from 94 cm is below the critical 3° . However, the results from 74 cm and 46 cm are also judged to be credible dates, but not as robust. Therefore, these three palaeomagnetic dates are selected. It is noted that the MAD value for the sample from 24 cm, rejected as being in stratigraphic disagreement with the stable Pb marker at the top of this section, was 12.6° .

Depth (cm)	MAD	Age (AD)	Master curve age uncertainty (yr)
24	12.6	1585	±66
30	11.7	905	±84
46	6.2	625	±96
56	9.2	-135	±128
74	4.85	-375	±132
84	9.85	-695	±143
94	2.7	-1095	±157

Table 8.1. The MAD values associated with the deposition ages determined from the Taf palaeomagnetic data. Values used are the mean of the Taf-02 and Taf-03 data. Master curve uncertainty is estimated as outlined in section 5.1.5. (See Table 5.2). Ages selected in **bold**.

It is less straightforward to evaluate the robustness of the ^{14}C ages. What is known is that these ages have been produced from bulk carbon samples that may have contained an unknown amount of 'young' carbon from disintegrated microscopic root material that may not have been fully removed by the processing of the samples (see Chapter 3). Therefore, it is very unlikely that any of the ^{14}C age will be too old, but they may be too young. There are a number of groups of results where the calibrated ages ranges overlap, and yet the samples are from different levels (e.g., 79.5 cm, 84.5 cm and 89.5 cm) or stratigraphic order can not be maintained because the calibrated ages reverse (e.g., 64.5 cm, 69.5 cm and 74.5 cm). In both these situations the younger or deeper ages of a group are consider to be unreliable.

The ^{14}C age of 1890 BC to 1680 BC at 108.5 cm is in isolation, and although it can not be accepted as being robust, it can not be rejected. The ^{14}C marker at 99.5 cm is in stratigraphic agreement with this age, and the overlying palaeomagnetic marker at 94 cm. It is also the shallowest of three ^{14}C dates with similar calibrated ages and so is taken to be the most secure. From this point up to 34.5 cm all the ^{14}C dates, because of the chronological reversals and the stratigraphic disagreements

apparent in this section, are not considered accurate due to the 'young carbon' issue discussed above. However, the upper extremity of this group can be used as a 'youngest possible' limiting line, and this interpretation supports the selection of the palaeomagnetic date at 46 cm as being a robust age marker. When this marker is joined to the stable Pb marker at 25 cm the ^{14}C dates at 34.5 and 30.5 cm are in some agreement with this solution. Although the date at 34.5 is underlain by a chronological reversal it is in stratigraphic agreement with the chronology indicated by the palaeomagnetic date and the stable Pb marker at 25 cm, and the isolated ^{14}C date at 30.5 cm

The Taf age markers selected are tabulated in Table 8.2, and plotted as an age-depth model in Figure 8.3.

Depth (cm)	Lower age (BC-AD)	Upper age (BC-AD)	Marker	Description
0	2003	2003	Sediment	Present day marsh surface
4.3	1983	1989	^{137}Cs	1986 Chernobyl fallout over Wales
9.5	1972	1982	Stable Pb	1977 decrease in European leaded petrol
11.5	1955	1965	stable Pb	Late 1950s – early 1960s peak in atmospheric Pb over the UK
25	1885	1895	Stable Pb	Late 1800s maximum of Pb smelting in the Swansea Valley
30.5	1395	1445*	^{14}C	509 ± 33 ^{14}C yr BP
34.5	1218	1299*	^{14}C	746 ± 37 ^{14}C yr BP
46	529	721	Palaeomag.	AD 625 $\pm$ 96
74	-507	-243	Palaeomag.	375 $\pm$ 132 BC
94	-1252	-938	Palaeomag.	1095 $\pm$ 157 BC
99.5	-1420	-1210*	^{14}C	3047 ± 45 ^{14}C yr BP
108.5	-1890	-1680*	^{14}C	3456 ± 56 ^{14}C yr BP

Table 8.2. The age markers selected for the Taf combined chronology. * = ^{14}C best relative calibration curve area range from Calib 4.0 using the INTCAL98 curve (Stuiver *et al.*, 1998).

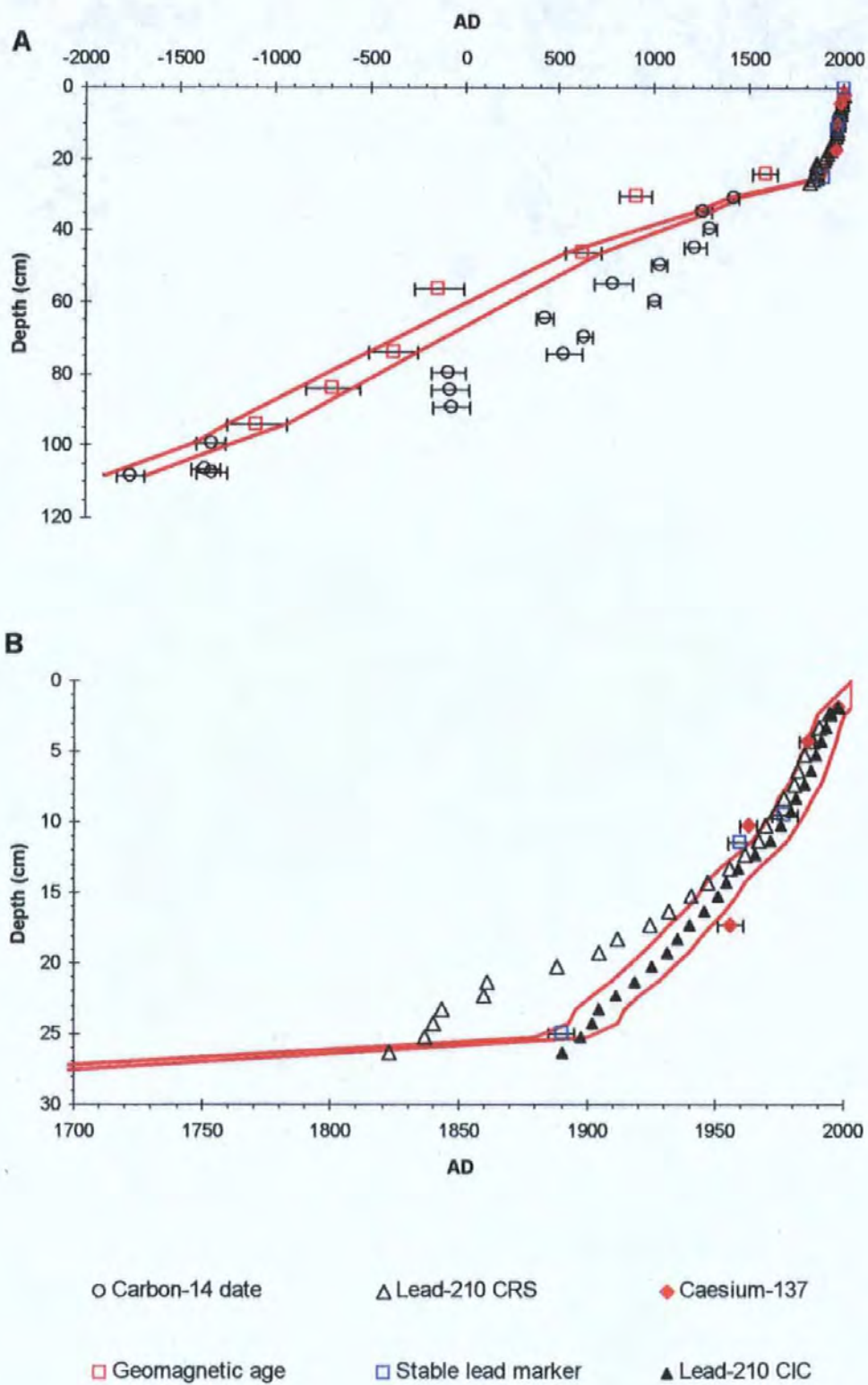


Figure 8.3. The Taf combined chronology. A, 1890 BC to AD 2003, B, The last 300 yr.

8.3. The Arne chronology. The dating information available for the Arne site is shown in Figure 8.4. By considering all the chronological data it is now possible to resolve the issue that emerged when only the ^{14}C dates were considered. In Chapter 3 two calibration were solutions presented for the Arne pre-bomb ^{14}C dates, but the independent age markers at 40 cm (Pollen), 50 cm (SCP) and 55 cm (Stable Pb) can be used to constrain the ^{14}C data. The date derived from the pollen analysis is awarded an uncertainty of only ± 5 yr, but chronological precision of the stable Pb and SCP markers is lower. This notwithstanding, they are viewed as reliable estimates, and together they form a chronological boundary zone, i.e. all the ages for the sediments above this level must be younger and all the dates from the levels below these three markers must be older. This information confirms that Arne-03-47.5 is out of stratigraphic order, and this indicates that solution 1 presented in Chapter 3 should be rejected. What is more, if solution 2 is accepted the stable Pb marker from 55 cm is in near perfect agreement with the ^{14}C date from the same level, i.e. AD 1825 $\pm$ 20 and AD 1825 $\pm$ 11 respectively (Figure 8.5).

The chronology from the pollen marker at 40 cm up to the ^{14}C bomb date at 26.5 cm is very well constrained by four independent dating methods that are all in good agreement (Figure 8.4). In Chapter 3 there was some uncertainty as to the most accurate calibration for Arne-03-26.5 (AD 1963.13 $\pm$ 0.11), but the stratigraphic order, and close proximity, of the other markers (e.g., SCP, ^{137}Cs and stable Pb) support the original solution. However, there is some disagreement between the ^{14}C bomb calibrated dates, Arne-03-26.5 and Arne-03-25 and the ^{137}Cs bomb peak marker from 20.5 cm (Figure 8.5). In this situation, assuming no contamination of the samples or the effects of unknown analytical errors, and in the light of the concerns about the post deposition migration of ^{137}Cs , it is proposed that the two ^{14}C dates are likely to be more accurate than the single ^{137}Cs marker.

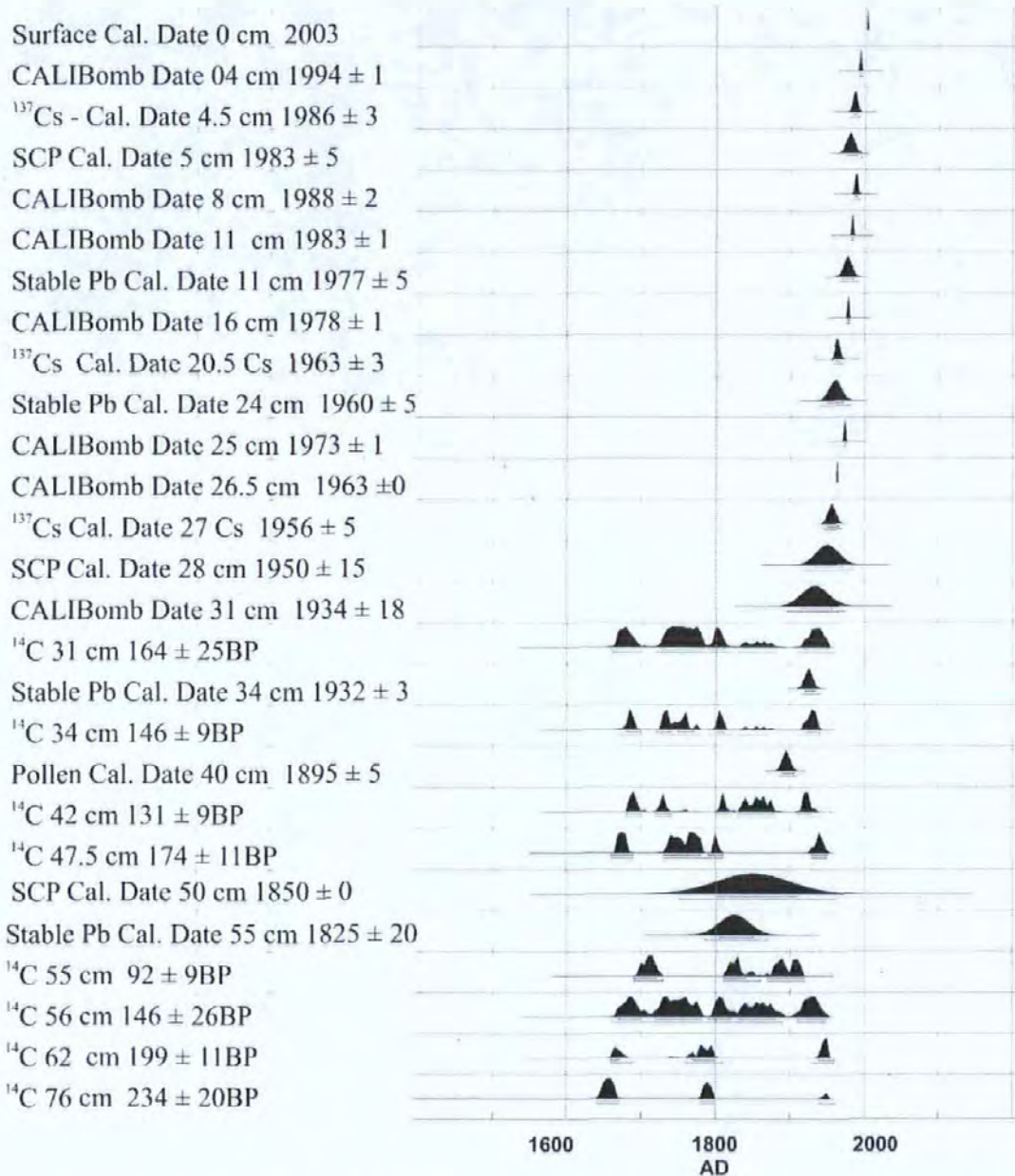


Figure 8.4. The individual Arne age markers, and the distribution plots calculated by OXCAL v3.10 (Bronk Ramsey, 2005). Note: the ages are shown in stratigraphic order, and no vertical age scale is implied. CALIBomb calibrations used for post bomb ^{14}C dates.

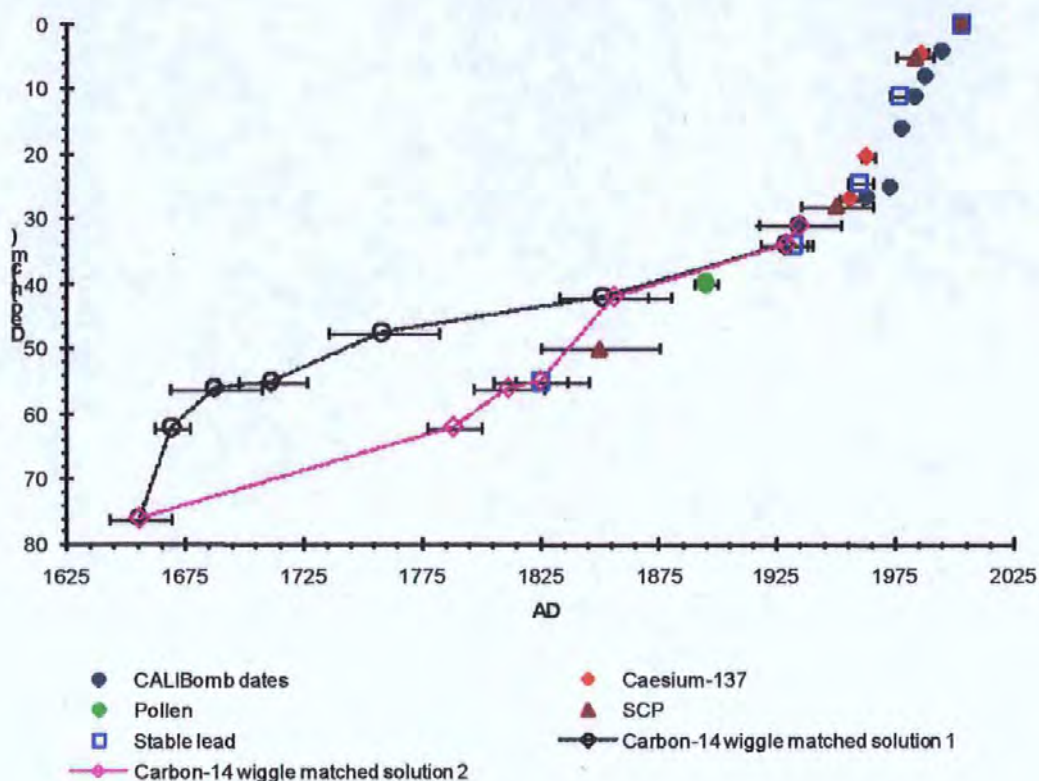


Figure 8.5. The Arne chronological markers showing the ^{14}C two solutions from Chapter 3. The ^{210}Pb chronologies are omitted from this plot.

The precision of the lower section can not be reduced to less than the ^{14}C uncertainty. At 55 cm the two age markers agree as to the mid age (1825-1826) but the ^{14}C date has a smaller age range (20 yr) than the error attached to the stable Pb marker in Chapter 7 of ± 20 yr. Therefore, the ^{14}C date gives the most precise solution at this level. Above 55 cm, the pollen marker from 40 cm and the stable Pb marker 34 cm refine the chronology significantly. The SCP marker at 50 cm is a relatively low precision marker so it is sufficient for the chronology to pass through the age range. It is proposed that the ^{14}C dates from 55 cm and 56.5 cm, supported by the stable Pb marker from 55 cm, constitute a robust anchor point for the lower section of the Arne chronology. From this point upward two options are possible, (1) to incorporate the whole of ^{14}C age range at 42 cm, or (2) to bypass this marker and use the pollen marker at 40 cm as the anchor point. The second option is selected because it still falls within the error range of the ^{14}C age at 42 cm, and it offers a simpler solution. Calib and CALIBomb produced the same calibration of Arne-03-3, i.e. AD 1933 $\pm$ 18, but the independent markers (e.g., stable Pb) indicate that this uncertainty can be confidently reduced. The stable Pb marker from 34 cm is dated as 1930 to 1935, so at this level, in contrast to the situation at 55 cm, the most

precise solution is obtained by using the stable Pb marker to constrain the chronology. From this level to the surface the CALIBomb ages are proposed to offer a plausible chronology with a realistic level of precision. When the upper SCP markers are examined this chronology passes through the range of the markers at 28 cm and at 5 cm. The stable Pb (1960 $\pm$ 5 at 24.5 cm) and the ^{137}Cs (1963 $\pm$ 5 at 20.5 cm) markers do not agree precisely with the bomb calibrated ^{14}C dates, but it is proposed that these data have more uncertainty attached to them than the ^{14}C data.

The questions surrounding reliability of ^{137}Cs as a high-resolution chronological marker in salt-marsh sediments have been highlighted already (Chapter 4), and this issue is discussed again in Section 8.5. The stable Pb marker at 24.5 cm is not precise, and could be significantly influenced by local factors. It is interpreted as the signal of the regional maximum of atmospheric Pb, but there is strong evidence (e.g., the Taf Pb record, and references in Chapter 7) that local historic industrial emissions can overprint and distort the regional record of Pb deposition. The markers selected (Table 8.3) are shown as an age-depth model in Figure 8.6.

Depth (cm)			Marker	Description
	Lower age (AD)	Upper age (AD)		
0	2003	2003	Sediment	Present day marsh surface
4	1992	1996	^{14}C #	1.1262 $\pm$ 0.0035 F ^{14}C
8	1984	1992	^{14}C #	1.1825 $\pm$ 0.0038 F ^{14}C
11	1981	1985	^{14}C #	1.2390 $\pm$ 0.0039 F ^{14}C
16	1976	1980	^{14}C #	1.3363 $\pm$ 0.0043 F ^{14}C
25	1971	1975	^{14}C #	1.4609 $\pm$ 0.0049 F ^{14}C 1972.1 to 1973.9 – falling limb of nuclear weapons test fallout in the Northern Hemisphere
26.5	1963	1963	^{14}C #	1.4637 $\pm$ 0.0049 F ^{14}C 1963.0 to 1963.2 – rising limb of nuclear weapons test fallout in the Northern Hemisphere
34	1930	1935	Stable Pb	The introduction and expansion of the widespread use of leaded petrol in Europe between AD 1930 and AD 1935
40	1890	1900	Pollen	1895 $\pm$ 5 - documented first local appearance of an exotic pollen marker
42	1833	1870	^{14}C *	131 $\pm$ 9 ^{14}C yr BP
55	1814	1836	^{14}C *	92 $\pm$ 9 ^{14}C yr BP
62	1777	1800	^{14}C *	199 $\pm$ 11 ^{14}C yr BP
76	1643	1669	^{14}C *	234 $\pm$ 20 ^{14}C yr BP

Table 8.3. The age markers selected for the Arne combined chronology. ^{14}C calibration by Calib*, and CALIBomb#.

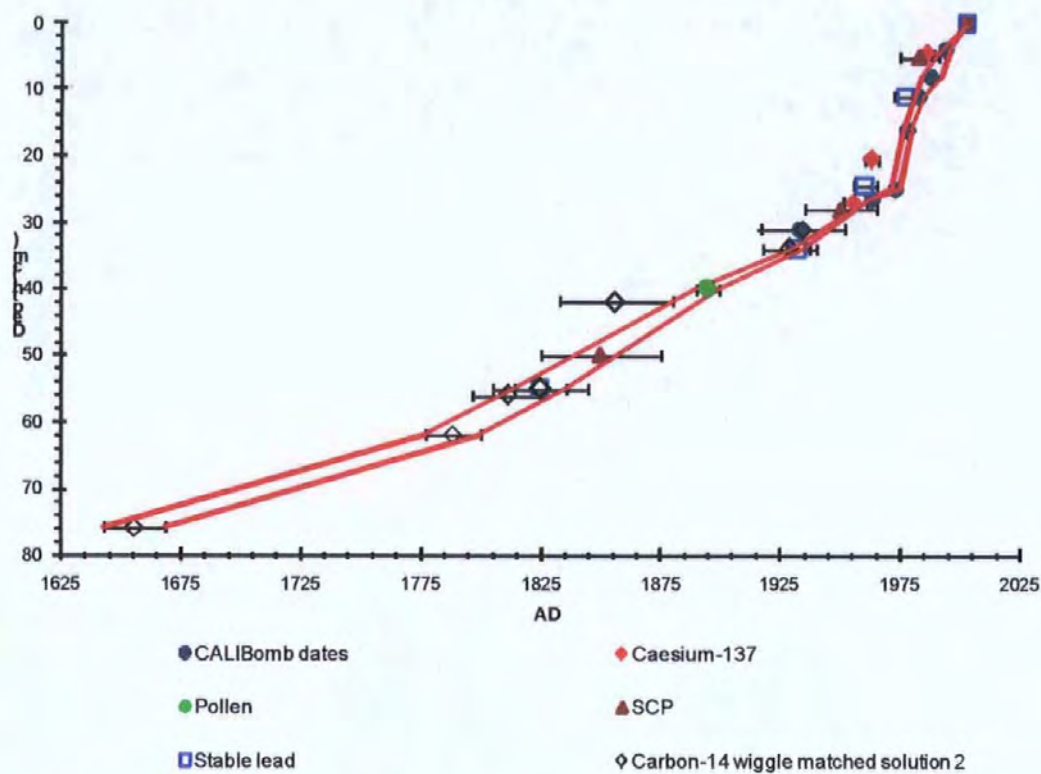


Figure 8.6. The Arne combined chronology.

8.4. The Viðarhólmi chronology. The different dating results from the Viðarhólmi salt-marsh site are shown in Figure 8.7. A number of levels in the section have two or more age markers in close agreement. The same approach was used here as applied to the data from the other two sites. However, in contrast to the Taf data, the MAD values for all the Viðarhólmi palaeomagnetic ages produced in Chapter 5 are below 5°.

The sequence of all the chronological markers, and their relative age ranges, is shown in Figure 8.8. There are a number of levels that have two or more independent dating methods in close agreement. Three ^{14}C dates constrain the oldest part of the lower section. They are in correct stratigraphic sequence, and agree with the stable Pb marker that is allocated the age of AD 50 $\pm$ 50 (Chapter 7). This Pb marker effectively constrains the calibration of ^{14}C date from the sample from 145 cm as AD 82 -100. A second closely dated point is the Landnám Tephra, or Settlement layer, at 81.5 cm, dated to AD 875 $\pm$ 6 yr; (Grönvold *et al.*, 1995; Wastegård *et al.*, 2003). This is considered one of the primary, high precision, age markers in the sequence (Figure 8.7).

A lower tephra layer is found at 87 cm but the identification and dating of this layer is not as secure as the Landnám Tephra. However, it confirms the ^{14}C ages from this lower section. In the lowest levels, the ^{14}C dates offer a valid chronology, but this can be further refined by combining the stable Pb marker from 137.5 cm. Above this level the section is secured by the tephra markers at 81.5 cm and 63 cm. The sea rafted pumice layer (AD 1225.5 $\pm$ 0.5) at 63 cm is in good agreement with a proximal ^{14}C age and an overlying geomagnetic date. This agreement of three independent methods produces a very precise, and robust, solution for this level. The proposed chronology passes through the ^{14}C date at 51 cm, the age range of a palaeomagnetic marker at 50 cm and a stable Pb marker at 45 cm. These three markers are not included in Table 8.3 but they do confirm the validity of this section of the proposed chronological solution for the Viðarhólmi sequence.

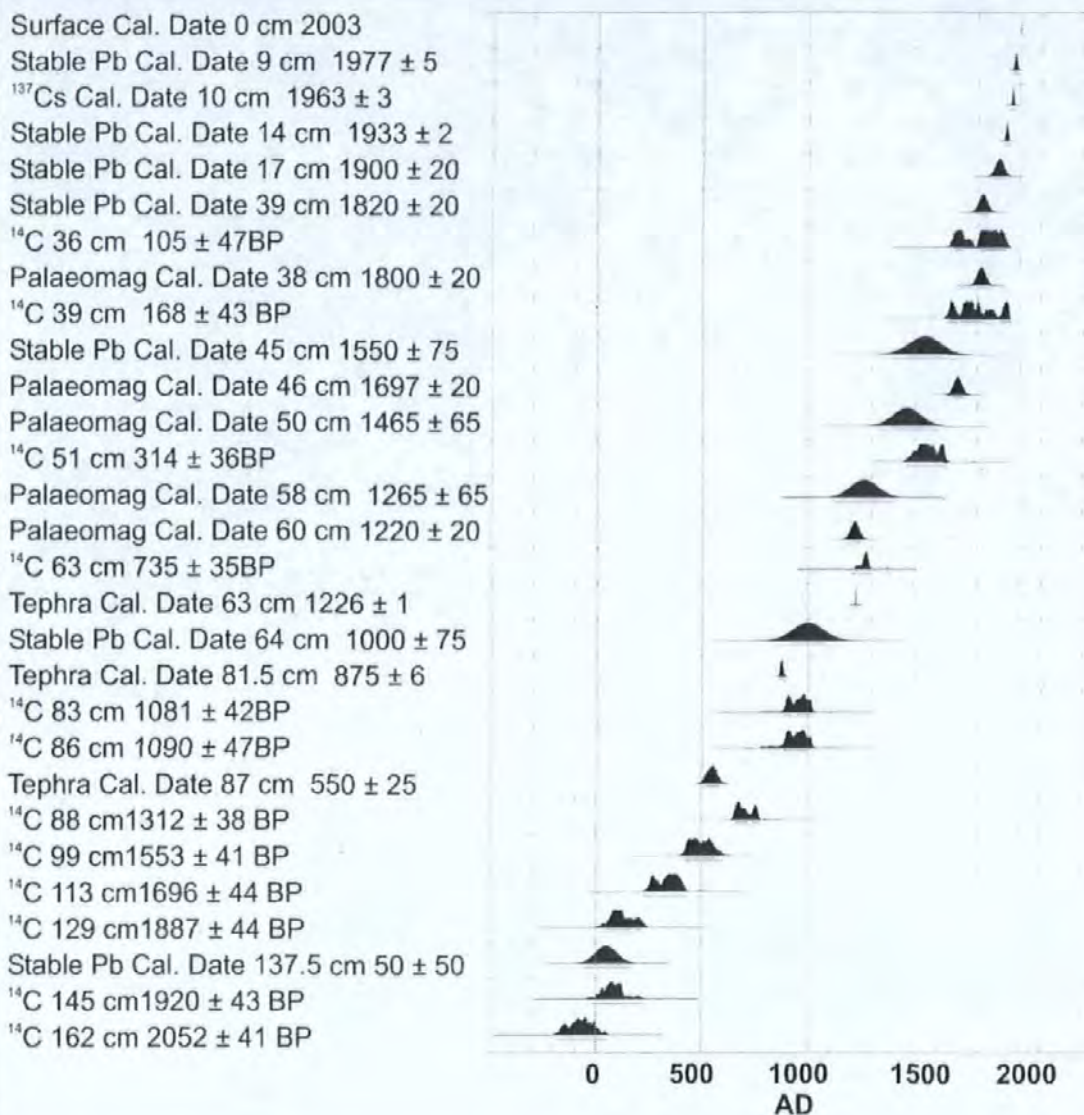
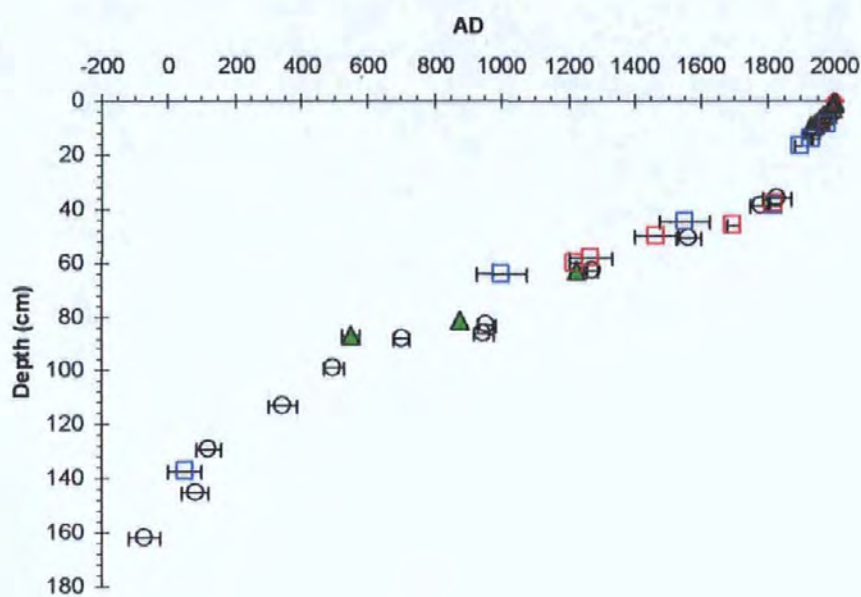
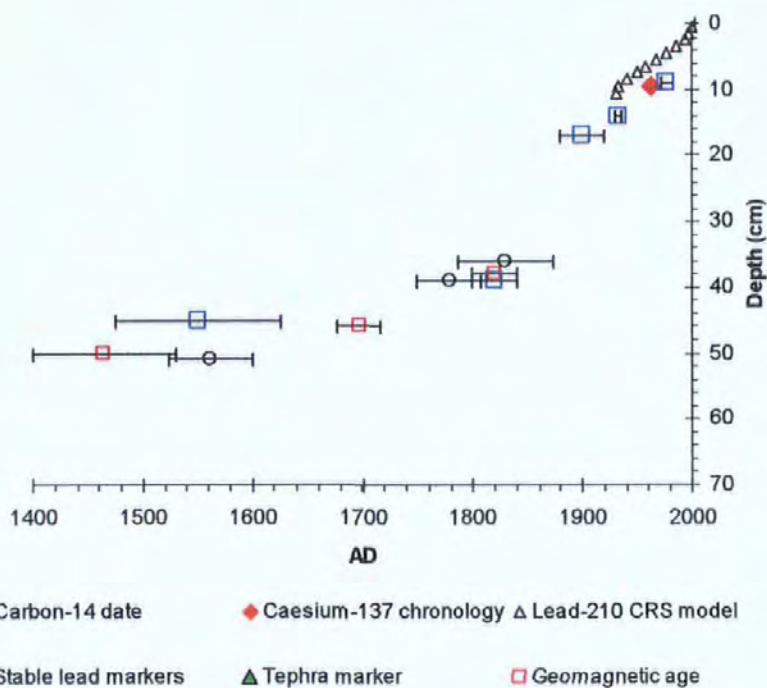


Figure 8.7. . The individual Viðarhólmi age markers, and the distribution plots calculated by OXCAL v3.10 (Bronk Ramsey, 2005). Note: the ages are shown in stratigraphic order, and no vertical age scale is implied.

A palaeomagnetic date (MAD 2.6°) is used at 46 cm, and at 38 cm (MAD 2.5°). The upper palaeomagnetic marker is in stratigraphic agreement with the stable Pb marker from 39 cm, and they both are assigned the age of 1820 $\pm$ 20. Above this level the northwestern European history of the atmospheric fallout from leaded petrol provides robust markers for 14 cm and 9 cm (Table 8.3). The stable Pb marker from 9 cm and the ¹³⁷Cs marker (1963) at 9.5 cm are in agreement, but of the two markers the stable Pb is viewed as the preferred solution here.



A



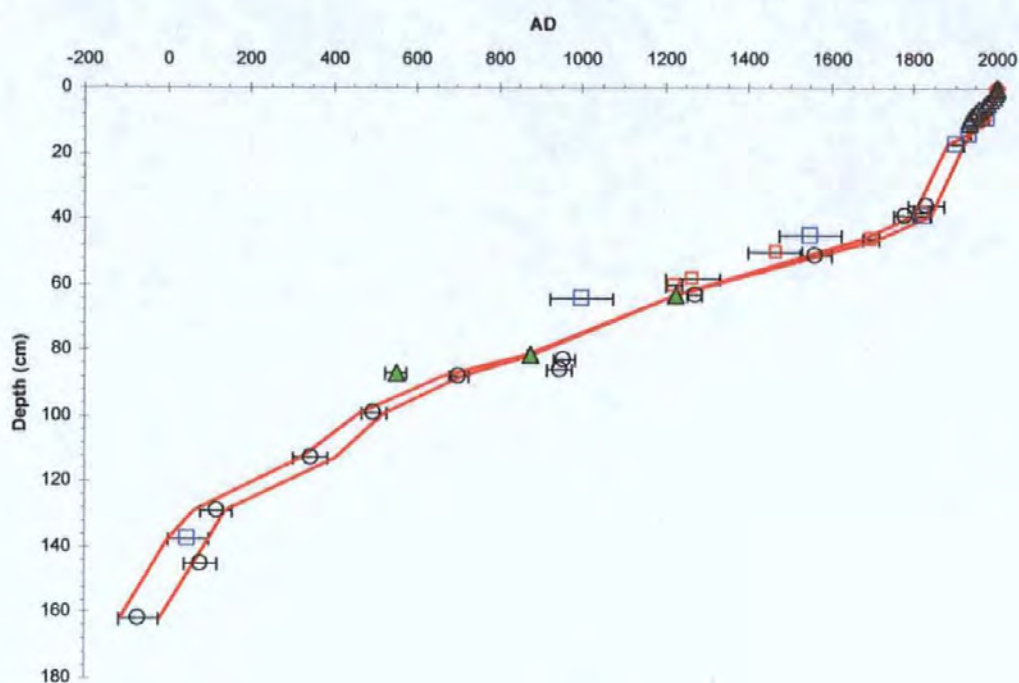
B

Figure 8.8. The Viðarhólmi chronological markers. Lead-210 CRS model shown for comparison purposes only.

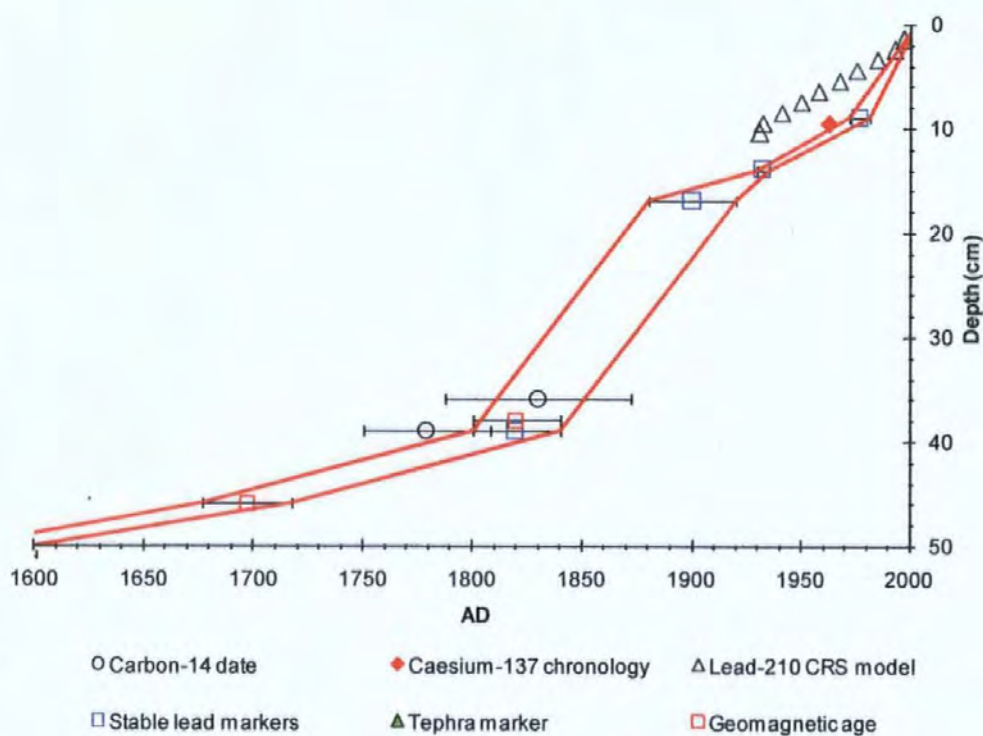
The markers selected (Table 8.4) are used to produce the final chronology shown as an age-depth model in Figure 8.9. The ^{14}C ages, the tephra markers from 81.5 cm and 63 cm, the ^{137}Cs markers, the stable Pb marker from 39 cm and the palaeomagnetic age from 38 cm are all used in Gehrels *et al.* (2006). Additional palaeomagnetic and stable Pb data are used here, but the resulting chronology is essential the same apart from some refinements for the section covering the last 50 yr, and the consolidation of the base of the chronology by the use of the new stable Pb marker identified as signalling the time of the Roman Empire.

Depth (cm)			Marker	Description
	Lower age (AD)	Upper age (AD)		
0	2003	2003	Sediment	Present day marsh surface
9	1972	1982	Stable Pb	1977 $\pm$ 5 - decrease in European leaded petrol
14	1930	1935	Stable Pb	1930s widespread use of leaded petrol in Europe
17	1880	1920	Stable Pb	Late 1800s early 1900s industrial expansion.
38	1800	1840	Palaeomagnetic	1820 – observed and documented abrupt shift in regional magnetic declination
46	1677	1717	Palaeomagnetic	Late 1600s – early 1700s magnetic inclination plateau
63	1225	1226	Tephra	Mediaeval Layer AD 1226
81.5	869	881	Tephra	Landnám, or Settlement layer, AD 875 $\pm$ 6
88	661	710	^{14}C	1312 $\pm$ 38 ^{14}C yr BP
99	464	524	^{14}C	1553 $\pm$ 41 ^{14}C yr BP
113	323	406	^{14}C	1696 $\pm$ 44 ^{14}C yr BP
129	66	140	^{14}C	1887 $\pm$ 44 ^{14}C yr BP
137.5	0	100	Stable Pb	Pb signal from the Roman Empire – AD 50 $\pm$ 50
162	-112	-17	^{14}C	2052 $\pm$ 41 ^{14}C yr BP

Table 8.4. The age markers selected for the Viðarhólmi combined chronology.



A



B

Figure 8.9. The Viðarhólmi combined chronology. Panel B last 400 yr.

8.5. Evaluation of the site chronologies

8.5.1. The Taf. This chronology covers the last 3800 yr and can be best considered in two sections; that above and that below 25 cm. The older, lower, section relies on a combination of geomagnetic age markers and ^{14}C dates. Both these methods have some inherent uncertainty attached to the initial analysis of the sediments, but in the case of the Taf the lack of discrete organic samples was an additional handicap. This problem was surmounted, to some extent, by the use of bulk carbon samples, but this technique has inevitably resulted in some loss of sampling precision, and some uncertainty as to the provenance of the carbon assayed.

The quality of the sediment samples was also an issue with the palaeomagnetic dating. For a measurable geomagnetic NRM signal to be recorded by the sediments the evidence presented in Chapter 5 indicates that a significant level of magnetic susceptibility must exist in the sediments. In some of the Taf samples the intensity and K values confirmed that the magnetic susceptibility levels were too low for a robust NRM signal to be preserved. When these factors are considered the lower section of the Taf chronology is evaluated as being reliable within the envelope of uncertainty shown in Figure 8.3, but, to reduce this uncertainty additional, and ideally high precision, age markers are needed for the period from 200 BC to AD 1850. This notwithstanding, the result obtained for the lower section of the Taf sediment sequence spans over three thousand years, and is considered to be of sufficient quality to be useful, for example for a sea-level reconstruction.

The section above 25 cm is considered to have a more robust chronological solution than the lower part of the sequence. It uses several independent age markers, and is supported by the ^{210}Pb CIC chronology. The age marker at 25 cm is well constrained by comparisons with the history of Pb emissions, and a dated peat bog sedimentary record of Pb deposition. Above this level the agreement between the stable Pb at 11.5 cm and ^{137}Cs marker at 10.3 cm is excellent, confirming the reliability of the solution proposed for the upper section. Therefore, in contrast to the lower section of the chronology, the last 100 yr are very well dated in the Taf sediment sequence.

8.5.2. The Arne. The multi dating method approach has produced a high resolution sediment deposition chronology at this site for the last 400 yr. This sediment sequence benefits from the greatest number of dating methods, and these have been used to create a very robust chronology. Below 40 cm, three independent dating methods are used to constrain the ^{14}C dates, and thus improve the absolute precision and accuracy of the resulting chronology for this section. Between 40 cm and 25 cm six different dating methods are used to produce deposition ages for the sediments in this section, and above this level the high precision calibration achieved using CALIBomb, supported by the stable Pb and SCP markers, have resulted in a very tight set of dates.

The independent markers scattered through the Arne sequence have flagged up age markers that are possible outliers, and these can be examined closer, and discarded if necessary. For example, unlike the signal of the maximum deposition of Pb from petrol in 1977, the age of the stable Pb marker at 24.5 cm can be significantly influenced by local factors. It is interpreted as the signal of the regional maximum of atmospheric Pb, but there is evidence (e.g. the Taf Pb record, and references in Chapter 7) that high levels of local industrial emissions can overprint and distort the regional record of Pb deposition. Therefore, although of value, without the support of an empirical record of local Pb emissions, or a local well dated sedimentary record, its precision is not high. Significantly, when the location of the ^{137}Cs markers in this section is examined, there is close agreement between these data and the other dating methods. The ^{137}Cs data were not used to constrain directly the final combined chronology, but they do support it. Therefore, post deposition stability, and the vertical migration of caesium within the sediments, is not considered to be an issue with the Arne chronology.

The Arne chronology is evaluated as being of a very high standard in both robustness and chronological precision. The age uncertainty for most sections is significantly lower than that commonly possible when using each of the dating methods independently.

8.5.3. Viðarhólmi. The Icelandic chronology provides a closely dated record of sediment deposition during the last two millennia. It benefits from two very well documented tephra markers of Medieval age that give these parts of the chronology a precision of $\leq \pm 6$ yr. At the base of the sequence, the isotopic signature of stable atmospheric Pb deposition on the salt-marsh surface is used to signal the timing of the maximum use of this metal by the ancient Roman Empire around AD 50. Stable Pb is also used in the Viðarhólmi chronology to signal the timing of the 19th and 20th century industrial expansion and the use of leaded petrol in Europe. In addition, a very precise geomagnetic signal is used to locate sediments deposited in AD 1820 base on palaeomagnetic and stable Pb dating. This independent chronological information both supports and constrains the ¹⁴C dates that are available for the Viðarhólmi sediment sequence.

The Viðarhólmi chronology is considered to be robust, and most section have good chronological precision. Unfortunately, between 1820 and 1935 the chronology can only be confirmed by the location of two stable Pb markers correlated with the relatively low precision regional UK and European records for this period. However, above this level the chronological precision of the stable Pb markers is better. An earlier version of the Viðarhólmi chronology has been successfully used to reconstruct sea-level change at the site by Gehrels *et al.* (2006). The new version presented in section 8.4 uses a higher resolution, and longer, stable Pb data set, and subsequently has an additional stable Pb marker at 137.5 cm. This consolidates the earlier interpretation for the base of the sequence. Furthermore, the new Pb enrichment data confirm the robustness of the dating of the critical parts of the 18th and 19th centuries, and refines the deposition timing of the last 50 yr.

8.6. Evaluation of the dating methods

8.6.1 Carbon-14 dating. This is one of the traditional dating tools for late Quaternary salt-marsh based sea-level studies, and its use was examined at all three sites. This study has shown that when a high resolution chronology is sought there are issues to be considered associated with the availability of the correct carbon samples. In addition, there is the need to reduce the uncertainty integral to the calibration of the ^{14}C date to calendar ages. However, it has been shown that in most cases these problems can be surmounted, or at least reduced significantly.

Ideally, for ^{14}C dating to work well, a salt-marsh sediment sequence needs to contain numerous detrital plant fragments dispersed throughout the sediments. The Taf analysis shows that some useful chronological information can be obtained by using bulk sediment samples, but this may result in a reduction in the chronological precision of the ages obtained. It is shown that this is a way of producing a usable chronology when there are no alternatives methods available. In the case of the Arne, when the pre-bomb ^{14}C dates are evaluated individually, the age uncertainty with some samples is excessive. When a different approach is adopted, and these data are considered as an interrelated group, a much closer calibration can be achieved.

The use of the bomb carbon ^{14}C calibration method was shown to have great potential for producing very high precision salt-marsh chronologies. Apart from the cost (a high sample density is required to ensure that the bomb spike is found), it has much to commend it as a dating method for recent sea-level studies. When combined with a high sample density pre-bomb data set it can be used to produce a 'seamless' ^{14}C chronology. However, it is dependent on sufficient individual samples being regularly spaced in the sediment column. Furthermore, the selection of identifiable detrital organic carbon samples is viewed as imperative when this method is attempted. To exploit the full precision that this calibration approach can offer, the offset between the assimilation of the atmospheric carbon into the living plant tissues, and the subsequent entombment of the sample in the sediments must be minimal. Therefore, the bomb spike calibration will not work using the bulk sediment approach, and its application to very minerogenic sequences or those where the plant fragments are only from long lived perennials (e.g., trees) is unlikely to produce reliable results.

In summary, the use of ^{14}C dating has been examined at three salt-marsh sites. These investigations have found that this dating tool has a number of fundamental constraints, but when applied under the correct circumstances it can produce good results. Its success is dependent on the presence of organic carbon, but this can be minimal if a high precision chronology is not needed. Some reduction of ^{14}C calibration uncertainties is possible if groups of dates are processed together.

8.6.2. Radionuclide dating. These methods have produced mixed results, and, when all the results are considered, there is not a simple conclusion that can be drawn. When ^{210}Pb dating is considered, there was no clear agreement between the different models (e.g., CRS, CIC), and each of the sites produced different results. At the Taf, the ^{210}Pb CIC method is judged to have produced a better result than the more commonly used CRS model. However, this method failed with the Arne data, and the CRS model only produced a credible result here when the ^{137}Cs data was used to 'correct' the chronology. In Iceland, none of the ^{210}Pb models could produce a plausible chronology, and it is proposed that the natural ^{210}Pb concentration is too low at Viðarhólmi for this dating method to be successful.

The ^{137}Cs results are also complex. The Taf ^{137}Cs marker at 17.3 cm was not used to build the chronology. Uptake into solution by pore waters has been proposed as an explanation by a number of studies for the blurring and vertical displacement of ^{137}Cs markers in sediments (e.g., Kim *et al.*, 1997; Cochram *et al.*, 1998; Abril, 2004; Donders *et al.*, 2004). An additional complication is that, although the Taf ^{137}Cs marker at 17.3 cm is displaced from the ^{210}Pb CIC chronology, the 1963 marker at 10.3 cm and the 1986 marker at 4.3 cm are in some agreement with other data. This is inferring that these shallower markers have not been as susceptible to post deposition migration. It is possible that these early ^{137}Cs markers for the mid 1950s are inherently vague because they are only signalling the first appearance of ^{137}Cs in the record. This is not going to be as well defined, or reliable, as the more precise peaks that signal the later events. This could explain the disagreement between the ^{137}Cs marker at 17.3 cm and the stable Pb markers in the Taf sequence.

The situation is very different when the Arne data are examined. Here there was disagreement between the ^{14}C markers, the stable Pb markers and the ^{137}Cs marker for the location of sediments deposited around 1963. In contrast to the Taf sequence, it was the Arne ^{137}Cs bomb spike marker that was apparently vertically displaced in the stratigraphy, not the earlier mid 1950s marker.

It is shown by the investigation into the radionuclide dating methods at the three sites that these methods are useful, but should not be used in isolation. Lead-210 dating is shown to be capable of producing a very valid chronology (e.g., the Taf), but equally it can be of little use (e.g., Viðarhólmi). The findings from all three sites confirm that without additional independent dating information it is not possible to use ^{210}Pb dating with any confidence as a dating tool for salt-marsh sediments. Cesium-137 is often used to support a ^{210}Pb chronology, but the findings of this study confirm the concerns expressed in the literature (e.g., Kim *et al.*, 1997; Cochram *et al.*, 1998; Abril, 2004; Donders *et al.*, 2004) surrounding the post-deposition mobility of ^{137}Cs in water logged sediments.

Americium-241 is suggested as an alternative to ^{137}Cs as a marker for the timing of the 1963 bomb spike and it was measured at the Arne site. Here it was only detected in low levels, and it did not produce a single, well defined, peak. A single peak would be expected if the ^{241}Am detected was (1) stable in the sediments and (2) it was only marking the 1963 maximum of nuclear fall out in the Northern Hemisphere. A complication at the Arne is the documented history of the licensed discharge of fission products and transuranic radionuclides from the near by Winfrith UKAEA nuclear research establishment between 1958 and 1995. There is a small possibility that the undifferentiated alpha-emitting radionuclides in this discharge included ^{241}Pu or ^{241}Am and this activity may have contributed to the radioactive loading of the Arne sediments and have masked or blurred the 1963 bomb signal.

It has been shown that ^{137}Cs and ^{241}Am can be used to locate the documented signals of fallout from atmospheric atomic weapons tests, and later discharges of radionuclides (e.g., Chernobyl). Lead-210 dating can be used to model a continuous chronology, but the investigations reported here confirm that ^{210}Pb chronologies for salt-marsh sediments are not dependable unless they are verified using an independent age marker. There are some complex issues, not found in terrestrial

environments and specific to salt marshes (e.g., low initial concentrations, multiple deposition pathways and the effects of pore water chemistries) involved with these dating methods that may preclude their use at some sites. However, as long as the limitations of these methods are considered, radionuclides have great potential as a dating tool for salt-marsh sediments, but are best used with other, independent, methodologies.

8.6.3. Palaeomagnetic dating. This method produced results with the Taf and Viðarhólmi sediment sequences, but it is felt that the lithology at the Arne did not favour the preservation of a robust NRM signal. Palaeomagnetic dating relies on the quality of the geomagnetic data, but it is also dependent on the ability to calibrate reliably these data into calendar ages. As discussed in Chapter 5, this involves correlating the raw data with established palaeomagnetic master curves, and there is a shortage of accurately dated, high resolution, palaeomagnetic calibration curves that cover the last 4000 yr. In addition, a secure calibration using a master chronology ideally requires a continuous set of results to facilitate the identification of the short term secular variations in the data. Unfortunately, as shown by the investigations reported here, not all these conditions can be met at all sites. In addition, it has been shown that the success of this method is not constant for all sections of a sediment sequence.

It is shown that if the conditions for palaeomagnetic dating to work can be met it offers a dating method that is not dependent on organic carbon samples. Subject to the availability of a robust calibration data set, palaeomagnetic dating can be used over all time periods. Again, subject to the constraints of the calibration data available, if a secure NRM signal can be isolated, in some time periods a high precision result can be obtained (e.g., Viðarhólmi). Therefore, it is proposed that this dating method is proved as usable in salt-marsh sediments, but because of the lack of good quality calibration data it will not be applicable in many instances. However, this is not a failing of the basic method, and it is felt that the results presented from the Taf and Viðarhólmi show the potential of this method to date minerogenic salt-marsh sediments. In the case of Viðarhólmi, because of the excellence of this chronology, the palaeomagnetic dates used here could offer a means to help date other Icelandic magnetic material.

8.6.4. Tephra, pollen and SCPs. Being independent of the need for organic carbon samples, these methods can be used in minerogenic salt-marsh sediments. Pollen and SCP analysis ideally require a continuous sample set so that the deposition history can be fully elucidated at a site, but they are both relatively cheap to apply, and do not require highly specialised laboratories. In contrast, a tephra horizon can be sampled in isolation, but the analysis is highly specialised. In addition, to produce a date, the geochemical 'fingerprint' of the tephra must be confidently matched to existing data. Therefore, if the geochemistry of a tephra layer is not well constrained, or the documented knowledge of it is of poor quality, it may not be possible to confidently attribute a robust age.

In common with tephra, pollen and SCP analysis require pre-existing knowledge of the local deposition histories. This condition precluded the use of the SCP record found by this study in the Icelandic sediments. However, when existing knowledge of the local deposition histories is available, as in the case of the Arne, excellent results can be obtained. One advantage is that the size of these particles makes post-deposition migration in the sediment pore space unlikely, and that once entombed, the signal is secure. In addition, tephra, pollen and SCPs are geochemically stable, and although they can be degraded, the character of the signal they mark will not be changed. The investigations carried out by this present study show that, even though these methods will not work in some locations (e.g., not in a tephra fall zone), all three of these dating methods can be used to constrain a salt-marsh sediment chronology. Under ideal circumstances very high precision is possible (e.g., the Icelandic Medieval tephra layer and the Arne pollen marker). It is proposed that, in sediment sequences where they can be used, the unique properties of these methods make them ideal limiting age markers to constrain strings of ^{14}C ages.

8.6.5. Stable atmospheric Pb deposition histories. This method was investigated at all three sites. The results were excellent. By combining stable Pb concentration data with the isotopic analysis of the samples it was possible to locate the signals of the rise of industrial emissions, both local and regional, and the appearance, increases and subsequent decline, of the use of leaded petrol in Europe. There are a number of constraints apparent with transforming the raw data into dates using this method, but these are the same as any 'specific event' dating tool such as

pollen or tephra insomuch as age calibration is required using an existing well-dated data set (e.g., the Taf result in Chapter 7), or documented record.

The results presented from each of the three sites show the potential of this novel dating tool as a means of obtaining age markers that cover the last 200 yr. The use of this method at the Taf site show how signals of documented industrial events in the 19th century can be detected and used to constrain this important period. In later times, the leaded petrol signal is well documented, and using the combined concentration and isotopic analysis this study has confirmed that it can be confidently isolated. At all three sites it was possible to use isotopic fingerprinting of the Pb in the sediments to locate age markers for the 19th and 20th centuries. In addition, under ideal circumstances, it is shown that it is possible to detect the more subtle signal of the use of Pb by the ancient Roman Empire. It is felt that, with a suitable sediment sequence, and an appropriate calibration record, this dating method could be extended back to the Bronze Age. It is proposed that the use of stable Pb analysis has much to commend it as a dating tool for late Holocene salt-marsh sediments.

Chapter 9

Conclusions and future work

The objective of this project was to test new methods for dating salt-marsh sediments. The intention was that all these methods should be suitable for use in high resolution investigations of sea-level changes during the late Holocene, with particular emphasis on the past 200-300 years. Eight individual dating methods have been investigated and evaluated. In Chapter 8 they were used to construct a 'definitive chronology' for three sites: (1) the Taf Estuary in south Wales, (2) the Arne Peninsula, in southern England and (3) Viðarhólmi, western Iceland. This final chapter will draw conclusions from these findings, identify the need for any future work, and suggest how the dating methods can be further developed.

9.1. Conclusions

This work has shown the promise of some of the novel dating methods, for example the use of stable Pb analysis, and has also highlighted and confirmed some fundamental issues previously reported surrounding some commonly used dating methods, such as ^{210}Pb dating. The conclusions drawn for the individual dating methods are presented below.

9.1.1. Radioisotopic dating 1: ^{14}C . There are two broad conclusions regarding this method:

(1) This dating method is shown by the investigations reported in Chapter 3 of this thesis to be capable of producing very good results when applied to salt-marsh sediments containing sufficient organic carbon. The ^{14}C dating method performed better on the relatively organic sediments from Viðarhólmi than on the very minerogenic sediments from the Taf site. This confirms the findings of previous studies that have used the ^{14}C dating method in salt-marsh environments.

(2) This thesis confirms that sediments deposited in the time period AD 1700-1950 can be problematic to date because of ambiguities with sections of the calibration curves, i.e. multiple age solutions. However, the work on the Arne sediments demonstrated how use of a high-precision analytical approach, combined with the use of extra chronological information to constrain calibrations, can reduce calibration age uncertainties to an acceptable range.

The more specific conclusions concerning ^{14}C dating to emerge from this study are:

- The results from the Arne confirm that the use of a 2 ‰ analytical procedure using the Accelerator Mass Spectrometer can reduce the initial ^{14}C age uncertainty between AD 1700 and AD 1950 to less than ± 20 ^{14}C yr.
- It was found that by combining the results from three 2 ‰ analytical replicates the range of 1 sigma ^{14}C ages can be reduced to ± 9 ^{14}C yr.
- A reduction in the ^{14}C analytical uncertainty to less than ± 10 yr for ages between AD 1700 and AD 1950 can produce more than 45% reduction in the spread of the calibrated calendar dates.
- During the Arne analysis it was shown that one 0.03 g (dry weight) organic carbon sample (grass stem) is large enough to provide sufficient refined CO_2 for three replicate graphite targets.
- It was found at the Arne that the use of the empirical post-bomb record of atmospheric carbon to calibrate ^{14}C dates after AD 1950 can produce a theoretical chronological precision of better than ± 0.3 yr in salt-marsh sediments.

9.1.2. Radioisotopic dating 2: ^{210}Pb and ^{137}Cs . This thesis has not produced any new information on these methods, but the investigations reported in Chapter 4 confirmed previous work (e.g., Abril, 2004) that there is a need for a multi-method approach when using ^{210}Pb and ^{137}Cs . One overall conclusion from Chapter 4 is that at some sites radionuclides can produce robust dating results, but there are a number of constraints that are specific to an individual site (e.g., lithology) and other issues that are regional (e.g., extent of fallout zones). It is also confirmed that there is a need for a better understanding of the post-depositional behaviour of radioisotopes in salt marshes. The results from the three sites were very different and thus confirmed some of the site-specific issues that surround these dating methods. For example, the ^{210}Pb CIC chronology at the Taf site was shown to be robust, but the same approach at the Arne was unsuccessful. This is attributed to the more steady-state depositional conditions at the Taf site. In contrast, the poor performance of the radionuclide methods at Viðarhólmi is attributed to its geographic location. The specific conclusions for the two main radionuclide methods are:

(1) Lead-210

- It is confirmed that this method is not suitable for use at a dynamic salt-marsh site, like the Arne, because any changes in the sediment source, sediment

characteristics or sediment accretion rates will potentially prohibit the reliable use of ^{210}Pb dating.

- The results of this study confirm that for reliable use there must be a significant level of activity in the surface sediments at the site sufficient to maintain ^{210}Pb activity above detection levels deeper in the sequence. This critical level will depend upon the sensitivity of the detectors used, but the results from the three sites investigated here suggest that a minimum of unsupported value of 100 – 150 Bq kg^{-1} at the sediment surface should still provide a detectable ^{210}Pb inventory after five half lives (i.e. $5 \times 22.3 \text{ yr}$).
- The results from the Viðarhólmi site indicated that as a result of low local ^{210}Pb production some Icelandic sites may not be able to satisfy the required surface ^{210}Pb activity.
- This study confirms that when conditions are favourable, as at the Taf site, a robust chronology can be produced for the last 100 yr, but, to be credible, a ^{210}Pb chronology must be substantiated by independent chronological information.

(2) Caesium-137

- The results presented by this study from the Viðarhólmi and Arne sites confirm that it is imperative that the regional depositional history of radionuclides, the timing of all the potential contributions from different sources and the relative activity levels must be understood. For example, will the site have contributions only from weapons tests or is Chernobyl also a potential contender? Alternatively, as in the case of the Arne site, is there a history of radionuclide discharge nearby?
- It is suggested that a contiguous sample set that covers all the major changes in ^{137}Cs deposition is needed for a secure interpretation.
- The results from the Viðarhólmi salt-marsh, and to a lesser extent from the Arne site, confirm post-depositional vertical mobility of ^{137}Cs in salt-marsh sediments, but that, in some cases, ^{241}Am may be used to confirm this situation.

9.1.3. Palaeomagnetic dating. Chapter 5 reports the first successful palaeomagnetic dating of salt-marsh sediments. This was achieved with the Taf and Viðarhólmi sediments. This study finds that fine minerogenic sediments deposited on a salt-marsh surface can be aligned by the geomagnetic field, and a stable NRM signal can be preserved. In addition it is found that the NRM signal preserved can be robust enough to be used for an estimate of the deposition date.

The different characteristics of the sediments from the three sites produced very different results. This highlighted that, although this method is applicable to salt-marsh sediments, there are some constraints and restrictions that are both site and region specific. These are detailed below, and some of these issues prevented the use of this dating method at the Arne site where a stable NRM signal was not preserved. The conclusions drawn fall into two groups: (1) those concerned with the preservation of the NRM signal, and (2) those concerned with the conversion of the data into dates using a 'master curve'.

(1) To preserve the raw NRM signal:

- It is suggested that zero, or very low water flows, must have been in place at the site for time spanned by the sediment column.
- A steady sedimentation rate is needed, with no breaks in accretion or periods of erosion.
- The sediment lithology must have a moderate to high magnetic susceptibility, as in the case of the Taf and Viðarhólmi sediments.

(2) For the data to be successfully converted into ages:

- The results from the Taf show that the NRM signal must be robust (e.g. low MAD values).
- It is concluded that, for a reliable calibration, a suitable Master curve must exist and a data set must be produced at sufficient resolution to detect short-term secular variations.
- It is proposed that the Viðarhólmi data can be used as a 'master' Curve to date other Icelandic sections.

9.1.4. Dating using stable particle deposition: Tephra, pollen and SCPs. All these 'unique event dating' methods produced credible dating results in Chapter 6, and this study confirms the value of these 'independent' dating tools. Final age estimates for the deposition of the salt-marsh sediments are totally dependent on the quality, and chronological precision, of the pre-existing information available. Other, more specific, conclusions are:

(1) Tephra. This study confirms that within the geographical range of Icelandic tephra falls this method offers a very precise dating method for salt-marsh sediments.

- The investigation at Viðarhólmi showed that close to the volcanic source, a regional tephra fall may not always be detectable in a minerogenic salt-marsh sediment sequence.

(2) Pollen. No new information was produced regarding the use of pollen as a dating tool but the investigation at the Arne confirmed that, to be used as an age marker, the change, or changes, in a pollen diagram must be well defined and unambiguous. In addition, it was found that poor pollen preservation may prevent the use of this method in very minerogenic salt-marsh sediments (e.g., the Taf site).

(3) SCPs This study produced some new information surrounding the use of SCPs.

- It was found that SCPs are well preserved in recent salt-marsh sediments at the Arne and Viðarhólmi sites.
- This is a low-cost dating method that can be used as a reconnaissance tool for the deposition history of the last 150 yr.
- For high resolution calibrations, and robust results, a local, well dated, deposition record is needed, such the ones use at the Arne site
- The Viðarhólmi SCP data presented here can be used as a 'master' curve to date other Icelandic sediment sections.

9.1.5. Dating using stable particle deposition: Stable Pb. The investigation of this novel method produced excellent results at all three sites. The two primary overall conclusions arising from this work are that stable Pb analyses can be successfully applied to salt-marsh sediments, but, in common with the other event dating methods, it needs a robust calibration data set. If the Pb enrichment signal has a sufficiently distinct isotopic signature it is possible to distinguish phases of contributions from different pollution sources with high confidence. For example, at the Taf site it was possible to isolate the signal of 19th century metal working in the Swansea Valley, and at the Arne site it was possible to trace the history of use of leaded petrol in southern England during the 20th century. Analyses of the Viðarhólmi sediments found an Pb isotope signature near the base of the sequence that was consistent with the isotopic character of the Pb ores (Rio Tinto field) exploited during the Roman Empire, and this was used to date this level to AD 50 ± 50. At Viðarhólmi a peak of Pb deposition was detected related to the burning of UK coal during the 1950s and early 1960s.

In addition, the stable Pb investigation reported in Chapter 7 has produced the following conclusions:

- It is confirmed that this method can be applied with only Pb concentration data, but for its full potential, both concentration and isotopic data are needed.
- This study shows that best results are obtained at sites with a low background natural presence of Pb, like the Viðarhólmi site.
- The Icelandic stable Pb chronology presented here is supported by the other dating methods. It is of high analytical quality, and can therefore be used as a 'master' chronology to date other Icelandic sediment sections.

9.2. Future work and development

9.2.1. Carbon-14 dating. When ^{14}C dating is considered as a tool for the dating of salt-marsh sediment deposition, three areas are identified to be potential targets for further work.

(1) The further development of the high-precision approach to the analysis of the carbon sample. This should be pursued to reduce the uncertainty of the initial ^{14}C date. As yet it is not clear what, if given unconstrained laboratory resources, is the ideal number of analytical replicates for different time periods

(2) More understanding is needed of the validity of the use of group, or multi-sample, calibrations, and how wiggle-matching practices can be used to reduce the final age ranges of pre-bomb ^{14}C dates.

(3) The use of the post-bomb atmospheric carbon record to calibrate ^{14}C samples should be developed further. Consideration should be given to refining the understanding of the carbon pathway for different materials, i.e. assimilation to entombment lags. Issues such as the growth periods and leaf fall times of individual plant species may need to be quantified to interpret fully a high-resolution post bomb ^{14}C analysis. This could take the form of combined sediment and dendrochronological ^{14}C analyses to pinpoint the local responses to atmospheric ^{14}C concentrations.

9.2.2. Lead-210 and ^{137}Cs . Further work on this topic should include a study of the physical characteristics (e.g., lithology, grain size) of the salt-marsh sediments and the associated performance of each of the radionuclide dating methods. The findings from a study of this type could then be used to refine ^{210}Pb models, and help select the best dating methods to use at a site. In addition, this type of information can be used to

discount the use of radionuclides at some sites, and therefore allow the investigator to devote resources to an alternative way of dating recent sediments (e.g., bomb spike ^{14}C or SCPs).

9.2.3. Palaeomagnetic dating. Cycles of tidal flooding and subaerial exposure can have some influence on the establishment, and preservation, of magnetic grain alignments. It is felt that, to improve the reliability of this method, more research can be justified into the time needed for a NRM signal to 'lock-in' in fine-grained water-logged sediments. In addition, further work is needed to produce more, well dated, and chronologically precise, palaeomagnetic calibration data sets.

9.2.4. Dating using stable particle deposition: Tephra, pollen, SCPs and stable Pb. SCP and stable Pb analysis would benefit from an initiative to produce new calibration data. In the case of SCPs this could be done relatively cheaply using pre-dated archived material, or in association with other palaeoenvironmental analysis. One method of developing a robust, and well dated, stable Pb master curve would be using a tree-ring calibration, as suggested in Section 9.2.1 for constructing a combined sediment and dendrochronological ^{14}C analysis.

9.2.5. Constructing combined chronologies. A multi-method dating approach improves both chronological precision and reliability when dating salt-marsh sediments. Indeed, further development is needed of more objective methods for selecting the most robust age markers to build a multi-method chronology. This is an area of active research (e.g., Telford *et al.*, 2003; Heegaard *et al.*, 2005), and would involve developing statistical methods of loading or weighting each of the age markers so that their individual power of age determination, and some measure of robustness, can be quantified.

Appendix 1: Sediment physical analysis data from each site

Taf-02	Grain size %			Total carbon analysis		
Depth (cm)	Sand	Silt	Clay	% Organic carbon	% Non organic carbon	% Non-carbonate minerogenic
0	0.84	85.38	13.78	59.65	0.00	40.35
2	1.96	87.00	11.04	60.82	0.00	39.18
4	1.56	86.80	11.64	59.01	0.00	40.99
6	0.31	82.73	16.96	49.77	0.00	50.23
8	1.68	84.38	13.94	45.25	0.00	54.75
10	2.55	83.19	14.25	36.91	0.00	63.09
12	1.22	84.34	14.43	29.93	0.00	70.07
14	2.96	83.42	13.62	28.47	0.00	71.53
16	3.59	82.64	13.78	32.95	0.00	67.05
18	1.80	83.89	14.31	20.94	0.00	79.06
20	1.38	83.36	15.26	24.32	0.00	75.68
22	0.80	84.35	14.85	16.38	0.00	83.62
24	4.88	81.55	13.57	16.27	0.00	83.73
26	9.10	77.64	13.26	17.38	0.00	82.60
28	8.31	77.07	14.63	14.63	0.00	85.37
30	10.08	76.80	13.12	11.84	0.00	88.16
32	5.08	80.10	14.83	9.91	0.00	90.09
34	4.54	80.69	14.77	12.28	0.00	87.72
36	3.48	82.32	14.21	11.65	0.00	88.35
38	2.66	83.69	13.65	10.35	0.00	89.65
40	2.14	84.16	13.70	9.17	0.00	90.83
42	2.37	82.70	14.93	8.96	0.00	91.04
44	1.99	83.26	14.75	8.26	0.00	91.74
46	2.60	82.32	15.08	9.04	0.00	90.96
48	3.63	81.83	14.54	9.43	0.00	90.57
50	1.84	82.20	15.96	8.00	0.00	92.00
52	1.07	81.66	17.27	7.13	0.00	92.87
54	1.87	83.61	14.52	7.42	0.00	92.58
56	0.63	81.69	17.67	7.21	0.00	92.79
58	0.71	82.63	16.67	7.87	0.00	92.13
60	1.37	80.69	17.94	8.34	0.00	91.66
62	1.40	81.62	16.98	7.84	0.00	92.16
64	0.19	82.72	17.09	8.96	0.00	91.04
66	0.96	83.21	15.83	10.05	0.00	89.95
68	0.97	83.77	15.26	7.42	0.00	92.58
70	1.73	83.53	14.74	6.53	0.00	93.47
72	3.15	82.20	14.65	6.88	0.00	93.12
74	2.75	81.64	15.61	7.75	0.00	92.25
76	1.19	80.76	18.04	7.98	0.00	92.02
78	1.46	79.64	18.89	8.14	0.00	91.86
80	2.84	82.36	14.81	6.23	0.00	93.77
82	2.44	79.10	18.46	7.25	0.00	92.75
84	1.39	76.68	21.93	6.92	0.00	93.08
86	0.53	74.12	25.35	7.34	0.00	92.66
88	0.97	80.03	19.00	6.81	0.00	93.19
90	0.97	78.11	20.93	7.79	0.00	92.21
92	2.91	77.64	19.45	6.39	0.00	93.61
94	1.52	81.18	17.30	8.35	0.00	91.65
96	2.70	79.07	18.23	6.44	0.00	93.56
98	2.04	81.92	16.04	6.44	0.00	93.56
100	3.24	72.87	23.89	5.60	0.00	94.40
102	3.13	78.21	18.67	4.71	0.00	95.29

Appendix 1: Sediment physical analysis data from each site

Arne-03	Grain size %			Total carbon analysis		
Depth (cm)	Sand	Silt	Clay	% Organic carbon	% Non organic carbon	% Non-carbonate minerogetic
2.00	19.67	67.72	12.61	14.31	0.00	85.69
4.00	0.29	87.30	12.41	22.31	1.00	77.69
6.00	19.77	71.02	9.21	25.87	2.00	74.13
8.00	14.21	76.32	9.48	21.67	3.00	78.33
10.00	18.95	71.09	9.97	24.55	4.00	75.45
12.00	14.41	72.18	13.41	19.93	5.00	80.07
14.00	9.03	75.13	15.84	17.54	6.00	82.46
16.00	11.69	73.00	15.30	18.68	7.00	81.32
18.00	11.65	72.82	15.52	18.04	8.00	81.96
20.00	0.22	81.34	18.44	15.46	9.00	84.54
22.00	7.02	76.54	16.44	11.09	10.00	88.91
24.00	9.20	74.27	16.52	13.80	11.00	86.20
26.00	4.98	79.17	15.84	12.02	12.00	87.98
28.00	9.03	77.42	13.55	12.82	13.00	87.18
30.00	17.05	70.59	12.36	16.38	14.00	83.62
32.00	6.19	79.89	13.92	16.91	15.00	83.09
34.00	13.89	72.61	13.50	12.22	16.00	87.78
36.00	7.24	78.10	14.66	10.91	17.00	89.09
38.00	5.78	78.50	15.72	10.39	18.00	89.61
40.00	17.22	68.75	14.03	8.78	19.00	91.22
42.00	14.57	70.76	14.67	8.84	20.00	91.16
44.00	9.73	75.39	14.89	8.90	21.00	91.10
46.00	8.65	76.91	14.44	9.49	22.00	90.51
48.00	11.54	73.59	14.87	9.71	23.00	90.29
50.00	16.34	69.95	13.71	10.69	24.00	89.31
52.00	40.76	49.16	10.08	9.25	25.00	90.75
54.00	24.17	62.59	13.24	7.49	26.00	92.51
56.00	30.21	58.84	10.95	4.62	27.00	95.38
58.00	90.22	9.78	0.00	2.27	28.00	97.73
60.00	93.95	6.05	0.00	0.01	29.00	99.99
62.00	94.87	5.13	0.00	0.92	30.00	99.08
64.00	96.10	3.90	0.00	0.18	31.00	99.82
66.00	94.37	5.63	0.00	0.00	32.00	100.00
68.00	90.78	9.22	0.00	0.00	33.00	100.00
70.00	51.55	41.69	6.77	0.00	34.00	100.00
72.00	46.02	43.52	10.47	0.00	35.00	100.00
74.00	48.25	40.53	11.21	0.00	36.00	100.00
76.00	41.21	47.36	11.43	0.00	37.00	100.00
78.00	34.27	55.28	10.45	0.00	38.00	100.00
80.00	35.53	52.17	12.30	0.00	39.00	100.00
82.00	25.34	66.07	8.59	0.00	40.00	100.00
84.00	32.00	60.86	7.14	0.00	41.00	100.00
86.00	25.56	65.95	8.48	0.00	42.00	100.00
88.00	31.37	57.00	11.63	0.00	43.00	100.00
90.00	49.00	41.37	9.63	0.00	44.00	100.00
92.00	46.55	44.66	8.78	0.00	45.00	100.00
94.00	44.98	45.13	9.89	0.00	46.00	100.00
96.00	42.19	48.58	9.23	0.00	47.00	100.00
98.00	45.74	44.80	9.47	0.00	48.00	100.00

Appendix 1: Sediment physical analysis data from each site

Viðarhólmur 03	Grain size %			Total carbon analysis		
Depth (cm)	Sand	Silt	Clay	% Organic carbon	% Non organic carbon	% Non-carbonate minerogenic
2.00	37.16	55.32	7.52	21.29	0.00	78.71
4.00	31.81	60.35	7.85	16.55	1.00	83.45
6.00	32.92	58.85	8.23	18.63	2.00	81.37
8.00	26.71	65.47	7.83	16.61	3.00	83.39
10.00	26.22	66.42	7.36	18.92	4.00	81.08
12.00	30.91	61.81	7.28	14.46	5.00	85.54
14.00	27.64	65.43	6.93	15.26	6.00	84.74
16.00	35.65	56.40	7.95	13.03	7.00	86.97
18.00	32.07	60.77	7.16	16.16	8.00	83.84
20.00	33.19	59.02	7.79	9.74	9.00	90.26
22.00	35.32	57.82	6.86	9.00	10.00	91.00
24.00	28.45	64.10	7.45	14.99	11.00	85.01
26.00	24.38	67.61	8.01	14.12	12.00	85.88
28.00	28.86	64.72	6.42	12.05	13.00	87.95
30.00	17.87	75.44	6.69	19.02	14.00	80.98
32.00	28.72	65.53	5.75	18.07	15.00	81.93
34.00	37.59	56.47	5.94	23.48	16.00	76.52
36.00	29.90	63.79	6.31	19.92	17.00	80.08
38.00	26.62	67.31	6.07	19.58	18.00	80.42
40.00	19.41	73.79	6.80	19.02	19.00	80.98
42.00	31.40	62.92	5.68	15.90	20.00	84.10
44.00	31.30	62.95	5.75	20.30	21.00	79.70
46.00	16.20	77.03	6.76	27.20	22.00	72.80
48.00	23.88	69.24	6.89	31.54	23.00	68.46
50.00	16.16	76.82	7.02	33.94	24.00	66.06
52.00	33.57	62.78	3.65	32.37	25.00	67.63
54.00	27.53	66.69	5.78	31.05	26.00	68.95
56.00	23.25	70.25	6.50	28.86	27.00	71.14
62.00	21.39	73.49	5.12	18.76	28.00	81.24
64.00	33.89	57.99	8.11	26.91	29.00	73.09
66.00	22.87	71.66	5.47	26.35	30.00	73.65
68.00	22.69	71.88	5.43	26.86	31.00	73.14
70.00	15.72	80.52	3.76	21.15	32.00	78.85
72.00	15.04	81.37	3.60	17.82	33.00	82.18
74.00	16.14	79.99	3.86	20.26	34.00	79.74
76.00	16.18	79.95	3.87	21.02	35.00	78.98
78.00	14.60	81.90	3.50	18.11	36.00	81.89
80.00	17.41	78.42	4.17	20.88	37.00	79.12
82.00	8.40	89.59	2.01	17.60	38.00	82.40
84.00	29.17	63.84	6.98	33.06	39.00	66.94
86.00	18.03	77.65	4.32	28.80	40.00	71.20
88.00	18.67	76.87	4.47	27.21	41.00	72.79
90.00	7.94	90.16	1.90	9.06	42.00	90.94
92.00	59.57	26.17	14.26	34.07	43.00	65.93
94.00	13.17	83.68	3.15	15.71	44.00	84.29
96.00	13.87	82.81	3.32	22.52	45.00	77.48
98.00	20.30	74.83	4.86	24.71	46.00	75.29
100.00	38.32	52.51	9.17	34.80	47.00	65.20
102.00	17.81	77.92	4.26	24.20	48.00	75.80
104.00	17.59	78.20	4.21	25.02	49.00	74.98
106.00	20.49	74.61	4.90	29.97	50.00	70.03

Appendix 1: Sediment physical analysis data from each site

108.00	16.78	79.20	4.02	22.72	51.00	77.28
110.00	16.99	78.95	4.07	19.30	52.00	80.70
112.00	12.88	84.04	3.08	19.48	53.00	80.52
114.00	7.48	90.73	1.79	8.80	54.00	91.20
116.00	14.08	82.55	3.37	20.45	55.00	79.55
118.00	6.94	91.40	1.66	7.69	56.00	92.31
120.00	10.33	87.20	2.47	21.16	57.00	78.84
122.00	14.97	81.44	3.58	19.54	58.00	80.46
124.00	4.76	94.10	1.14	5.93	59.00	94.07
126.00	3.32	95.88	0.80	4.74	60.00	95.26
128.00	2.16	97.33	0.52	3.09	61.00	96.91
130.00	15.07	81.32	3.61	24.22	62.00	75.78
132.00	17.41	78.42	4.17	27.82	63.00	72.18
134.00	21.39	73.49	5.12	24.38	64.00	75.62
136.00	11.75	85.44	2.81	22.38	65.00	77.62
138.00	18.35	77.26	4.39	21.74	66.00	78.26
140.00	17.92	78.24	4.00	19.48	67.00	80.52

Appendix 2. Dating methodology raw data

Magnetic data: Taf Estuary, South Wales: 51° 46'N 004° 25'W 2002						
Taf-02						
Sample depth (cm)	Raw declination (Degrees)	Declination after rotation to field site north (Degrees)	Inclination (Degrees)	Intensity (mAm ⁻¹)	MAD (Degrees)	Low -field magnetic susceptibility (K) (SI units)
2	no data	no data	no data	no data	no data	1.6
4	no data	no data	no data	no data	no data	-0.1
6	no data	no data	no data	no data	no data	-0.1
8	no data	no data	no data	no data	no data	0.8
10	30.80	54.30	65.90	0.48	16.12	1.2
12	no data	no data	no data	no data	no data	1.3
14	no data	no data	no data	no data	no data	2.9
16	no data	no data	no data	no data	no data	1.5
18	no data	no data	no data	no data	no data	2
20	37.30	60.80	77.50	0.44	11.20	4
22	15.60	39.10	58.10	0.39	9.60	3.2
24	24.30	47.80	62.40	0.39	10.20	4.6
26	63.10	86.60	63.80	0.42	18.66	3.7
28	19.60	43.10	55.90	0.36	10.69	4.3
30	63.20	86.70	59.30	0.43	16.60	4.5
32	22.90	46.40	50.70	0.34	9.05	5.5
34	23.40	46.90	54.20	0.36	8.10	5.3
36	40.00	63.50	45.80	0.34	7.40	5.4
38	20.50	44.00	62.20	0.36	7.60	6.9
40	33.40	56.90	63.50	0.44	8.20	5.8
42	no data	no data	no data	no data	no data	7.1
44	13.80	37.30	51.60	0.45	8.80	6.2
46	29.90	53.40	48.40	0.42	9.20	7.9
48	9.40	32.90	47.50	0.52	6.50	7.3
50	355.00	15.50	76.60	0.51	3.10	7.6
52	12.80	36.30	62.80	0.59	3.90	8.5
54	no data	no data	no data	no data	no data	7.6
56	7.70	31.20	47.70	0.45	9.20	6.3
58	40.80	64.30	60.30	0.51	4.10	9.8
60	22.30	45.80	53.90	0.53	9.78	8.4
62	25.50	49.00	59.00	0.54	8.20	7.7
64	11.20	34.70	60.10	0.65	9.05	6.3
66	21.80	45.30	46.00	0.68	4.02	7.7
68	26.00	49.50	49.80	0.72	1.40	6.4
70	31.80	55.30	58.40	0.58	8.20	5.7
72	357.60	21.50	48.90	0.55	7.20	7.4
74	49.60	73.10	59.40	0.68	7.20	7.6
76	51.90	75.40	53.60	0.53	2.69	8.9
78	29.80	53.30	45.90	0.76	5.40	7.9
80	48.90	72.40	58.50	0.51	4.90	9.6
82	25.70	49.20	58.20	0.59	5.40	8.9
88	no data	no data	no data	no data	no data	7.8
90	61.40	84.90	69.00	1.06	2.30	9.9
92	57.40	80.90	77.80	1.13	1.30	8.2

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

94	74.20	97.70	68.00	0.80	2.80	8.6
96	16.50	40.00	53.20	0.88	2.10	8.3
98	20.50	44.00	59.80	0.56	3.10	10
100	36.60	60.10	60.40	1.07	2.90	9.9
102	54.70	78.20	67.30	1.05	2.80	11.2
Magnetic data: Taf Estuary, South Wales: 51° 46'N 004° 25'W 2003						
Taf-03						
Sample depth (cm)	Raw declination (Degrees)	Declination after rotation to field site north (Degrees)	Inclination (Degrees)	Intensity (mAm ⁻¹)	MAD (Degrees)	Low -field magnetic susceptibility (K) (SI units)
2	no data	no data	no data	no data	no data	0.6
4	no data	no data	no data	no data	no data	1.5
6	no data	no data	no data	no data	no data	1.6
8	no data	no data	no data	no data	no data	0.7
10	no data	no data	no data	no data	no data	1.9
12	no data	no data	no data	no data	no data	1.4
14	no data	no data	no data	no data	no data	3.2
16	no data	no data	no data	no data	no data	1.9
18	no data	no data	no data	no data	no data	2.6
20	22.7	35.2	63.8	0.447	20.9	3.9
22	48.6	61.1	75.9	0.316	7.6	4.6
24	39.5	52	59.6	0.338	15	3.8
26	14.9	27.4	43.9	0.409	20.1	5.3
28	22.6	35.1	65	0.262	11.3	4.5
30	58.4	70.9	55.5	0.42	6.8	5.4
32	42.1	54.6	38.4	0.298	18.8	5.2
34	no data	no data	no data	no data	no data	1.6
36	no data	no data	no data	no data	no data	2.9
38	41.4	53.9	49.6	0.26	13.8	5.7
40	42.7	55.2	39.8	0.399	17.6	8.9
42	no data	no data	no data	no data	no data	6.1
44	30.9	43.4	57.8	0.462	5.8	6.6
46	43.9	56.4	64	0.406	3.2	7.1
48	42	54.5	75.6	0.517	3.5	7.3
50	23.50	36.00	72.40	0.62	5.30	8.1
52	18.4	30.9	54.5	0.761	3.7	7.3
54	no data	no data	no data	no data	no data	7.1
56	15.1	27.6	60.3	0.466	8.1	7.3
58	28.9	41.4	65.5	0.624	13.2	8.1
60	44.1	56.6	44.5	0.663	10.3	7.4
62	25.8	38.3	55.2	0.689	6.6	4.2
64	17.7	30.2	59.7	0.969	9.5	7.4
66	27.3	39.8	75.7	1.03	5.3	6.2
68	49.3	61.8	59.8	1.15	2.5	5.6
70	46	58.5	56.2	0.871	6.1	7.2
72	50.4	62.9	67.6	0.73	2.5	7.3
74	45.6	58.1	59.7	1.04	2.9	9.5
76	40.3	52.8	51.5	0.689	4.7	7.6
78	no data	no data	no data	no data	no data	5.9
80	32.2	44.7	46.8	0.628	2.6	8.5

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

82	33	45.5	49.7	0.82	5.2	9.8
84	28.6	41.1	65	1	11.4	8.4
86	47	59.5	50.9	1.39	3.5	7.5
88	23.2	35.7	67.6	1.24	2.4	11.4
90	50.7	63.2	57.7	1.77	2.1	7.9
92	48.9	61.4	58.1	2.14	1	8.2
94	67.1	79.6	62.2	1.34	2.6	8.0
96	37.5	50	58.6	2.04	3.7	9.5
98	59.5	72	50.8	0.737	4.7	9.4
100	45.7	58.2	60.4	2.25	1.8	12.6
102	62.7	75.2	66.3	2.84	2.2	10.3

Magnetic data: Arne Peninsular, Poole Harbour, Southern England: 50° 41'N 02° 02'W 2003

Arne-03						
Sample depth (cm)	Raw declination (Degrees)	Declination after rotation to field site north (Degrees)	Inclination (Degrees)	Intensity mA m^{-1}	MAD (Degrees)	Low -field magnetic susceptibility (K) (SI units)
2	70.2	357.5	19.7	0.16	7.2	0.7
4	no data	no data	no data	0.07	no data	-0.2
6	no data	no data	no data	0.13	no data	-0.2
8	189.3	116.6	52.9	0.03	10.9	-0.4
10	no data	no data	no data	0.02	no data	-0.4
12	202.6	129.6	22.3	0.02	11.9	0.3
14	309.7	237	62.5	0.02	11.8	0.3
16	no data	no data	no data	0.03	no data	0.6
18	230.1	157.4	87	0.07	12.2	0.2
20	80.9	8.2	62.7	0.06	8.8	0.6
22	352	279.3	52.8	0.08	2.2	1.4
24	42.7	330	57.5	0.12	6.7	1.6
26	331.4	258.7	65.8	0.07	6.1	1.5
28	232.1	159.4	-26.6	0.21	5	0.8
30	296.8	224.1	46.1	1.12	1.2	2.6
32	266	166.7	27.2	2.40	4.6	7.2
34	70.2	357.5	35.1	1.68	2	6.3
36	250.7	182	72.2	5.30	2.8	7.9
38	238.6	165.9	69	5.52	0.8	49.2
40	237.5	164.8	65.3	2.23	2.9	65.6
42	266.7	194	65.9	2.15	1.4	32.7
44	265.1	192.4	63.6	0.21	1.4	24.2
46	199.4	126.7	46.4	0.91	2.9	6.6
48	277.9	205.2	52	0.28	2.1	1.5
50	261.1	188.4	61.5	0.72	1.7	1.5
52	110	37.3	42.1	0.04	4.5	1.6
54	no data	no data	no data	0.72	no data	1.5
56	no data	no data	no data	0.08	no data	1.7
58	no data	no data	no data	0.41	no data	0.6
60	no data	no data	no data	0.50	no data	0.2
62	no data	no data	no data	0.35	no data	0.6

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

64	no data	no data	no data	0.62	no data	0.3
66	283.8	211.1	49	0.24	8	1
68	no data	no data	no data	0.21	no data	1
70	no data	no data	no data	0.70	no data	1.4
72	262.7	190	13.6	0.30	2.8	3.2
74	no data	no data	no data	0.28	no data	3.1
76	no data	no data	no data	0.20	no data	3.2
78	156.6	83.9	-71.3	0.28	5.6	3.3
80	306.3	233.6	81.6	0.31	6.6	4.2
82	357.5	284.8	67.6	0.51	10.8	4
84	no data	no data	no data	0.42	no data	3.5
86	19.2	306.5	62	0.50	7.2	3.8
88	no data	no data	no data	0.36	no data	3.6
90	236.2	163.5	30.6	0.52	6.7	3.1
92	no data	no data	no data	0.16	no data	3.1
94	no data	no data	no data	0.16	no data	3
96	287.4	214.7	27.5	0.43	6.5	3.8
98	no data	no data	no data	0.19	no data	3.8
Magnetic data: Arne Peninsular, Poole Harbour, Southern England: 50° 41'N 02° 02'W 2004						
Arne-04						
Sample depth (cm)	Raw declination (Degrees)	Declination after rotation to field site north (Degrees)	Inclination (Degrees)	Intensity mAm⁻¹	MAD (Degrees)	Low -field magnetic susceptibility (K) (SI units)
2	86.2	346.5	14.9	0.11	14.4	1.0
4	278	205.3	27	0.04	16.3	0.0
6	194.3	121.6	3.9	0.05	16.9	0.0
8	234.2	161.5	38.4	0.10	12.1	0.9
10	257.2	184.5	79.3	0.04	15.6	0.0
12	235.7	163	31.5	0.05	15.6	0.0
14	253.3	180.6	-23.4	0.02	10.6	0.0
16	239.7	167	10.7	0.05	18.8	0.6
18	271.9	199.2	59.7	0.04	7.8	0.3
20	327.1	254.4	66.1	0.26	4.1	1.3
22	15.5	302.8	25.6	0.11	16.3	0.9
24	200.3	127.6	51.1	0.07	18.2	0.1
26	231.2	158.5	42.6	0.02	12.6	0.0
28	253.2	180.5	63.7	1.67	2.4	1.1
30	305.3	232.6	16.3	0.02	9.9	0.1
32	no data	no data	no data	0.05	no data	0.1
34	241.3	168.6	69	0.27	2.4	8.7
36	122.3	310.4	54.2	0.06	6.9	0.0
38	257.8	185.1	51.4	0.23	6.3	21.3
40	242.1	169.4	58.3	0.55	1.9	33.1
42	260	187.3	75.7	0.19	4.3	14.2
44	no data	no data	no data	0.03	no data	31.6
46	no data	no data	no data	0.04	no data	9.2
48	no data	no data	no data	0.06	no data	2.1
50	no data	no data	no data	0.06	no data	3.1
52	no data	no data	no data	0.24	no data	1.2

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

54	no data	no data	no data	0.20	no data	2.1
56	277.2	204.5	52.3	1.29	7.2	22.2
58	200.3	127.6	45.6	1.77	9.3	16.0
60	no data	no data	no data	0.49	no data	0.3
62	no data	no data	no data	0.26	no data	0.8
64	no data	no data	no data	0.24	no data	0.4
66	no data	no data	no data	0.24	no data	1.4
68	no data	no data	no data	0.31	no data	1.3
70	no data	no data	no data	0.24	no data	1.9
72	no data	no data	no data	0.20	no data	4.4
74	no data	no data	no data	0.35	no data	4.3
76	no data	no data	no data	0.26	no data	4.4
78	no data	no data	no data	0.32	no data	4.0
80	no data	no data	no data	0.21	no data	5.8
82	no data	no data	no data	0.50	no data	5.5
84	no data	no data	no data	0.12	no data	4.9
86	no data	no data	no data	0.22	no data	3.3
88	no data	no data	no data	0.61	no data	5.0
90	no data	no data	no data	0.88	no data	2.3
92	no data	no data	no data	0.95	no data	4.3
94	no data	no data	no data	0.10	no data	4.2
96	no data	no data	no data	0.08	no data	5.3
98	no data	no data	no data	0.09	no data	5.3

Magnetic data: Viðarhólm, Western Iceland: 64° 47'N 22° 27'W 2003

Vid-03						
Sample depth (cm)	Raw declination (Degrees)	Declination after rotation to field site north (Degrees)	Inclination (Degrees)	Intensity mAm ⁻¹	MAD (Degrees)	Low-field magnetic susceptibility (K) (SI units)
2	164.4	334.15	52	26.3	2.5	112.5
4	169.2	338.95	54.9	27.7	2.8	110.3
6	167	336.75	60.3	36.3	2.1	132.6
8	165.5	335.25	85.9	27.1	3.7	152.6
10	169.3	339.05	62.9	44.8	2	148.4
12	164.1	333.85	61	49.8	2.6	162.1
14	161.4	331.15	61.5	48.2	1.7	159.4
16	159.3	329.05	64.3	72.2	2.7	282.3
18	167.4	337.15	62.1	60.2	2.6	182
20	161	330.75	57.2	61.3	3.2	178.1
22	163.1	332.85	57.4	54.4	3.9	187.1
24	160.3	330.05	60.3	54.1	3	186.6
26	164.2	333.95	61.6	49.8	2.6	164.6
28	160.8	330.55	62.5	57	1.7	179.6
30	156.7	326.45	63.5	52.7	1.5	169.6
32	160.8	330.55	57.8	33.6	3.2	103.1
34	160.3	330.05	71.7	35.6	2.4	134.4
36	156	325.75	71.4	21.1	1.5	76
38	147.7	317.45	73.8	23.2	2.3	82.4

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

40	122.1	291.85	77.9	15.1	2.1	59.7
42	138.2	307.95	73.6	14	2	49.4
44	132.8	302.55	65.7	15.3	3.5	55.4
46	159.3	329.05	73.1	15	2.6	49.2
48	132.2	301.95	63.4	10.1	2.5	37.9
50	153.3	323.05	67	7.46	3.6	33.6
52	221.8	31.55	73.3	4.13	1.8	21.1
54	255.5	65.25	77	5.19	3.7	23.3
56	218.7	28.45	82.8	6.01	5.1	29.9
58	163.8	333.55	48.2	8.89	3.2	29.2
60	66.9	236.65	74.4	3.23	4.1	31.6
62	19	188.75	27	12.9	1.7	57.4
64	178.4	348.15	63.2	9.26	3.5	37.3
66	169.2	338.95	64.1	2.72	3.9	15.9
68	211.3	21.05	59.7	3.28	3.9	19.7
70	162.1	331.85	76.6	3.37	4.2	23
72	123.6	293.35	79	5.04	3	30.3
74	146	315.75	53.8	3.77	5	24
76	183.2	352.95	65.8	3.43	4.6	22.6
78	175.8	345.55	40.3	3.29	4.5	20.7
80	218	27.75	51	3.6	1.8	21.9
82	237.9	47.65	44.3	1.42	4.2	15.1
84	197.2	6.95	57.7	2.47	4.6	14.2
86	169.3	339.05	62.9	1.95	2.3	15.8
88	163.4	333.15	59.2	1.88	2.8	13.9
90	216.3	26.05	64.3	9.7	2.7	56.2
92	178	347.75	67.2	9.72	1.9	28.2
94	270.2	79.95	74	4.38	3.6	26.5
96	236.6	46.35	82.3	2.55	2.9	21
98	256.5	66.25	51.7	2.77	3.5	17.1
100	301	110.75	67.9	2.54	4.4	11.7
102	167.6	337.35	68.7	1.48	3.4	10.2
104	175.8	345.55	51.4	2.73	2.8	19.7
106	174.6	344.35	71.3	1.86	5	13.8
108	168.3	338.05	55.9	1.82	6.1	12.5
110	148.6	318.35	67.9	3.21	0.6	18.5
112	312.3	122.05	79.7	2.75	2.7	21.1
114	201.8	11.55	43.6	3.72	3	22.2
116	241.5	51.25	72.5	4.14	0.6	30.5
118	213.1	22.85	72.4	7.97	4.4	44.8
120	109.4	279.15	16.4	2.8	7.8	29.1
122	177.7	347.45	79.7	2.9	3	19.2
124	213.9	23.65	53	8.52	2.8	53.8
126	278.2	87.95	66	10.2	1.6	73.8
128	173.2	342.95	69.9	6.24	4.4	45.4
130	212.9	22.65	49	3.3	5	26.9
132	136.1	305.85	78.2	2.27	3.9	18.4
134	203.5	13.25	35.4	2.11	1.3	12.2
136	264	73.75	75.4	1.48	4.2	14.3
138	180.3	350.05	58.2	2.23	3.9	13.4
140	228.4	38.15	73	1.81	2.4	14.8

Appendix 2.1. Palaeomagnetic data

Appendix 2. Dating methodology raw data

Arne 2003 Pollen and SCP counts							
Depth (cm)	Total pollen grains counted	Total land pollen	<i>Spartina</i>	<i>Pinus</i>	<i>Spar. %</i>	<i>Pinus %</i>	SCP
1	418	368	21	53	5.7	14.5	70
2	480	423	7	56	1.8	13.3	107
3	320	279	18	35	6.5	12.5	59
4	356	315	8	70	2.5	22.2	37
5	363	312	30	29	9.6	9.3	104
6	361	306	10	30	3.3	9.8	70
7	367	296	12	41	4.1	13.9	56
8	356	309	11	52	3.6	16.8	45
9	370	316	8	58	2.5	18.4	50
10	380	314	10	42	3.2	13.4	73
11	374	327	11	26	3.4	8.0	79
12	409	327	13	39	4.0	11.9	104
13	392	314	4	40	1.3	12.7	104
16	350	253	3	42	1.2	16.6	158
18	248	178	2	20	1.2	11.2	92
20	365	305	5	23	1.6	7.5	86
24	336	307	3	12	1.0	3.9	40
26	349	319	4	16	1.4	5.1	38
28	345	309	7	22	2.4	7.2	45
30	352	305	12	24	3.9	7.9	32
32	334	290	11	22	3.9	7.6	17
34	313	272	10	17	3.7	6.3	18
36	349	311	10	20	3.2	6.4	12
38	353	313	9	10	3.0	3.2	18
40	371	319	4	50	1.4	15.7	30
41	318	265	1	30	0.5	11.2	59
42	345	305	1	14	0.3	4.6	39
44	371	317	1	27	0.3	8.5	50
46	362	313	1	33	0.3	10.5	31
47	392	331	0	32	0.0	9.7	28
48	367	307	0	31	0.0	10.1	15
50	362	308	0	30	0.0	9.7	1
54	375	320	0	32	0.0	10.0	1
57	318	233	0	28	0.0	12.0	1
60	414	366	0	39	0.0	10.6	0
62	285	244	0	23	0.0	9.5	0
64	172	133	0	13	0.0	10.1	0
65	51	10	0	0	0.0	0.0	0
68	22	0	0	0	0.0	0.0	0

Appendix 2.2. Pollen and SCP data.

Viðarhólmi 2003 Pollen and SCP counts							
Depth (cm)	Total identifiable grains	Lycopodium marker	Total sample LPG identified	Charcoal	SCP <10	SCP >10	Total SCP
0.5	107	33	74	8	35	18	53
1	119	50	69	15	40	22	62
1.5	121	41	80	18	39	19	58
2	107	50	57	11	15	9	24
2.5	84	26	58	19	7	6	13
3	110	48	62	20	5	5	10
3.5	107	51	56	17	3	1	4
4	75	56	19	24	12	7	19
4.5	92	44	48	42	24	17	41
5	97	54	43	14	12	9	21
5.5	88	49	39	15	11	8	19
6	85	54	31	30	12	7	19
6.5	90	51	39	21	9	4	13
7	67	48	19	20	6	3	9
7.5	103	28	75	22	1	1	2
8	99	48	51	20	4	1	5
9	77	54	23	20	6	4	10
10	68	47	21	12	3	1	4
10.5	81	44	37	15	0	0	0
12	61	46	15	12	0	0	0
16	64	21	43	16	0	0	0

Taf-02: as mg/kg or ppm

Depth (cm)	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd	Pb
0.5	24.643699	9224.885589	15597.958016	2.032832	8.141451	142.674776	29.528586	46.380425	37.581505	0.214242	0.161957	61.999582
1.0	18.766831	6533.206024	15515.780070	1.381634	8.459827	322.468875	18.575200	49.799808	48.590195	0.135726	0.146069	35.304313
1.5	17.633284	6058.629997	15140.629869	1.165616	3.932178	346.333662	15.699776	46.096962	50.323633	0.120115	0.148091	31.322277
2.0	16.614247	5763.514677	15997.635225	1.098787	6.638982	221.717339	16.090411	48.188258	4.682192	0.110763	0.165127	31.841083
2.5	19.176700	7514.027833	17325.629423	1.408111	8.700835	219.756581	18.493439	50.147515	56.260437	0.124453	0.186839	33.328284
3.0	18.021467	7114.678066	17676.011049	1.331167	7.964196	160.402946	18.274646	46.295692	58.013154	0.125090	0.181480	33.128826
3.5	19.503098	7608.912258	17870.367311	1.475350	15.418156	128.357732	19.351663	45.430852	55.691479	0.141020	0.201419	35.991372
4.0	18.365022	7355.147749	17453.630184	1.355764	5.727051	188.289588	19.141788	46.539379	56.018389	0.140393	0.162042	34.427635
4.5	19.471974	8034.931629	18384.904026	1.609994	6.748601	131.381904	21.128818	45.822748	58.794249	0.138403	0.243796	38.857751
5.0	18.638567	7820.011940	17573.714627	1.678567	6.170985	110.204100	22.889950	44.466070	56.133333	0.164378	0.191801	40.180683
5.5	21.653189	7093.079809	15343.958537	1.549660	8.601310	85.349876	23.164769	40.949189	51.027663	0.147663	0.247975	40.961768
6.0	17.872519	7279.349614	17820.292288	1.522905	5.308458	76.198380	24.412982	38.684190	52.309126	0.163111	0.252918	45.303586
6.5	19.055556	8541.551926	18813.173991	1.850995	4.946663	88.636475	25.409307	39.613313	52.554083	0.169738	0.229978	51.779587
7.0	18.433359	7174.914063	15544.514844	1.931797	4.174453	73.706172	25.590234	38.953516	42.552734	0.181641	0.204648	51.336185
7.5	19.498364	7557.924162	15920.009276	1.698051	6.142751	79.832454	27.569163	42.013538	41.544970	0.189157	0.221836	58.371908
8.0	19.923933	7942.588689	16648.055784	1.732674	4.450874	82.861620	28.654627	42.231748	42.260283	0.223265	0.225154	64.275308
8.5	23.341852	9840.228496	18111.867892	2.038897	6.774760	90.645227	31.087722	44.722653	47.871963	0.299803	0.222942	77.801957
9.0	23.707083	10044.011707	18073.739707	2.072741	5.139746	91.039141	30.326244	43.130146	46.452683	0.283707	0.174790	83.754393
9.5	23.694159	9925.640232	17738.475048	2.094932	6.612998	89.782515	29.133849	41.362089	43.541586	0.307544	0.172495	89.214945
10.0	24.965113	10110.440700	16473.370302	2.292172	5.838830	95.041450	29.269698	41.864928	39.840382	0.312496	0.199135	89.012642
10.5	25.388925	10237.023787	17169.917412	2.223178	4.572636	95.409248	29.347669	40.388582	37.143673	0.294196	0.159049	60.623140
11.0	23.123943	9356.504265	16437.519621	2.088872	3.803071	86.782104	29.994692	37.126445	34.599052	0.309763	0.164512	82.889340
11.5	24.791105	9372.837209	15877.906849	2.054947	3.868213	86.659879	30.548965	38.886652	34.709780	0.323797	0.158993	88.673068
12.0	24.455758	9384.000000	15594.917051	2.047444	4.531315	87.023501	32.937057	39.332640	34.863917	0.325430	0.123897	85.204534
12.5	26.529074	9768.536862	15665.012476	2.235690	5.473195	93.643781	29.834026	38.835917	30.795841	0.258979	0.119433	72.471569
13.0	27.937386	10048.220305	16098.457067	2.297040	14.143039	100.127857	31.258527	40.817916	29.173855	0.250431	0.109847	72.894745
13.5	31.578359	9507.148936	15855.339412	2.057305	22.467275	100.615765	33.574468	48.109828	2.432665	0.247092	0.145086	72.712476
14.0	30.687344	10210.503906	16509.003906	2.144688	21.077344	109.558359	32.830078	50.277734	27.479141	0.215508	0.127344	70.944544
14.5	26.450435	10094.422925	16420.177866	2.193834	18.773913	105.086719	37.330040	50.873913	29.204190	0.236245	0.173913	78.821357
15.0	47.182822	10369.449427	16011.672668	2.120484	16.025401	103.097637	35.683797	50.871751	31.033689	0.212779	0.176759	81.159293
16.0	33.165475	11917.238811	17744.416857	2.696531	20.823783	117.400614	31.850376	52.340150	31.161032	0.187272	0.116041	74.806155

Appendix 2.3. The elemental concentration data

17.0	31.879739	11968.233681	18369.340731	2.634360	20.834726	116.189060	35.500653	54.090470	40.107023	0.209021	0.138642	95.020117
18.0	30.246959	10912.246458	16346.510708	2.374853	16.676639	108.363519	35.802636	53.183921	38.703104	0.196784	0.191367	109.107624
19.0	36.582902	12866.273145	20384.655286	3.032856	17.467367	131.294576	36.892318	57.089035	35.577124	0.159829	0.139462	95.844268
20.0	36.673734	12507.936946	19138.147783	2.930601	20.546995	124.795823	41.160591	58.211232	34.375015	0.166975	0.124532	101.392985
21.0	36.732458	12379.584721	19276.415279	2.954123	18.451714	127.431694	42.955926	58.966112	34.227855	0.177747	0.153575	115.162142
22.0	37.626701	12317.194319	19407.249839	2.952744	13.254229	133.274138	40.301485	58.609813	27.697844	0.163344	0.144093	101.465991
23.0	43.122243	13808.864401	20113.381722	3.274325	21.085318	148.414147	34.461894	66.556648	21.207496	0.127364	0.128274	92.623438
24.0	38.665630	12371.347396	18732.913645	3.086777	15.234542	132.525801	46.926170	65.225181	27.182571	0.156506	0.106790	152.914186
25.0	37.174778	11153.612272	17562.552219	2.915561	7.996606	128.878355	44.273499	61.923368	26.187963	0.144791	0.094778	178.832128
26.0	39.210996	12103.143426	18726.314741	3.034422	10.294024	132.059522	44.161355	59.884861	25.859203	0.159243	0.101992	146.594170
27.0	41.959625	12474.084450	18499.886059	2.958338	5.677480	131.207534	33.878686	52.966890	21.943673	0.118914	0.079223	95.958995
28.0	47.999845	15036.462136	19061.378641	3.523262	11.028350	138.978408	36.833010	59.382913	23.412272	0.149786	0.104078	71.230304
29.0	49.758914	13339.215473	18699.579233	3.449094	23.453546	136.637014	28.684764	56.400814	22.886977	0.127737	0.065395	83.047723
30.0	49.654156	15522.176955	20552.695473	3.726091	16.303704	143.238436	28.825103	57.411934	24.932757	0.145556	0.097119	99.842812
31.0	52.005222	14187.977120	19519.401077	3.209314	22.254913	145.223176	21.337147	55.926380	21.232813	0.125855	0.063553	72.793284
32.0	52.285551	15395.465306	20327.775510	3.534041	13.811429	145.824245	21.324490	56.453469	20.508816	0.166408	0.071102	60.007361
33.0	49.168961	14292.510463	18764.891938	3.401331	21.907925	136.947952	17.884734	52.409331	19.746113	0.179362	0.057057	44.137784
34.0	51.797955	14183.871052	17460.000000	3.422364	10.463562	131.319857	14.866167	51.857115	16.195350	0.153839	0.041576	30.850420
35.0	48.875172	14809.637931	18160.364721	3.372573	14.529708	137.534244	13.625332	48.664854	16.984058	0.140729	0.053952	27.805584
36.0	47.515642	14073.526564	17948.776059	3.102246	10.708003	134.634593	12.123067	46.285541	19.911204	0.141103	0.045595	31.856638
37.0	47.327093	13790.960887	17516.186441	2.950091	25.548110	131.291812	11.360495	43.459322	19.035176	0.104707	0.058435	25.717614
38.0	47.375542	14129.294699	17853.032598	2.879842	11.702865	139.981324	10.133026	45.167336	18.873862	0.105775	0.051050	29.641633
39.0	47.592655	14027.500998	17813.592814	2.865629	14.769661	146.854052	9.518962	44.595210	16.122395	0.095689	0.041198	22.628623
40.0	47.548505	13515.891785	18410.973276	2.829324	15.534675	147.859875	9.915539	46.286110	15.015480	0.117862	0.051310	23.656100
42.0	46.272032	13687.925049	18226.055227	2.749665	13.245759	157.423826	9.169625	44.856410	14.203787	0.076095	0.027456	22.650112
44.0	45.061892	13460.382503	17775.401831	2.776155	11.514954	153.192024	10.191251	44.724720	14.090173	0.104049	0.025799	23.201641
46.0	42.739562	12747.489041	17006.732877	2.542356	14.711507	145.179205	9.634932	44.100411	12.528740	0.408370	0.022192	22.007411
48.0	43.042513	12060.999659	16405.483100	2.351820	8.184910	147.764862	9.195630	45.030113	11.425032	0.079850	0.015323	22.540676
50.0	46.947781	13585.845205	17672.486301	2.875233	8.095068	162.110712	8.566438	44.429178	10.917781	0.102616	0.018164	23.569055
52.0	46.017231	12681.828783	16022.628763	2.552689	14.961070	145.312134	8.044816	42.345552	9.827398	0.071719	0.007946	19.485498
54.0	43.343840	12623.556000	16305.220000	2.545760	14.399200	148.827760	8.178000	38.844400	11.090640	0.067960	0.016080	20.967213
56.0	47.558813	14693.281761	18318.406135	3.131364	12.378126	125.819940	8.104301	43.657352	14.652884	0.085428	0.014565	22.783408
58.0	44.969063	14958.522259	19407.607973	3.060120	12.221262	155.260465	7.994950	47.245316	16.233887	0.097874	0.022007	25.225063
60.0	42.520604	14155.472306	18094.964753	2.992870	7.917422	199.655589	8.722659	44.917221	17.007049	0.099698	0.042699	25.057885

62.0	43.758369	14768.994903	18251.070336	3.297778	5.955963	148.846075	8.340061	41.470744	16.570846	0.087870	0.010520	23.162569
64.0	37.808813	13621.361311	18311.114754	3.130151	8.716721	150.548852	8.047475	42.140459	16.815738	0.093443	0.027148	21.982767
66.0	37.257702	13315.068931	16775.524476	3.326194	7.086913	129.168831	11.530070	37.525275	18.221778	0.073167	0.017263	19.529617
68.0	38.687890	13550.916585	17177.919529	3.141825	8.767419	119.585868	6.623749	37.254956	13.660451	0.068577	0.017507	15.206883
70.0	38.909629	13265.022416	16902.275008	2.919425	5.204282	130.496487	5.553965	40.511342	12.750753	0.054480	0.003131	17.881378
72.0	37.729443	13131.088146	16754.103343	2.851388	7.268490	126.543060	5.176900	38.868085	0.228815	0.061560	0.003485	17.726255
74.0	37.673318	13573.697637	17706.992554	2.969427	8.614438	147.249595	5.622791	42.540758	13.316931	0.064526	0.007536	21.239055
76.0	38.333625	14167.713147	17474.402390	2.948924	6.702390	200.735060	6.467729	47.452988	15.003984	0.081873	0.014343	22.499150
78.0	39.115999	14069.073691	17870.256752	3.212191	12.570190	196.163388	6.823875	49.179193	15.189063	0.076706	0.021607	21.342928
80.0	39.112147	13454.808681	16740.200334	2.759720	6.480801	161.967947	6.432321	45.558731	12.773289	0.078090	0.012100	17.925689
82.0	41.559344	15224.206089	20330.846437	3.243324	9.328203	213.039144	7.248177	49.102844	14.870525	0.082503	0.024329	21.200214
84.0	42.255721	15586.949309	19268.235681	3.332113	15.007900	218.687953	6.301777	44.834891	15.705069	0.077933	0.005372	17.513970
86.0	43.586178	15949.294790	18748.537815	3.509970	7.435966	154.828235	7.766319	46.107025	14.101513	0.006623	0.002743	16.056282
88.0	38.101739	13984.569170	17747.332016	2.908221	8.820158	163.733202	7.499605	45.654941	12.735178	0.060988	0.008379	17.209302
90.0	36.641463	13417.077486	17607.216495	2.971387	6.877951	246.642501	8.242368	46.254872	13.767875	0.078736	0.012930	22.243911
92.0	39.669569	13239.592157	17623.823529	2.844627	10.405882	287.390196	8.178039	46.787059	13.639216	0.089216	0.012627	20.917464
94.0	37.556147	13108.077592	17442.441472	2.765940	7.206020	265.944482	8.369498	44.992776	13.444816	0.074849	0.021351	21.460682
96.0	38.941622	13629.911668	17553.361898	2.765379	12.290705	292.621622	9.909295	47.741727	14.990112	0.080488	0.021595	23.337983
98.0	37.868132	13133.227242	17454.113284	2.662900	12.256912	288.244774	9.731895	45.518678	12.768712	0.070843	0.011976	19.503520
100.0	38.830614	14123.121759	17494.223827	2.792964	7.504431	301.927798	8.606761	45.411355	36.594683	0.085658	0.008664	20.717900
102.0	36.375828	12266.165950	16288.561983	2.467359	9.582149	271.832727	6.820760	41.457322	10.710744	0.072952	0.015709	16.081798

Arne-03-02: as mg/kg or ppm

Depth (cm)	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd	Pb
1	17.2672999	7011.41113	11688.114	0.19310719	26.0230665	46.0949796	13.7845319	76.7259159	32.3218453	0.23625509	0.50645862	30.9432972
2	6.39329084	7852.41194	12186.7024		0 37.8678296	30.956055	13.4145589	76.295203	38.066689	0.26825897	0.67153304	33.6601275
3	1.17194171	5927.49576	9675.55405		0 10.755676		0 14.29102	62.635039	42.5038292	0.17827177	0.74016943	36.4963877
4	0	4974.98024	9523.24111		0 6.3201581		0 15.0924901	61.7193676	36.3019763	0.18197628	0.74158103	45.1979051
5	0	5906.66151	10392.7975		0 9		0 14.4964451	86.072643	36.2522411	0.16710974	0.55001546	46.2522566
6	3.86467144	8262.86272	11583.7866		0 13.3780091		0 11.6111906	74.5491217	42.2553025	0.22032531	0.53098243	42.8174496
7	4.71556285	9068.60519	12639.5011		0 9.47161142		0 13.0137184	59.2438464	42.9920578	0.24354447	0.64280932	41.7790745
8	4.2007772	8699.49482	12308.4715		0 9.18264249		0 20.9238342	61.1852332	39.7088083	0.21	0.60862694	30.2399093
9	3.634714	8231.43984	12605.0493		0 14.2445759		0 9.87140039	47.2781065	43.1100592	0.23447732	0.62887574	34.3789744
10	2.11259356	7127.64074	13469.7559		0 24.3865929	9.98893589	13.9267166	51.2372275	47.4001952	0.24148389	0.6639245	38.2755744
11	1.17352651	6300.96806	13534.5933		0 32.6651301		0 14.3367797	40.8442542	48.6179783	0.29650313	0.8203622	41.8376161
12	4.37637795	7484.52756	15666.8504		0 15.2086614		0 15.8283465	35.2244094	26.1354331	0.28677165	0.66070866	42.3952887
13	5.03183144	7688.82982	15128.8687		0 15.7886548		0 17.3655754	38.2794165	43.6372123	0.31056078	0.75625284	48.0067553
14	7.14962867	7628.04004	15310.4811		0 20.873103		0 17.5307717	37.1236681	43.9795932	0.36670326	0.73317404	46.4775073
15	4.23654304	7637.98571	15022.9874		0 15.7318816		0 18.5303845	35.1180674	48.0179653	0.3398707	0.62805036	47.1523784
16	4.45658409	7419.309	14000.1825		0 16.1186441		0 17.3209909	37.8344198	44.0276402	0.38503259	0.8746545	50.6195698
17	6.85600794	8955.98808	15671.8173		0 16.8619662	3.94041708	19.4097319	49.1082423	47.2786495	0.37195631	0.88031778	52.6781993
18	7.33329028	9170.17759	16224.9144		0 13.7436229	4.89764288	19.638618	75.9405877	48.0945431	0.41784953	1.14544398	56.913413
19	8.70338693	10110.1745	16262.9353		0 20.2846391	6.43722203	19.1162504	100.002737	48.3629148	0.41070133	1.04941498	60.8213616
20	9.24012158	10102.0061	16978.2371		0 18.2654509	8.25126646	20.6054711	98.070922	46.7614995	0.43460993	1.02784195	62.4183857
21	13.2395094	11057.4693	18102.1821	0.23023886	23.3841188	14.1226598	24.0402841	92.4170433	44.314009	0.40377017	0.9281601	62.2662492
22	14.5968656	11998.6796	19195.9186	0.41149717	24.2440814	17.621874	26.3223741	79.4624875	44.4724241	0.49792598	1.06283428	64.9085829
23	15.0049489	12157.0571	18969.5018	0.60114814	30.1959749	12.9224678	26.3770373	63.6265259	44.2246123	0.49900363	0.91700429	62.1645793
24	16.6792946	13319.4121	19960.9928	0.8419595	34.1541476	16.7028086	27.2386675	63.3272371	47.6410189	0.41635532	0.82150229	55.2125539
25	16.5549738	13235.6152	19960.9162	0.80120419	28.1034031	20.0811518	22.3837696	68.7290576	44.6874346	0.55617801	1.1058377	64.2476571
26	15.3988893	13292.4012	19693.0938	0.81792878	32.1424371	18.9741914	21.5709899	85.3799412	48.2759882	0.40551454	1.20595884	63.7506828
27	14.0092654	12217.088	18374.7717	0.73636003	30.6750496	19.0046327	19.0935804	82.5109199	49.1452019	0.35118465	1.11827929	63.8851224
28	12.9866753	11905.1154	17648.5408	0.82537537	28.0519987	19.2187195	17.3951251	76.5121872	51.7064673	0.35816705	0.98129347	58.0113227
29	8.78144397	8219.54917	13695.0539	0.74893172	27.3910487	14.1600784	19.4148318	77.4609605	47.8682783	0.40865077	0.90801699	46.1355243
30	7.07808531	8489.75578	13759.8697	0.29322045	23.7694562	13.6138066	17.9136438	84.8674699	45.1412569	0.4088831	0.88161511	45.1777401
31	6.47831043	8699.97989	12484.2642	0.02832048	23.0063694	21.1357694	16.1088837	85.5206168	37.107878	0.36221254	0.77004358	42.5413476

32	7.55795796	8723.4034	13130.6507	0.0402002	22.7067067	20.5405405	13.8874875	73.997998	33.7313313	0.3445045	0.8152953	40.6342476
33	9.34843093	9405.38337	13670.8379	0.46835328	26.0148819	22.5247493	14.5055969	74.9155613	31.92132	0.32859269	0.70276286	40.2267357
34	13.1512325	11651.8205	15429.7135	2.43517655	35.0086609	65.9960027	15.9013991	81.3057961	37.7188541	0.40317122	0.86342438	42.501972
35	12.5575758	10920.7964	14117.1717	2.03959596	27.7818182	57.8505051	12.7515152	64.969697	33.1313131	0.32509091	0.65050505	41.9632727
36	11.9010309	10915.0396	13929.8969	2.28783505	26.2185567	61.7896907	12.956701	67.1257732	32.7010309	0.28478351	0.61608247	39.474543
37	16.9310232	10438.3018	7884.92972	3.33834586	33.5952926	61.7535142	11.658712	50.4792416	28.3622099	0.31563256	0.70768225	36.8718274
38	8.91105121	8736.78073	11628.0323	2.12991914	21.4123989	50.8867925	9.77628032	48.3234501	24.7843666	0.29539084	0.69622642	35.7381806
39	7.50423645	8310.92453	6874.48276	2.02719212	20.0827586	50.009064	11.5625616	43.791133	25.8364532	0.33363547	0.68413793	35.3336355
40	7.895459	7126.67926	9361.64652	2.22280301	18.5821627	51.9516498	11.9411957	40.0731787	23.5530872	0.24878144	0.58333878	30.9411696
41	6.20472016	7928.64639	9888.06473	1.91773432	29.1301416	54.4895482	12.8415374	41.0492245	24.9386379	0.29478085	0.69669589	33.9281591
42	6.95366098	8059.7677	9885.65697	1.94663992	21.223671	55.4944835	12.4292879	41.2678034	23.3580742	0.30435306	0.7558676	34.0190304
43	6.23732371	7518.38806	8934.07675	1.56484093	18.222368	51.2823877	11.9330928	45.4417842	19.7258117	0.33870777	0.77376189	29.7772778
44	7.39029776	8322.10278	9651.38842	3.56507193	19.7845433	47.927735	12.2689863	47.4058213	22.9642021	0.37682168	0.85112078	33.2388491
45	7.6476386	8430.78891	9938.39836	2.09938398	19.8028747	44.2053388	11.4168378	45.7330595	22.9075975	0.35425051	0.68501027	31.8380972
46	7.23805748	8257.27294	9776.01586	2.39365709	19.9960357	43.8850347	12.7492567	47.9682854	22.8186323	0.30469772	0.68424182	30.5751305
47	7.05219707	7976.95246	9107.85619	2.29454061	16.5858855	43.677763	14.3648469	43.8215712	20.436751	0.30782956	0.79893475	33.8984421
48	3.89695979	6663.73495	7415.75678	2.54906832	14.5302386	44.3439032	12.7178817	44.8931023	20.0300752	0.31406342	0.83949003	30.1506767
49	13.2674683	7935.90029	8102.2159	4.79532012	28.921677	48.881378	13.119272	44.8176796	23.1108222	0.26230744	0.6481638	25.1644199
50	12.4662577	9386.08221	8580.7771	5.68261759	16.1145194	50.1022495	15.5092025	59.8364008	26.2413088	0.41169734	1.01431493	33.1530061
51	8.1092969	8800.65485	8933.02233	3.68997001	14.6591136	35.9800067	14.6991003	34.9403532	25.8953682	0.34492502	0.75814728	30.3868444
52	4.90923588	7373.41037	7301.26246	4.12863787	13.7142857	28.4651163	13.833887	36	22.3574751	0.30482392	0.64504983	29.4720664
53	3.71480363	6569.57543	6683.5851	3.36918429	9.90936556	23.7099698	12.4874119	27.9879154	20.3746224	0.01482377	0.59859013	26.9053105
54	3.26347915	6774.75931	7201.62767	3.76480163	9.00101729	23.7151577	11.5564598	24.4313327	20.0284842	0.01904374	0.60142421	25.4428349
55	0	3736.36115	3657.48266	2.88382557	1.06005946	8.2061447	10.6878097	12.3290387	12.0594648	0.01102081	0.39643211	17.8100165
56	0	3348.45993	2958.68324	3.55525697	0	5.66583809	8.88411152	10.9398724	9.97245549	0.14132348	0.23540477	13.3795499
57	0	1675.52878	1096.21622	4.29324324	0	0	5.80621622	5.19972973	4.08081081	0.06689189	0.13297297	7.23206757
58	0	1053.22278	496.657682	5.14366577	0	0	5.3296496	4.87196765	2.01105121	0.04358491	0.10431267	3.94033693
59	0	978.517296	313.638171	5.81630219	0	0	5.82664016	5.88151093	1.84254473	0.05097416	0.10019881	9.77830351
60	0	823.326336	167.483703	6.06571056	0	0	5.80052151	18.1799218	1.26179922	0.03864407	0.19009126	0.93518905
61	0	389.030984	0	1.83510638	0	0	2.9537234	10.037234	0.81861702	0.02026596	0.10132979	1.69378989
62	0	364.272912	33.5669833	1.11470685	0	0	1.36469047	5.17183099	0.54422535	0.01116279	0.05046839	0.02254831
63	0	485.257274	37.2346003	1.17719528	0	0	2.57221494	4.98715596	0.56044561	0.02178244	0.05433814	1.2840498
64	0	659.602705	0	1.46418668	0	0	2.99573892	8.23807913	1.17037538	0.02589111	0.08684478	2.00978018
65	0	562.18893	91.4592419	1.36866823	0	0	2.92975512	8.26836632	0.71017779	0.0235894	0.07680644	1.98823214

66	0	498.36	157.368078	0.66285342	0	0	2.22488599	4.44039088	0.67661238	0.0262671	0.06136808	1.61007166
67	0	821.369897	376.329897	0.45583505	0	0	2.91958763	4.42721649	1.75010309	0.03035052	0.06053608	2.44839863
68	4.58384106	1079.13457	0	1.40503311	9.45695364	0	0	3.14463576	2.52715232	0.04784106	0.10656954	3.47974834
69	0	1659.1495	807.402512	0.87243886	17.3932584	0	5.0720423	9.13681428	2.84097819	0.08581626	0.20391276	5.25473893
70	0	2465.48514	1295.93604	1.28954031	28.389074	0	5.3356429	11.8560959	3.86142572	0.14326449	0.29108594	6.28275816
71	0.11563414	3840.25379	2102.14213	1.38646719	28.7249235	2.48242095	7.03270996	21.5518531	5.1117307	0.2433458	0.46114927	8.08597076
72	1.3787062	4762.73127	2488.94879	2.33854447	27.9137466	3.48598383	12.032345	80.0296496	6.38247978	0.30824798	0.77959569	11.2199596
73	1.65226527	4863.75128	2511.09652	2.09349967	26.3401182	2.8664478	10.3847669	67.0045962	6.62560735	0.30429416	0.60598818	10.3548391
74	1.3180778	4575.54312	2275.25335	2.20464204	25.1454724	2.57495914	12.1608369	80.5753514	6.19653482	0.27711017	0.56653808	10.6769663
75	0.64285132	4375.48758	2254.17515	1.76130346	21.6863544	1.07861507	8.85539715	84.7250509	5.86558045	0.27551935	0.59478615	9.13131025
76	0	4415.96072	2193.98798	1.83727455	21.498998	1.25450902	9.49098196	67.3827655	6.05611222	0.2943487	0.6101002	9.67963928
77	0.37595868	4490.82841	2285.34538	1.72214332	22.4583602	1.91814074	10.3266624	67.6152356	5.90471272	0.28911556	0.63145255	10.1810329
78	0	3896.10543	2306.63984	1.47364185	25.3440644	3.11066398	8.08853119	44.1448692	5.19839034	0.2649497	0.60531187	9.02107311
79	0	3629.21573	2064.81356	1.20894915	25.480678	2.47240678	7.1739661	46.820339	4.83579661	0.24260339	0.55574237	8.42740339
80	0	3850.98237	2255.52632	1.51342105	23.7078947	2.75605263	8.47894737	43.8315789	4.91052632	0.30489474	0.61981579	9.21738158
81	0	3504.24797	2329.03654	1.39295681	29.1189369	4.01541528	6.68172757	52.7362126	44.8186047	0.27125581	0.55662458	8.37901661
82	0.03232884	3649.25418	2323.98922	1.34070081	52.0916442	7.54447439	5.94097035	56.7816712	4.83072776	0.24113208	0.5596496	8.92885445
83	0	2749.99553	1986.07096	0.58738502	64.1392904	8.09724047	4.6021025	45.8239159	3.8956636	0.22959264	0.48417871	7.83339028
84	0	2242.2348	1788.53503	0.38731478	68.8944016	8.27891385	2.49413342	33.0351995	3.20455917	0.1481998	0.39672813	6.28522963
85	0	2207.32708	1954.55746	0.38980185	59.0647292	8.4332893	3.90277411	39.9550859	3.33130779	0.14837517	0.37180978	6.85760898
86	0	2539.11743	2132.63434	0.51412844	53.7090433	7.84560944	4.55072084	40.7732634	3.56461337	0.15664482	0.42314548	6.87183486
87	0.44871327	4219.58338	2678.82472	1.34954407	35.047619	5.11448835	7.84761905	102.532928	5.41357649	0.19550152	0.5885309	10.517001
88	0	3755.03285	2067.24976	1.26180758	21.5199223	1.54635569	7.97667638	61.3333333	4.8303207	0.1750826	0.52641399	8.1700162
89	3.24328604	3538.56364	2094.3583	2.37703728	33.7314418	8.90795117	7.84929066	81.1613329	5.34081161	0.16881557	0.51238535	8.21538766
90	0	4401.96216	2566.02238	1.74486267	28.3947101	3.73794507	8.67548321	48.6429298	5.49420142	0.20850458	0.5876704	8.47095287
91	0	3223.60705	1811.77253	0.89870303	17.39142	0.22619222	7.26624543	60.6025939	4.00744929	0.15978716	0.4318723	8.6800266
92	0	3138.39192	1803.91134	0.81355932	16.7327249	0.29178618	8.20599739	136.662321	4.0482389	0.14409387	0.5085528	9.26363755
93	0	3597.46976	1879.86348	1.1483959	21.7474403	0.25507167	7.04273038	141.870307	4.51986348	0.18610239	0.77578157	11.7750307
94	1.46897932	5116.13956	2576.11741	1.39933289	34.5590394	2.66577718	10.2308205	76.7791861	6.63162108	0.18028019	0.60448299	11.0543162
95	3.13322204	6328.87693	3325.54257	1.95365609	44.7786311	5.80808013	8.53422371	79.2200334	8.23772955	0.20610351	0.77657429	13.1755726
96	3.20630137	6541.57068	3388.76712	2.02356164	52.3726027	8.30136986	7.59205479	42.0328767	8.35068493	0.21715068	0.61569863	11.6235753
97	3.05096753	6129.41502	3196.58905	2.04814693	43.3164972	6.35618235	12.2558216	96.0314857	7.49675303	0.18434897	0.76360774	13.020938
98	3.06868077	6278.27674	3314.40081	2.22275932	31.5649547	4.50835851	14.0100705	164.914401	7.67693857	0.17901309	0.87661631	14.5890702

Viðarhólmi-03: as mg/kg or ppm

Depth (cm)	Li	Al	K	Sc	Ti	Mn	Cu	Zn	Sr	Ag	Cd	Pb
1	16.6991063	29780.8663	49811.3208	9.43793446	3458.98709	371.711063	60.4099305	33.2202582	285.05716	0.32810328	0.26772592	1.64407812
2	16.7405476	31366.3615	52122.5554	9.67668232	3810.95176	420.697236	65.4297262	32.833116	296.221643	0.39817471	0.31994785	2.02827901
3	24.4726655	33646.179	50143.2937	10.7164686	4282.51273	395.483572	68.1624448	31.6327334	152.569671	0.32597623	0.21758913	1.48005433
4	20.9068826	34271.3927	51540.8372	10.3184615	4037.00972	482.334737	60.7193603	31.7226721	159.825911	0.36680162	0.23562753	1.92091768
5	16.1308399	32589.0541	52082.6391	10.1298606	3858.04039	496.307433	59.8885359	31.8891533	171.847671	0.38027882	0.22278137	2.7683101
6	16.1730314	33266.782	49827.3206	9.88980061	3841.06009	440.24338	63.0118905	30.8840825	164.394728	0.36174383	0.23197026	2.95153768
7	17.0475553	35023.5794	50807.4486	9.9129002	4044.23871	369.069042	62.6832498	31.2478232	167.007368	0.3841929	0.22665774	3.35619558
8	18.8409704	36562.1321	53080.5396	10.805903	4451.24555	386.994663	65.8127305	32.6502695	171.254717	0.37196765	0.20943396	3.54366577
9	19.0981432	35797.2175	52004.9873	10.5543501	4173.5069	368.183077	68.0279125	33.3242706	163.118037	0.38514589	0.20291777	4.5668435
10	19.563366	39455.3592	56656.6548	11.8364042	4853.29395	409.665482	67.8783995	33.6417709	173.073336	0.36174383	0.18654951	3.68421764
11	19.4266442	39051.7396	52899.5081	11.8448297	4570.69032	374.516074	65.7174314	32.7642496	165.923777	0.32215852	0.17645868	2.75129848
12	19.8285714	37849.1184	54647.2931	11.6598367	4490.37306	424.31298	64.888498	31.2469388	171.334694	0.32163265	0.16	2.33931973
13	25.8511283	38037.1869	53798.2626	12.4432199	4714.07774	403.839731	71.0448582	31.9925901	176.370495	0.34597508	0.18187942	2.11438195
14	22.6246649	41119.4397	59503.7003	12.3565416	4823.08874	434.463861	68.5161475	31.8317694	181.435657	0.32815013	0.15844504	1.76595174
15	25.90625	40543.1016	59760.1047	12.6041406	4863.83359	439.205781	69.2878203	32.4042969	183.191406	0.32734375	0.1640625	1.86640625
16	21.8527567	40290.6596	88736.5604	12.2205084	4646.05375	511.125837	57.9109224	31.9927369	175.253879	0.26622648	0.12994388	1.20356553
17	24.474934	43318.0765	59638.2063	13.3324274	5256.49631	421.490818	71.3100871	32.7526385	194.55277	0.32058047	0.1646438	2.04934037
18	22.2444971	41087.8456	57665.7777	12.8113512	5043.58171	402.126705	72.5676207	29.7277345	198.457162	0.34459871	0.19505588	1.88201829
19	25.5578254	44872.6221	60306.7682	13.9834992	5486.95117	422.497582	70.5279025	33.7482702	198.788797	0.34319605	0.18187809	1.86280066
20	24.2763158	43148.8184	57594.4216	13.7236579	5221.34763	387.144789	65.2013763	30.2190789	198.856579	0.32289474	0.15947368	1.60973684
21	22.4611399	40744.9508	55455.6482	12.3212176	4620.2386	384.313523	70.2500596	30.5265544	187.138601	0.36295337	0.20207254	1.69093264
22	25.4117647	41350.7988	52354.5797	12.9268508	4859.04998	378.667585	72.6071446	43.4273643	189.913552	0.36425089	0.17783555	1.50718232
23	29.8787062	37152.4286	49708.572	8.3719407	3520.51779	268.611914	73.0903585	34.3483827	132.845013	0.36469003	0.19892183	1.49245283
24	29.3524004	31832.621	41579.5171	6.58165475	2955.42962	201.089602	73.5349622	32.4228805	105.319714	0.40531154	0.20102145	1.51092952
25	32.6644068	28893.6976	41721.709	5.99292203	2679.62603	178.074631	75.9770115	29.920678	100.299661	0.38969492	0.21152542	1.30630508
26	34.8897959	33342.9959	36035.0482	7.12759184	3122.2098	185.537469	70.1946204	32.4714286	108.15102	0.34530612	0.19020408	1.30802721
27	28.0711462	37126.6166	42674.2561	8.21604743	3300.95415	236.903874	72.2438024	32.7094862	131.924901	0.35889328	0.17786561	1.46693017
28	53.7950249	35411.0806	43918.7534	8.75088557	3415.48816	231.867383	72.5081871	31.0268657	137.6199	0.3558209	0.19343284	1.4240796
29	35.0473595	36695.1986	44093.7109	8.92399319	3544.5645	235.243666	71.0501479	31.0548552	144.233049	0.33771721	0.17499148	1.12763203
30	33.8372562	36722.3968	43515.4814	9.04099529	2917.04667	204.882367	66.8904452	28.872226	144.762609	0.39462004	0.18318763	1.2796234
31	34.0468909	34532.2487	40312.2805	8.81818552	3636.86608	170.424791	74.9344832	32.6829766	134.218145	0.44933741	0.19979613	1.81501869

32	32.6172107	32122.7854	41948.9092	8.00261128	3267.02829	165.842453	75.6387023	35.0365974	130.31454	0.40830861	0.18278932	1.65565447
33	34.9090909	32422.1194	46309.0372	7.63335142	3403.56065	194.233433	63.572654	36.6166893	113.149254	0.3109905	0.14002714	1.11994573
34	31.4696277	30047.1613	36770.4251	7.49886349	3369.33272	148.909262	75.0790934	32.0398432	108.623122	0.39895493	0.18262573	1.31338994
35	32.9990115	33817.5974	29031.6447	8.56669522	3725.10603	171.505819	72.0303736	30.1107084	147.6257	0.35980231	0.16052718	1.22490939
36	22.0273973	17132.1109	29447.057	3.86205145	1802.37113	109.442085	75.4467705	29.0898764	61.467424	0.42258603	0.17641163	1.18864016
37	23.4376238	22095.1842	26204.3042	4.48657426	2051.25307	109.056158	70.0898297	32.8534653	62	0.37782178	0.14178218	1.29821782
38	17.7795276	19366.2756	27010.1843	4.0907874	2004.4937	107.545984	64.4003228	28.4074803	55.9488189	0.46771654	0.19212598	1.05695538
39	51.0142954	32189.3833	30798.8569	6.867774	3242.78312	105.445936	72.8564275	31.8400272	103.895167	0.49257999	0.20258679	1.1264806
40	33.4705295	29592.5714	35914.7229	8.57350649	3289.61271	171.935584	69.8513487	36.3380619	111.473806	0.29002997	0.15264735	0.95146187
41	33.3700306	30155.1111	31949.6815	8.83800204	3557.29085	164.023976	67.1979613	34.3877676	113.583364	0.30246687	0.1598369	0.90562012
42	35.9196787	33957.996	36536.7847	9.90168875	3767.97422	202.838876	74.5393574	36.8417671	131.79245	0.33004016	0.15983936	0.92946452
43	34.7387631	35604.7624	37851.9475	10.5745995	3877.90029	230.943751	69.8356201	38.581683	133.40853	0.35030754	0.14518418	0.85205813
44	30.9768379	33939.7422	38999.635	9.88326284	3649.64987	208.52721	65.9025176	34.3750252	128.726365	0.35359517	0.26586103	0.83559584
45	28.6113886	28937.2268	33740.8967	8.85322677	3313.58873	151.875644	87.4337662	35.8585415	107.078202	0.46185814	0.2005994	1.02338994
46	32.5426963	29028.6439	32125.3793	8.73197748	3219.82561	177.440609	80.0427029	34.7530971	106.831719	0.34994369	0.17568731	1.1564889
47	33.0898785	28344.6275	35628.3806	8.4891498	3119.24883	170.854656	73.1069231	34.1024291	107.437571	0.31352227	0.16923077	0.92963563
48	32.5882904	31086.4757	35659.5918	9.31744396	3578.13768	171.031516	77.1525326	37.5910338	113.76546	0.36309133	0.16139177	0.9566544
49	33.5092505	28371.869	32719.2843	8.61642134	3330.40294	153.387306	76.6404186	38.0147198	106.132667	0.33804186	0.16448346	1.04910196
50	35.9968952	26472.6636	31397.969	8.05234153	3000.21136	147.015912	75.74674	37.1150065	98.2551817	0.35332471	0.17852523	1.0127555
51	35.6171391	24653.0903	29894.0409	7.45874753	2870.09015	120.320765	73.0813843	33.9484509	98.8678181	0.40358603	0.18747528	1.09276203
52	44.9363726	26335.4727	32278.335	9.45419227	4083.46664	148.032111	74.9946878	34.0269574	113.050862	0.41561943	0.23072349	1.1322894
53	31.4962664	24731.0716	30014.9748	8.82672048	3607.88884	155.483754	70.9481736	30.8508577	105.73998	0.33759839	0.2332997	1.05329297
54	27.2297458	26297.9374	32572.2505	8.62943249	3593.95092	162.978865	69.8137378	30.1499022	114.430841	0.32031311	0.22544031	0.94828441
55	23.42706	24777.7131	33579.6948	7.62653103	3358.10564	140.228281	60.4574161	26.6258393	111.158006	0.34604273	0.22461851	0.86111902
56	28.6486202	27087.2129	34510.6833	8.7469908	4074.06489	152.25138	65.0357819	28.0024967	116.992431	0.31080158	0.18212878	1.00507227
57	34.8903749	28584.0851	33621.925	9.87566363	4365.77289	273.722796	65.3998379	25.3831814	117.516028	0.34950355	0.20911854	1.30612631
58	26.7376365	26753.2195	39905.5015	10.5136842	4021.66618	510.43138	69.3442304	24.4818272	109.620973	0.34256207	0.24230387	0.99683548
59	10.3902149	27059.0003	54974.7174	13.7368066	3495.88546	680.017587	78.2178248	26.3535868	115.426433	0.24372893	0.28641322	0.52212893
60	16.25021	22531.01	47985.3053	12.5498675	2840.6635	534.285363	60.3970662	20.5620679	122.198695	0.14283683	0.17214863	0.30275929
61	13.01288	24475.1474	39370.5525	11.0264269	2954.90471	469.177247	57.6557437	20.8825106	126.539706	0.23474338	0.17103629	0.643949
62	17.315696	24462.4798	35444.0671	10.672537	2999.62274	417.220533	54.244462	20.9409674	124.055597	0.26708786	0.17611056	0.70294176
63	30.0758893	29158.5889	36237.9842	11.2127273	4047.64609	188.383794	61.6498419	27.6810277	126.312569	0.32110672	0.16758893	1.05515152
64	29.6167164	26472.1313	31260.5373	9.57938308	4579.71924	148.143682	58.8155622	24.7693532	110.157532	0.3719005	0.16318408	0.98024544
65	40.7389691	29085.0433	34450.3505	9.64461856	3946.61633	138.726186	80.154268	30.116701	116.606515	0.35975258	0.16494845	0.89465292

66	42.9175553	28576.5527	34260.8973	8.75742523	3517.50765	137.793628	74.4242263	27.5551365	120.222679	0.29430429	0.1443433	0.69708713
67	36.4092092	26879.3714	33930.7708	8.64392392	3624.64248	137.261662	79.1888288	28.3615616	111.86018	0.29085085	0.14014014	0.68209543
68	31.4427317	27508.7727	35661.3073	9.33002927	3720.79789	144.316488	81.7850146	27.9543415	118.466654	0.36776585	0.1795122	0.75689106
69	29.6790556	25874.3595	33090.9005	9.59522428	3824.03154	140.847622	84.5763642	33.281484	105.539616	0.37655312	0.57956155	0.79252614
70	29.2873747	27675.8437	34582.004	8.91711423	4145.30846	176.517435	67.7250902	31.9170341	107.242806	0.29675351	0.38076152	0.70736139
71	25.8551952	31144.1019	39177.5381	8.92185308	3979.03823	237.62184	54.4701919	27.5710126	121.656175	0.2431767	0.12547981	0.64283256
72	24.5060052	30176.7219	37363.7467	9.63767624	4101.51877	213.215796	53.6452089	24.0599217	117.638695	0.2586423	0.11984334	0.65569191
73	28.283436	28259.7977	32169.3744	11.5792026	5147.959	144.315462	84.3205575	25.9966288	120.727702	0.41947488	0.36252836	0.88280065
74	21.1863712	29315.738	33591.3066	12.5153291	5638.58866	158.866424	71.3625273	22.3220642	130.110804	0.28517367	0.31756533	0.76276546
75	22.4120839	27039.0629	32414.0367	11.5350197	5102.44207	117.773159	79.34746	20.811114	118.85599	0.50895413	0.49541284	0.8695806
76	21.0631069	25391.8023	32279.6369	10.9014391	4691.54445	141.924573	86.2704936	22.083228	116.405003	0.52391661	0.49630128	0.90583726
77	17.9826237	24545.739	30512.0027	12.0587446	4833.1628	143.368874	76.6019422	19.5003388	101.424271	0.49037795	0.43998672	0.90533378
78	14.3699396	24148.8314	28472.6797	13.1433445	4845.61894	143.748717	70.9229174	18.5881531	100.775178	0.48775285	0.86232371	0.89656145
79	15.259712	24993.2003	30557.4738	11.237199	4794.1928	166.074503	65.6572147	17.5639791	101.501466	0.37870681	0.4578534	0.80299738
80	9.68201044	21779.1188	26757.0627	11.5995039	4427.62833	141.672219	77.6267781	15.0115927	95.1267885	0.45134726	0.79895561	0.81134465
81	10.7107755	20983.4082	26122.3265	9.90097959	3942.5351	146.667918	63.2681796	11.9712653	94.4858776	0.3756898	0.27836735	0.69644898
82	8.76384285	19669.6005	32858.2502	9.3565137	2970.17273	239.816335	59.5075761	15.2642852	75.5696534	0.24738462	0.2044239	0.77661274
83	21.9055786	21684.0201	30204.5619	8.88457525	4000.21846	148.148388	68.4710528	15.3831171	101.173405	0.36780201	0.31464883	0.83410033
84	23.1032223	19174.446	27059.0211	8.60532971	4958.75364	125.439728	67.9566445	14.5735962	93.1979878	0.41703875	0.30591434	0.79794697
85	29.9761789	23995.6707	31991.748	8.65747967	4502.11829	137.209919	58.5394472	14.361626	108.004228	0.40668293	0.2	0.82857724
86	36.7706876	26864.1847	35025.4224	8.85555992	4421.69391	166.02609	56.8986405	17.1039686	108.09053	0.39467191	0.16738703	0.74039293
87	32.2695945	24082.8289	32245.183	10.0088625	4499.78675	140.74635	67.5003126	16.5893571	103.61638	0.44171711	0.22710188	0.7674118
88	30.1161973	23313.6949	31534.6749	9.55664162	3967.80568	141.262228	51.4369317	16.0455799	100.473205	0.37338386	0.14740281	0.71517805
89	36.7892417	29617.5329	37856.2993	8.97771486	4094.32194	235.444449	53.470997	20.6793124	109.561335	0.27762993	0.09868554	0.63267947
90	32.9302345	29899.8369	37292.4363	8.82258919	4143.2053	263.134108	54.8040938	21.4187971	114.042977	0.24972069	0.11498471	0.58455997
91	38.3810697	33712.6676	42491.415	9.74843602	4504.75735	330.156967	54.1937874	23.5326743	131.086148	0.24391605	0.211239	0.58184157
92	27.9735941	26496.0283	35482.0094	10.4938908	3766.36993	184.384248	63.4418233	18.4206069	104.419582	0.40314498	0.2063385	0.63262306
93	38.4021507	30838.1082	31973.3289	9.14333886	4088.36814	167.329466	65.8773475	21.3194557	107.092094	0.44624228	0.18001991	0.73427149
94	50.8862286	32605.5256	39098.4363	9.12118265	4139.76781	272.85272	59.7662444	26.8213929	124.766255	0.29741393	0.21366623	0.67134034
95	45.5917019	35274.6626	39613.1722	9.76330312	4588.60463	262.290594	67.1126042	29.2163545	126.521813	0.37882779	0.29325277	0.70774085
96	43.0536242	32467.3461	36332.0221	9.54115272	4129.16092	203.166291	66.1961732	26.6217909	116.323178	0.4214028	0.2852491	0.71076522
97	41.465901	32312.6139	34130.5743	10.2167921	4167.60832	202.509465	70.3394218	28.6453861	117.897188	0.38037228	0.30732673	0.69820462
98	44.9810872	34211.0154	40549.6205	9.63995897	4465.72759	261.307241	64.6592985	30.3300923	125.985805	0.29474462	0.20266667	0.68908034
99	42.0853368	30802.2412	32509.9047	9.89710154	3933.70135	187.447808	67.0418824	27.8131844	111.083957	0.37086034	0.23581991	0.6989024

100	37.513865	30883.1697	31934.4376	10.0030266	4114.19673	163.818569	65.3607526	26.1470757	112.347812	0.40181595	0.2208589	0.69187457
101	41.7382919	32097.922	33611.1769	10.3365434	4480.91903	189.779314	67.2254364	28.9426765	114.952414	0.38107868	0.19287155	0.74524546
102	42.5596063	33365.8858	35188.8583	10.4162992	4640.63425	200.604882	68.191748	36.2714961	121.295433	0.41040945	0.24015748	0.74526247
103	46.5271438	31126.4675	32564.5568	8.68971766	3858.91438	170.480525	76.5096678	51.9748917	108.84717	0.51074458	0.37032173	0.72999343
104	45.9474029	29198.0982	31689.0389	8.19525562	3535.05562	162.100777	67.8965399	30.5642536	106.376442	0.40835992	0.24458078	0.7191411
105	41.911498	29704.1903	33028.2186	8.97060729	3742.19069	158.678704	76.5210688	29.8500405	109.267368	0.44876113	0.25425101	0.78500675
106	42.9203891	30098.363	33000.8856	8.95165381	3786.0628	161.396739	72.9447997	30.1628715	113.716364	0.479211	0.30513251	0.79045958
107	39.7645624	27574.9656	31103.1268	8.74627335	3452.19705	132.20704	77.0135851	27.1896165	108.275477	0.48630875	0.40511308	0.83577843
108	42.4560704	29047.6442	31382.0919	9.01560117	3715.82053	142.067019	75.4670733	30.1582014	111.315894	0.50222483	0.49501466	0.78890844
109	50.9606013	27931.4042	31412.2446	8.16565767	3368.04004	160.602556	73.5525958	35.8850427	110.566614	0.28880355	0.45097369	0.73042706
110	41.8025859	29474.4848	32654.4242	8.74238384	3848.5701	163.368242	71.9220364	33.0220606	112.440566	0.34361212	0.39191919	0.72550842
111	40.6024658	31275.7388	33523.4631	8.57122293	3808.43284	200.120813	65.8992336	31.4839054	117.066258	0.34300566	0.35748084	0.68575808
112	41.7818539	31835.7327	34799.8404	8.92834589	3980.18571	203.9445	66.3490337	34.0134949	119.631785	0.37882738	0.50782837	0.68482149
113	41.1148184	32696.9225	35853.4226	9.46622179	4012.66175	206.26842	68.8529931	33.6549558	121.751992	0.36812561	0.29754661	0.72684331
114	37.9129242	35113.6414	40272.8532	9.08133013	4191.26053	271.951512	58.4174152	31.3209462	137.468577	0.27225231	0.21062736	0.57084676
115	39.6247047	34195.9136	38408.3405	8.89174485	4160.2116	264.975552	60.5074587	36.5046237	135.010408	0.26964563	0.26486669	0.6321836
116	39.2799734	34097.1411	38601.1002	9.54707406	4221.42377	250.150302	63.7673863	33.2126204	129.908947	0.25498505	0.25426769	0.6720558
117	36.2983871	34643.3105	38788.9492	9.1916129	4104.94185	267.043871	61.6947581	37.7967742	130.469032	0.24185484	0.31693548	0.65119624
118	33.9120158	32681.0545	36227.1546	7.87729481	3635.55711	263.034327	54.5251477	37.1645437	118.961208	0.2158109	0.25922521	0.56978332
119	35.976016	34655.0606	38932.6825	9.12	3971.05495	272.725703	59.2417055	36.8298468	128.93932	0.22776815	0.27661559	0.62876749
120	40.7721692	31962.6508	36252.3577	9.66515689	3876.77591	214.489277	70.7242838	37.0542974	121.785757	0.32324693	0.36507503	0.74200546
121	28.8854552	30495.9664	36631.4789	9.48681223	3569.87133	212.53697	75.1372523	35.9298623	118.413114	0.35544508	0.5393349	0.71278468
122	31.0094213	31508.2409	37880.186	9.53507402	3768.07098	221.373674	73.2448183	37.5246299	125.880162	0.33746972	0.39165545	0.74036339
123	28.2514735	32721.1827	38867.031	9.52267191	3942.73312	242.306012	68.5277014	34.0023576	132.009116	0.2859725	0.30176817	0.69717092
124	28.5328836	35160.3683	41579.7345	9.69519056	4118.55209	284.304405	62.6521417	35.8324452	143.256607	0.23789545	0.18698145	0.70406745
125	30.0695134	31751.9007	36773.225	8.19670308	3513.11055	255.995551	52.354717	34.0560079	121.057875	0.22315789	0.15491559	0.55860973

126	28.2536585	34331.8673	39600.622	8.79422439	4002.44129	284.202459	54.4792195	35.2530732	137.975883	0.22314146	0.11004878	0.59042602
127	26.1021898	29508.4579	33625.7176	7.33266092	3251.32945	235.886715	49.2911745	31.2684804	119.507578	0.22049104	0.14731254	0.53124088
128	27.4387118	34385.3079	39409.7643	8.95768649	4139.96285	280.250595	65.3840289	39.6461387	139.742307	0.3122445	0.20742688	0.63449228
129	22.6007501	25397.372	32304.0957	8.51627685	3202.01397	181.439673	66.1178316	26.1586089	110.53387	0.34768496	0.25202864	0.59609956
130	24.3092574	27408.1017	34537.7799	8.80374364	3378.334	197.789949	66.4915565	29.5975585	120.676785	0.35068159	0.25066124	0.7119566
131	24.0490296	28917.43	34825.9832	8.98680286	3533.50594	207.913708	60.3076609	28.2475996	120.27097	0.3357712	0.21001021	0.69280218
132	24.0324215	28520.9362	34527.495	8.85722391	3464.33872	208.822209	62.9799392	31.5039514	121.079311	0.34601824	0.27558257	0.72231003
133	19.8351759	23933.8332	30993.6056	8.08651256	3047.33902	172.248764	57.4886432	24.7380905	107.482693	0.3199196	0.26130653	0.76983585
134	21.0470157	26711.0677	33193.7022	8.50491497	3322.80992	191.291284	62.1019006	28.703968	112.182674	0.35363788	0.37532511	0.84946982
135	26.0612043	20507.5656	28334.2918	7.05911155	2395.36261	152.761619	67.2075025	29.1158934	93.8058045	0.37425469	0.36959526	0.85408358
136	20.9869084	21258.9768	29219.1718	7.15053374	2611.18058	164.619859	64.1301108	28.7355488	96.5813494	0.34876133	0.32467271	0.83368916
137	23.137577	21566.9035	28064.3097	7.11425051	2704.00649	166.188419	68.1737166	27.7355236	94.9335524	0.36213552	0.31211499	0.8773306
138	23.4625042	23232.6067	28567.327	7.59058025	2895.25177	179.519023	63.8492026	27.5816763	100.317557	0.31834408	0.32494062	0.8237394
139	23.6233723	25480.6317	31258.7355	8.45216694	3072.42303	204.688668	67.0729883	29.7840401	106.00195	0.3364808	0.30050083	0.82923539
140	23.8358974	25581.7067	32179.1155	8.40008205	3123.79725	208.602585	71.9602051	33.2045128	105.256697	0.3552	0.3585641	0.93113162

Taf-02 Stable Pb isotopes

Depth (cm)	206Pb/207Pb	Expanded Uncertainty	REU %	208Pb/206Pb	Expanded Uncertainty	REU %	208Pb/207Pb	Expanded Uncertainty	REU %
0.5	1.158269987	0.000304481	0.02628758	2.105960555	0.001103037	0.05237692	2.439404181	0.00062932	0.02579811
1	1.162770458	0.000288182	0.02478404	2.101310872	0.000969457	0.0461358	2.443239201	0.000569847	0.0233234
1.5	1.16146391	0.000291893	0.02513147	2.10257822	0.001062229	0.05052031	2.442114547	0.00063691	0.02608028
2	1.161038949	0.000308361	0.02655903	2.102842626	0.001123189	0.05341287	2.44141125	0.000645435	0.02643697
2.5	1.160392204	0.00032391	0.02791383	2.104030118	0.001120288	0.05324486	2.44153648	0.000647478	0.0265193
3	1.159134915	0.000329357	0.02841404	2.104480159	0.001172232	0.05570174	2.439376434	0.000685591	0.02810516
3.5	1.156093599	0.000346267	0.0299515	2.108441251	0.000990342	0.04697034	2.437561401	0.000630368	0.0258606
4	1.158429948	0.000281849	0.02433026	2.105270625	0.00095602	0.04541077	2.438808639	0.00056082	0.02299566
4.5	1.157757897	0.000298576	0.02578918	2.10569641	0.001054689	0.05008649	2.437905305	0.000614337	0.02519937
5	1.156747105	0.000373042	0.03224926	2.106249143	0.001318528	0.06260076	2.436397292	0.000745599	0.03060252
5.5	1.156837747	0.000279454	0.02415673	2.106715935	0.000967778	0.04593776	2.43696631	0.000564717	0.02317295
6	1.155299359	0.000288894	0.02500596	2.108770606	0.000972617	0.04612244	2.436181751	0.000583015	0.0239315
6.5	1.154505023	0.000425935	0.03689334	2.108822298	0.001584086	0.0751171	2.434645353	0.000952297	0.0391144
7	1.153713125	0.000456418	0.0395608	2.109038937	0.001668262	0.07910056	2.433225116	0.000968002	0.03978267
7.5	1.15264861	0.000260188	0.02257303	2.110088815	0.000947338	0.04489564	2.432191079	0.000546156	0.02245529
8	1.15025812	0.000251939	0.02190284	2.112447074	0.001039633	0.04921464	2.429839931	0.000629285	0.02589819
8.5	1.144751732	0.000271478	0.02371505	2.117665943	0.000990073	0.04675301	2.424272322	0.000567452	0.02340711
9	1.141682622	0.000305613	0.02676867	2.120453218	0.001079337	0.05090124	2.420903502	0.000589473	0.0243493
9.5	1.138813725	0.000364458	0.03200329	2.122768111	0.001135905	0.05351057	2.417437891	0.000675744	0.02795288
10	1.139725759	0.000260244	0.02283388	2.122480193	0.001007345	0.04746074	2.419078074	0.00054945	0.0227132
10.5	1.142348947	0.000258808	0.0226558	2.119889828	0.000941805	0.04442706	2.421683132	0.000535509	0.02211307
11	1.142016005	0.000284363	0.02490009	2.119517053	0.001053198	0.04969048	2.421545632	0.000585923	0.02419622
11.5	1.145826916	0.000312324	0.0272575	2.120451705	0.001034552	0.04878922	2.425364757	0.000645235	0.02660362
12	1.150469351	0.000256223	0.02227118	2.116693961	0.001127011	0.05324391	2.430655307	0.000539511	0.02219613
12.5	1.152169685	0.000370888	0.03219043	2.112661828	0.000923377	0.04370679	2.433099038	0.000794545	0.03265566
13	1.152168474	0.000268064	0.02326607	2.111754113	0.001321465	0.06257665	2.43292472	0.000579358	0.02381323
13.5	1.154464168	0.000262081	0.02270152	2.111604918	0.000985224	0.04665761	2.436433042	0.000542004	0.02224578
14	1.154943876	0.000291605	0.02524839	2.11032529	0.000918369	0.04351787	2.436694514	0.000591648	0.02428076
14.5	1.157407131	0.000293501	0.02535848	2.109915228	0.000960269	0.04551223	2.43851057	0.000588597	0.02413755
15	1.159729533	0.000264603	0.02281596	2.106828087	0.001036643	0.04920398	2.440773069	0.000581195	0.02381194

16	1.161155692	0.000304154	0.02619407	2.104597761	0.000982648	0.04669053	2.442501396	0.000634829	0.02599093
17	1.162546296	0.000312207	0.02685546	2.103508376	0.001092438	0.05193409	2.444199932	0.000635295	0.02599194
18	1.166800429	0.000283041	0.02425784	2.102484257	0.001095566	0.05210815	2.4485056	0.000572799	0.0233938
19	1.168795084	0.000291946	0.02497841	2.098582152	0.0009914	0.04724144	2.451281659	0.000582475	0.02376205
20	1.169297418	0.000298425	0.02552178	2.0972582	0.000970204	0.0462606	2.45164641	0.000620839	0.02532336
21	1.169273473	0.000392869	0.03359941	2.0965982	0.001046677	0.04992261	2.450667093	0.000879678	0.03589544
22	1.170774172	0.000457012	0.03903499	2.095924449	0.001224971	0.0584454	2.453159397	0.000605084	0.0246655
23	1.170483974	0.000261502	0.02234132	2.095330904	0.001151995	0.05497916	2.452560776	0.000531744	0.02168116
24	1.170393533	0.000326867	0.02792795	2.09524773	0.000905204	0.0432027	2.45226722	0.000686746	0.02800452
25	1.170577512	0.000271065	0.02315655	2.095200753	0.001052439	0.05023093	2.452926348	0.000571974	0.02331801
26	1.171235454	0.000284861	0.02432144	2.095561513	0.0009761	0.04657942	2.454059181	0.000617439	0.02515992
27	1.172113088	0.000377322	0.03219163	2.095175752	0.001027942	0.04906232	2.454279876	0.000808442	0.0329401
28	1.171757837	0.000337251	0.02878167	2.093893767	0.001343244	0.06415055	2.452854935	0.000612669	0.02497777
29	1.170740901	0.000352622	0.03011956	2.093318677	0.000995177	0.04754064	2.452584191	0.000711149	0.02899591
30	1.170850682	0.000288347	0.02462714	2.094899504	0.001223518	0.0584046	2.453271512	0.000608237	0.02479289
31	1.172909854	0.000305216	0.02602211	2.095245229	0.001029525	0.04913623	2.454901692	0.000631928	0.0257415
32	1.177242495	0.00033193	0.02819558	2.093001229	0.001070411	0.05114238	2.459613846	0.000669355	0.02721381
33	1.181507663	0.000321888	0.02724384	2.089301136	0.001132183	0.05418954	2.46384885	0.000673171	0.02732194
34	1.184249844	0.000877192	0.07407155	2.085279661	0.001101695	0.052832	2.465996886	0.001783377	0.07231869
35	1.18415967	0.000352436	0.02976255	2.082128658	0.003006208	0.14438145	2.465803217	0.000713925	0.02895303
36	1.18428408	0.000331794	0.02801646	2.082429803	0.001057818	0.0507973	2.466942509	0.000626611	0.02540032
37	1.184077164	0.000946424	0.07992925	2.083117669	0.00110573	0.05308055	2.466891262	0.001979641	0.08024843
38	1.184981312	0.000351531	0.02966555	2.08339038	0.003331154	0.159891	2.468639385	0.000704284	0.02852925
39	1.184919216	0.00028017	0.02364466	2.083356195	0.001197365	0.05747289	2.469852651	0.000595736	0.02412033
40	1.185718632	0.000341827	0.02882872	2.084307601	0.000956089	0.04587082	2.470846152	0.000666572	0.02697748
42	1.185345237	0.000331347	0.02795363	2.083928216	0.001114369	0.05347444	2.470601051	0.000758285	0.03069234
44	1.185535396	0.000327962	0.02766363	2.084288289	0.001066997	0.05119241	2.470068377	0.000695096	0.02814076
46	1.185755842	0.000276849	0.02334788	2.083434943	0.001150287	0.05521106	2.469539333	0.000604958	0.02449679
48	1.184827462	0.00039019	0.03293221	2.082772833	0.000951616	0.04568986	2.46876735	0.000781921	0.03167254
50	1.185877786	0.000391675	0.03302828	2.08365174	0.001327051	0.06368871	2.469975781	0.000728835	0.02950778
52	1.186666051	0.000324911	0.02738013	2.082825093	0.001269739	0.06096235	2.470900471	0.000755884	0.03059143
54	1.187515581	0.000277917	0.02340322	2.082164013	0.001190499	0.05717605	2.471195389	0.000599004	0.02423946
56	1.188427276	0.000287916	0.02422662	2.080989173	0.000929748	0.04467817	2.471349752	0.000597624	0.02418208
58	1.188777292	0.000280755	0.02361709	2.079512814	0.000982273	0.04723571	2.471962568	0.000576436	0.02327849
60	1.188670325	0.000307616	0.02587899	2.079519576	0.000922268	0.04435004	2.472923073	0.000719606	0.02909942

62	1.189890994	0.000298581	0.02509312	2.080330501	0.001016995	0.04888624	2.473913383	0.000608245	0.02458636
64	1.191261523	0.000409228	0.03435251	2.07894348	0.001020156	0.04907089	2.477379007	0.000772476	0.0311812
66	1.190099976	0.000402578	0.03382721	2.0797057	0.001323367	0.06363241	2.475363075	0.000814798	0.0329163
68	1.189887319	0.000383044	0.03219163	2.080051055	0.001383486	0.06651214	2.476760684	0.000813061	0.03282758
70	1.188577651	0.000371829	0.03128354	2.081608448	0.001322372	0.06352647	2.472705707	0.000781517	0.03160573
72	1.188140801	0.00035943	0.03025145	2.080390901	0.001290148	0.0620147	2.473148019	0.000686493	0.02775785
74	1.188991308	0.00032335	0.02719533	2.081514763	0.001001143	0.04809685	2.473996029	0.000622404	0.02515786
76	1.189510136	0.000299697	0.02519496	2.080518619	0.000990497	0.04760816	2.474928438	0.000577104	0.02331801
78	1.189308928	0.000279693	0.02351726	2.08066624	0.000970368	0.04663735	2.47346814	0.00058629	0.02370317
80	1.188349492	0.000353793	0.0297718	2.07984607	0.000935611	0.04498465	2.471042163	0.000717755	0.02904663
82	1.189970464	0.000400443	0.03365152	2.079353828	0.001196605	0.05754696	2.475302149	0.000827058	0.03341241
84	1.188596474	0.000324894	0.02733424	2.080224372	0.001360894	0.06542053	2.473777047	0.000625311	0.0252776
86	1.189001636	0.000279473	0.02350484	2.080906561	0.000972192	0.04671964	2.475535817	0.00056727	0.02291505
88	1.188241742	0.000315939	0.02658875	2.082127309	0.000935885	0.04494852	2.472975108	0.00057168	0.0231171
90	1.187249523	0.000384565	0.03239122	2.080642796	0.000967128	0.04647771	2.472031804	0.000895584	0.03622866
92	1.18652635	0.000408083	0.03439307	2.082136999	0.001127915	0.05417103	2.471986051	0.000696668	0.02818253
94	1.187015684	0.000282113	0.02376655	2.083461106	0.001109567	0.05325596	2.472391389	0.000601631	0.02433395
96	1.189770071	0.000307167	0.02581733	2.082858962	0.000969063	0.04652556	2.480846887	0.000661945	0.02668222
98	1.188889673	0.000306899	0.02581392	2.085099117	0.001054103	0.05055408	2.475056372	0.000618987	0.02500899

Appendix 2.4. The Pb stable isotope data

Arne-03 Stable Pb isotopes

Depth (cm)	206Pb/207Pb	Expanded Uncertainty	REU %	208Pb/206Pb	Expanded Uncertainty	REU %	208Pb/207Pb	Expanded Uncertainty	REU %
1	1.145014972	0.00028448	0.0248451	2.117995007	0.00094677	0.04470123	2.425271202	0.000565817	0.02333007
2	1.14586518	0.000285346	0.02490219	2.116581037	0.000931383	0.04400415	2.425266589	0.000578717	0.02386199
3	1.139197224	0.000346904	0.03045164	2.123850239	0.001086643	0.0511638	2.419810653	0.000670263	0.02769898
4	1.139598933	0.000279856	0.02455737	2.121163682	0.00104242	0.04914379	2.417275735	0.000603782	0.02497777
5	1.139074292	0.000287992	0.02528301	2.123212046	0.000972157	0.0457871	2.418472832	0.000558322	0.02308574
6	1.139249205	0.000261156	0.02292349	2.122706263	0.000934532	0.04402549	2.418202914	0.000548472	0.02268098
7	1.138299201	0.00026134	0.0229588	2.124261673	0.000941576	0.04432488	2.418164347	0.000555248	0.02296157
8	1.137834971	0.000281107	0.02470544	2.123639712	0.000940033	0.04426517	2.416442574	0.000576611	0.02386199
9	1.136433733	0.000303546	0.02671038	2.124553991	0.001070308	0.05037801	2.414134741	0.000656285	0.0271851
10	1.132833474	0.000270056	0.023839	2.128164722	0.000961752	0.04519159	2.410809748	0.000575228	0.02386036
11	1.131975226	0.000351365	0.03104	2.129077693	0.001287962	0.06049389	2.410184649	0.000712017	0.02954201
12	1.132795251	0.000261206	0.0230585	2.127856139	0.000924761	0.04345975	2.410422081	0.000543469	0.02254665
13	1.132876519	0.000275318	0.0243026	2.128224451	0.000936783	0.04401711	2.411014307	0.000565314	0.02344714
14	1.133769501	0.000268684	0.02369829	2.128252779	0.000978587	0.04598078	2.412922059	0.00056583	0.02344997
15	1.132888379	0.000257952	0.02276945	2.128400963	0.000961238	0.04516244	2.411319377	0.000545091	0.02260549
16	1.13413605	0.000260744	0.02299057	2.127410506	0.000936603	0.04402549	2.412637184	0.000535011	0.02217537
17	1.130515345	0.000262595	0.02322793	2.134443715	0.000943247	0.0441917	2.413853314	0.000549261	0.02275452
18	1.133086405	0.000262396	0.02315766	2.128715255	0.000951012	0.04467538	2.412018242	0.000569716	0.0236199
19	1.133086318	0.000261635	0.02309051	2.127961332	0.000934985	0.04393806	2.411156562	0.00054322	0.02252946
20	1.133086677	0.00029719	0.0262284	2.128630164	0.001051883	0.04941598	2.412089254	0.000639335	0.02650546
21	1.13328105	0.00026009	0.02295017	2.128757456	0.000943243	0.04430958	2.412536976	0.0005509	0.02283487
22	1.133985184	0.00066555	0.05869126	2.127933573	0.001760071	0.0827127	2.413044396	0.000993334	0.04116517
23	1.134806476	0.000263031	0.02317853	2.126938608	0.000942197	0.04429825	2.413621515	0.000572479	0.02371868
24	1.134949077	0.000253746	0.02235744	2.127144937	0.000936875	0.04404377	2.414220181	0.000536958	0.02224147
25	1.136080868	0.000258664	0.02276852	2.125929721	0.000932206	0.04384933	2.415245098	0.00053941	0.02233356
26	1.135497816	0.000254177	0.02238459	2.126329718	0.000922346	0.04337738	2.41443158	0.000525881	0.02178072
27	1.13563596	0.000268397	0.02363409	2.126757989	0.000936354	0.04402728	2.415020742	0.000551409	0.02283249
28	1.136672824	0.000274377	0.02413859	2.125304338	0.000920941	0.04333218	2.415996055	0.000556497	0.02303386
29	1.136746702	0.000277567	0.02441769	2.124974548	0.001036681	0.04878559	2.41545456	0.000595502	0.02465383
30	1.139093745	0.000285147	0.02503279	2.122401863	0.001010345	0.04760383	2.417614679	0.000568729	0.02352439

31	1.151247483	0.000258567	0.02245972	2.111352491	0.000918572	0.04350632	2.43077882	0.000535021	0.02201027
32	1.156737134	0.000268202	0.02318605	2.106702192	0.000926826	0.04399415	2.436964873	0.00054789	0.02248246
33	1.160565984	0.000276353	0.02381188	2.104037749	0.000932223	0.0443067	2.441827811	0.000567528	0.02324194
34	1.162465429	0.000261773	0.02251875	2.10150652	0.000934473	0.04446682	2.443024602	0.000563141	0.02305096
35	1.163084166	0.000259973	0.02235203	2.101123533	0.000909982	0.04330931	2.443795752	0.000537161	0.02198058
36	1.167250993	0.000261284	0.02238459	2.097419078	0.000911516	0.04345891	2.448288033	0.000555454	0.02268744
37	1.174344234	0.000268998	0.02290622	2.090106335	0.000904143	0.04325821	2.454598832	0.000546992	0.02228436
38	1.175668173	0.00026886	0.02286868	2.089020964	0.00092642	0.04434711	2.456009493	0.000573996	0.0233711
39	1.175918595	0.000282367	0.02401248	2.089762015	0.000919875	0.04401817	2.457425264	0.000587449	0.02390508
40	1.175287682	0.000280212	0.02384196	2.090313257	0.00091931	0.04397954	2.45664117	0.000564115	0.02296284
41	1.176522273	0.00028847	0.02451885	2.089760336	0.000945352	0.04523736	2.458872971	0.000577446	0.02348418
42	1.177681138	0.000288222	0.02447368	2.087758675	0.000978534	0.04687006	2.458845619	0.000582593	0.02369378
43	1.179865642	0.000305593	0.02590069	2.086494928	0.000952759	0.04566315	2.461860424	0.000572184	0.02324194
44	1.181434347	0.000286127	0.02421862	2.084838373	0.000953986	0.04575826	2.463256021	0.000604698	0.02454873
45	1.182807401	0.000273746	0.02314371	2.083605983	0.000906902	0.0435256	2.464607964	0.00057338	0.02326453
46	1.182809522	0.000284878	0.02408488	2.083671488	0.000952577	0.04571628	2.464617233	0.00058142	0.02359068
47	1.182846678	0.000266598	0.0225387	2.084171817	0.000905933	0.04346729	2.465357775	0.000562005	0.02279608
48	1.182771785	0.000292633	0.02474126	2.084418227	0.000933112	0.04476608	2.465457015	0.000572688	0.02322849
49	1.184132385	0.000270266	0.02282568	2.084285211	0.000925243	0.04439136	2.467981879	0.000584061	0.02366551
50	1.183299199	0.000268641	0.02270268	2.083656701	0.000910659	0.04370484	2.465414006	0.00058316	0.02284243
51	1.182685431	0.000281749	0.02382281	2.084501383	0.000918071	0.04404271	2.465312338	0.000586027	0.02295965
52	1.183242587	0.000290379	0.02454092	2.083230104	0.000927687	0.04453116	2.464792507	0.000580911	0.02356835
53	1.183186016	0.000278648	0.02355069	2.083549919	0.000897582	0.04307947	2.46514629	0.000551111	0.02235612
54	1.183720435	0.000314596	0.0265769	2.083393767	0.000935301	0.04489313	2.466342665	0.000566731	0.02297861
55	1.18388462	0.000297402	0.02512084	2.082760004	0.000942546	0.04525466	2.465807434	0.000566571	0.0229771
56	1.190712418	0.00042375	0.03558794	2.079579692	0.001070242	0.05146434	2.465901487	0.000636817	0.02581679
57	1.184190642	0.000308202	0.02602641	2.082328291	0.000933408	0.0448252	2.475822652	0.000898898	0.03630703
58	1.196413009	0.000332411	0.02778397	2.085994623	0.000941396	0.04512935	2.47308622	0.00065504	0.02648673
59	1.185614756	0.000362281	0.03055641	2.092812462	0.000965369	0.04612783	2.504060278	0.000668687	0.02670413
60	1.199892444	0.000370519	0.03087936	2.084221763	0.00096634	0.04636457	2.50097202	0.000630321	0.02520303
61	1.202798458	0.000334422	0.02780365	2.087021213	0.00093617	0.04485675	-2.510238197	0.000606435	0.02415848
62	1.20041611	0.000388886	0.03239597	2.078541655	0.000971368	0.04673307	2.49451158	0.000769508	0.03084805
63	1.197693888	0.000274877	0.02295051	2.07144358	0.000902606	0.04357377	2.480832034	0.000558403	0.0225087
64	1.202889818	0.000327144	0.02719651	2.077775028	0.001133145	0.05453647	2.49934006	0.000690295	0.02761907
65	1.202909	0.000272229	0.02263089	2.07418379	0.000921622	0.04443298	2.495059627	0.00055894	0.02232173

Appendix 2.4. The Pb stable isotope data

66	1.200642996	0.000271621	0.02262297	2.076440894	0.00093029	0.04480213	2.49301891	0.00056104	0.02250444
67	1.197312198	0.000288328	0.02408127	2.070639639	0.000968227	0.04675979	2.479131135	0.0005789	0.02335092
68	1.19692259	0.000272474	0.02276454	2.068044578	0.000921764	0.04457177	2.475321439	0.000553327	0.02235376
69	1.197963961	0.0002767	0.02309749	2.068760712	0.000926338	0.04477743	2.47823518	0.000555184	0.02240239
70	1.197539667	0.000267951	0.02237512	2.068140075	0.000916566	0.04431839	2.476679921	0.000556424	0.02246654
71	1.19811299	0.000303858	0.02536141	2.072902635	0.001015127	0.04897129	2.483536635	0.000621178	0.02501185
72	1.197806833	0.000307685	0.02568737	2.068590288	0.001037283	0.05014446	2.477771475	0.00061608	0.02486428
73	1.197201896	0.000267457	0.02234018	2.067283422	0.000899813	0.04352637	2.474892907	0.00054177	0.02189064
74	1.199935317	0.000272493	0.02270901	2.075811932	0.000902198	0.0434624	2.490769601	0.000550185	0.02208896
75	1.199144391	0.000298287	0.02487496	2.076181023	0.000928381	0.04471582	2.489635201	0.000574238	0.02306513
76	1.199604916	0.000280325	0.02336814	2.074059892	0.00090525	0.04364627	2.488047999	0.000562871	0.02262299
77	1.200012995	0.000274727	0.02289365	2.077678094	0.000910242	0.04381056	2.493199002	0.000571391	0.022918
78	1.198721017	0.000280119	0.02336814	2.078877185	0.00091032	0.04378901	2.49203045	0.000581557	0.02333666
79	1.200784288	0.000312254	0.0260042	2.077831746	0.00106433	0.05122311	2.495051391	0.000711718	0.02852519
80	1.200306235	0.000306339	0.02552178	2.078616268	0.001033218	0.04970701	2.494900681	0.000633819	0.02540458
81	1.212833703	0.000292111	0.02408498	2.078420987	0.000909666	0.04376715	2.520605585	0.000591643	0.02347226
82	1.216218015	0.00029419	0.02418893	2.088286028	0.000940119	0.04501869	2.539817988	0.000596144	0.02347191
83	1.229953481	0.000338834	0.02754852	2.104281377	0.000986278	0.04687006	2.588108623	0.000608153	0.02349798
84	1.198570848	0.000270327	0.02255407	2.071441468	0.000901057	0.04349901	2.482747251	0.000543141	0.02187663
85	1.197183796	0.000276212	0.02307184	2.069136361	0.000899824	0.0434879	2.477123495	0.000554411	0.02238124
86	1.198892186	0.000292959	0.02443584	2.069794746	0.000929229	0.04489475	2.586984164	0.000595541	0.02302067
87	1.200209342	0.00027528	0.02293604	2.06989389	0.000935028	0.04517277	2.484213176	0.000569855	0.02293905
88	1.200413222	0.000283834	0.02364466	2.070497777	0.000954078	0.04607963	2.485417682	0.000572505	0.02303454
89	1.198833243	0.000266474	0.02222775	2.071638398	0.00090823	0.04384114	2.483675389	0.00056957	0.02293254
90	1.201333733	0.000280145	0.0233195	2.070473541	0.000910256	0.04396368	2.487403488	0.000568346	0.02284895
91	1.197976898	0.000283363	0.02365345	2.073014579	0.000919298	0.04434595	2.483327812	0.000562564	0.02265365
92	1.197643148	0.000285663	0.02385208	2.071126968	0.000951398	0.04593624	2.480471062	0.000607184	0.02447857
93	1.197344508	0.00027126	0.02265517	2.069243115	0.000905512	0.04376053	2.477672474	0.000545508	0.02201697
94	1.198011377	0.00029147	0.02432947	2.072029789	0.000997108	0.04812228	2.482375439	0.000616604	0.02483928
95	1.197725216	0.000287696	0.02402019	2.072160939	0.000977597	0.04717767	2.481720601	0.000588379	0.0237085
96	1.195058807	0.00030518	0.02553681	2.071194425	0.001015736	0.04904108	2.475244391	0.000590771	0.02386717
97	1.196872051	0.000271914	0.02271875	2.070189567	0.000920557	0.04446728	2.477668217	0.000563995	0.02276313
98	1.194763097	0.00027257	0.0228137	2.070182332	0.00090028	0.04348796	2.473551592	0.000549901	0.02223123

Viðarhólmi 03 Stable Pb isotopes

Depth (cm)	206Pb/207Pb	Expanded Uncertainty	RSU %	208Pb/206Pb	Expanded Uncertainty	REU %	208Pb/207Pb	Expanded Uncertainty	RSU %
1	1.180957019	0.007696913	0.6517522	2.119042607	0.009760025	0.46058653	2.503486315	0.012528791	0.50045373
2	1.269031147	0.021699917	1.70995939	1.973278677	0.015903569	0.8059464	2.45062079	0.00062413	0.02546826
3	1.180265422	0.000380493	0.03223791	2.076285918	0.000976466	0.04702944	2.511418815	0.02874157	1.14443555
4	1.198087678	0.000789867	0.06592731	2.066390303	0.001214138	0.05875646	2.261242187	0.025986421	1.14920997
5	1.184542002	0.014015513	1.18320105	2.102083827	0.029586614	1.40748974	2.476228929	0.001135961	0.04587464
6	1.079819298	0.023481367	2.17271229	2.148919567	0.019431544	0.90424714	2.561603907	0.02009066	0.78430001
7	1.191921927	0.001123665	0.09427341	2.06662627	0.001604805	0.07765338	2.463263472	0.001652433	0.06708307
8	1.168744522	0.002216375	0.18963725	2.079275171	0.002986479	0.14363079	2.430110426	0.004593579	0.18902758
9	1.170110962	0.00041298	0.03529407	2.085436692	0.001081487	0.05185902	2.439893543	0.000946967	0.03881184
10	1.170538355	0.000537624	0.04592966	2.083098102	0.00106146	0.05095583	2.438836516	0.001041902	0.04272126
11	1.167896806	0.000587232	0.05028114	2.088884217	0.001123906	0.05380414	2.438791428	0.001014156	0.04158439
12	1.165261751	0.000312917	0.02685379	2.091795882	0.000929793	0.04444952	2.437365475	0.000640849	0.02629269
13	1.168741456	0.000302286	0.02586421	2.089507409	0.000956202	0.0457621	2.439677359	0.000880975	0.03611032
14	1.175410615	0.000379417	0.03227955	2.08237565	0.001018921	0.04893069	2.447507139	0.000696613	0.02846213
15	1.178374783	0.000488014	0.04141419	2.0796966	0.001724455	0.08291861	2.450661532	0.00114255	0.04662209
16	1.178835832	0.000689659	0.05850336	2.078873181	0.00667079	0.32088491	2.450592702	0.001168332	0.04767549
17	1.185204237	0.000456021	0.03847612	2.076466596	0.001051339	0.05063115	2.460956036	0.000969822	0.03940833
18	1.18796042	0.000571127	0.04807623	2.070996559	0.001126237	0.05438139	2.460312251	0.001090386	0.04431902
19	1.193960981	0.000512333	0.04291033	2.063837926	0.000970273	0.04701302	2.464079977	0.001026214	0.04164693
20	1.188922665	0.001414602	0.11898187	2.079351994	0.001842633	0.08861573	2.47521189	0.002776561	0.11217466
21	1.18951717	0.000628417	0.0528296	2.070074313	0.001278502	0.06176118	2.391123285	0.000605888	0.02533904
22	1.183234605	0.000826081	0.06981547	2.080876584	0.001270033	0.06103354	2.463367746	0.001210872	0.04915513
23	1.187910311	0.000341525	0.02875007	2.073371641	0.001024012	0.04938873	2.463254196	0.000719037	0.02919055
24	1.189148468	0.000628925	0.05288872	2.070717883	0.001178656	0.05692017	2.463640541	0.001333312	0.05411957
25	1.193177407	0.000400615	0.03357546	2.067170335	0.001034072	0.05002357	2.466415331	0.000818671	0.03319275
26	1.193960579	0.000297968	0.02495629	2.066906965	0.000949578	0.04594199	2.467922339	0.000599339	0.02428515
27	1.199245046	0.000395301	0.0329625	2.061981998	0.001015057	0.04922723	2.472625008	0.000854865	0.03457319
28	1.199663309	0.000576671	0.04806944	2.059720282	0.001007723	0.04892523	2.471166565	0.001164493	0.04712323
29	1.208138829	0.002324456	0.19239978	2.040438317	0.002680413	0.13136456	2.464658255	0.002887568	0.11715895
30	1.202458792	0.000451656	0.037561	2.057290582	0.001173294	0.05703102	2.473802567	0.000867579	0.03507065

31	1.200701188	0.000345412	0.02876751	2.05871285	0.000973713	0.04729718	2.472218612	0.000564963	0.02285248
32	1.200306784	0.000435152	0.03625343	2.059745214	0.000981217	0.04763778	2.472324246	0.00052829	0.02136817
33	1.196651221	0.00033151	0.0277031	2.055336339	0.000575406	0.02799572	2.471789276	0.000864666	0.03498137
34	1.194741831	0.000468253	0.0391928	2.066474605	0.001152909	0.0557911	2.468919566	0.00082656	0.03347863
35	1.196690255	0.000666525	0.05569736	2.062847912	0.001117227	0.05415946	2.468792228	0.001003539	0.04064897
36	1.200450858	0.000890309	0.07416452	2.054922181	0.001299509	0.06323882	2.466840353	0.001781484	0.07221723
37	1.206975176	0.000923225	0.0764908	2.050343206	0.001146134	0.05589962	2.475131863	0.00103241	0.04171113
38	1.201794744	0.000733003	0.06099237	2.057416147	0.001141857	0.05549954	2.471765932	0.001086566	0.04395911
39	1.210432486	0.001652661	0.13653474	2.047794111	0.00192771	0.09413593	2.478230487	0.002680791	0.10817358
40	1.204047398	0.000619466	0.05144866	2.056442971	0.001774849	0.08630674	2.475753003	0.001138319	0.04597868
41	1.205084327	0.000504447	0.0418599	2.055490764	0.00101537	0.04939794	2.476761182	0.000823909	0.03326557
42	1.207670991	0.001000624	0.08285572	2.050107709	0.001333623	0.06505134	2.475474556	0.002093169	0.08475824
43	1.206994352	0.00064779	0.0536697	2.052317829	0.001058228	0.05156257	2.477302622	0.00115807	0.04674724
44	1.210776431	0.000420071	0.03469436	2.049869406	0.001128132	0.05503435	2.482049321	0.00094752	0.03817489
45	1.210196553	0.000674378	0.0557247	2.045545984	0.001183692	0.05786681	2.475757429	0.001189187	0.04803324
46	1.20166119	0.000709244	0.05902199	2.056053886	0.00103027	0.05010908	2.470628978	0.001167851	0.0472694
47	1.216518326	0.000679864	0.05588609	2.039791989	0.001258106	0.06167814	2.481173441	0.001000277	0.04031467
48	1.21428404	0.000400797	0.03300689	2.044093564	0.000936148	0.0457977	2.481551033	0.000722104	0.02909892
49	1.209839534	0.000479372	0.0396228	2.051783999	0.00097558	0.04754791	2.481671094	0.000802233	0.03232632
50	1.213231578	0.000949888	0.078294	2.046123374	0.00169605	0.08289091	2.480679995	0.00184689	0.07445095
51	1.205751259	0.000459909	0.03814291	2.052655034	0.001398988	0.06815505	2.475058283	0.000944607	0.03816504
52	1.206135547	0.000803591	0.06662525	2.047496329	0.001295595	0.06327705	2.471033528	0.001277732	0.05170841
53	1.214528085	0.00075864	0.06246377	2.045826701	0.001172713	0.05732219	2.48378215	0.001362424	0.0548528
54	1.205304578	0.00079816	0.0662206	2.05508641	0.001121872	0.05458027	2.477730788	0.001135993	0.0458481
55	1.209474129	0.000625294	0.0516997	2.049363893	0.001090481	0.05321071	2.47879223	0.001059742	0.04275233
56	1.205078598	0.000362831	0.03010852	2.054969661	0.001019843	0.04962815	2.476103594	0.000739932	0.02988294
57	1.205739134	0.00128977	0.10696923	2.052457843	0.002383997	0.1161533	2.474140733	0.002264255	0.09151682
58	1.206850016	0.000725942	0.06015178	2.05515753	0.001146273	0.05577543	2.478848422	0.001145578	0.04621411
59	1.209276694	0.000498856	0.04125247	2.049864401	0.000981017	0.04785764	2.478906102	0.000941854	0.03799476
60	1.215788613	0.00123616	0.10167561	2.042472524	0.001608613	0.07875812	2.482657484	0.002416933	0.09735267
61	1.198395028	0.002172363	0.18127271	2.060496185	0.002244835	0.10894631	2.470220989	0.001968905	0.07970561
62	1.203560754	0.000469564	0.03901456	2.05709841	0.001093585	0.05316153	2.476141945	0.001002054	0.04046837
63	1.204789583	0.000720341	0.05978974	2.057408218	0.001156493	0.05621118	2.476862418	0.001256164	0.05071593
64	1.19126533	0.000604866	0.0507751	2.067790115	0.001171088	0.05663478	2.463741295	0.001003366	0.04072531
65	1.206870608	0.002178186	0.18048217	2.053327748	0.00306122	0.1490858	2.481606276	0.004739813	0.19099776

Appendix 2.4. The Pb stable isotope data

66	1.201131059	0.001073483	0.08937271	2.057401525	0.00151827	0.07379551	2.472793946	0.00202286	0.08180465
67	1.197129828	0.000475026	0.03968042	2.061685299	0.001223786	0.05935853	2.468590772	0.000998878	0.04046347
68	1.199621259	0.001023977	0.08535832	2.057990159	0.001247585	0.06062151	2.469449753	0.001545259	0.06257501
69	1.211283917	0.000690657	0.05701862	2.047668189	0.001294426	0.06321462	2.480284048	0.001077435	0.04343998
70	1.20850878	0.000930584	0.07700266	2.050696444	0.001536631	0.07493214	2.478401349	0.001883881	0.07601193
71	1.211120564	0.000952744	0.07866633	2.045243891	0.001712609	0.08373617	2.477971416	0.001525592	0.06156615
72	1.210391409	0.000808716	0.0668144	2.048312953	0.001308124	0.06386348	2.479289257	0.001309102	0.05280152
73	1.209429826	0.000549364	0.04542337	2.04861908	0.001247703	0.06090458	2.476879627	0.001075956	0.04343998
74	1.214516845	0.001749568	0.14405463	2.04137267	0.00303907	0.14887386	2.478271066	0.002603554	0.10505526
75	1.212610193	0.000758807	0.06257633	2.0424326	0.001519876	0.07441498	2.477835339	0.001444913	0.05831352
76	1.192829058	0.002321732	0.19464079	2.062415428	0.002172218	0.10532398	2.460747546	0.002360234	0.09591531
77	1.21500493	0.000999009	0.08222263	2.039675097	0.001798861	0.08819353	2.477239814	0.002638022	0.10649038
78	1.214095906	0.000685347	0.05644919	2.039836737	0.001179258	0.0578114	2.476205111	0.001233538	0.04981565
79	1.217182432	0.000720843	0.05922226	2.040847177	0.001143867	0.05604861	2.484602664	0.001832475	0.07375323
80	1.215199603	0.001670841	0.13749517	2.046993539	0.001740629	0.08503345	2.487086202	0.003080595	0.1238636
81	1.213602834	0.000923394	0.07608703	2.045213899	0.001523926	0.07451179	2.482214043	0.001294788	0.05216262
82	1.222736174	0.002447992	0.20020608	2.038161932	0.002734006	0.13414075	2.492343318	0.005039046	0.20218107
83	1.215203481	0.001022986	0.08418227	2.044973053	0.001355432	0.06628117	2.485063955	0.001587268	0.06387232
84	1.219252963	0.00085079	0.06977962	2.037931546	0.001259595	0.0618075	2.483137878	0.001363588	0.05491392
85	1.217692541	0.000952567	0.0782272	2.040489554	0.001118328	0.05480684	2.486120583	0.001389097	0.05587407
86	1.213629175	0.000655959	0.05404936	2.045715717	0.001152575	0.0563409	2.482460696	0.000890074	0.03585451
87	1.214900949	0.00145228	0.11953893	2.043454773	0.001857331	0.09089169	2.483466068	0.001446474	0.05824418
88	1.21427029	0.001071696	0.08825842	2.042415512	0.00123741	0.06058562	2.47953677	0.001710785	0.06899616
89	1.211776433	0.002569042	0.21200623	2.038360691	0.003211952	0.15757527	2.46829992	0.003533926	0.14317247
90	1.191942396	0.002436578	0.20442076	2.065894602	0.002713852	0.1313645	2.462451848	0.002172728	0.08823435
91	1.215061863	0.001034978	0.08517902	2.043972585	0.001074749	0.05258139	2.48253739	0.001666363	0.06712338
92	1.202850538	0.00077764	0.06464979	2.058832103	0.001271425	0.06175468	2.476941117	0.001066039	0.04303854
93	1.214236759	0.000824343	0.06788985	2.043331676	0.001577256	0.0771904	2.483394125	0.001359476	0.05474266
94	1.214388577	0.000821269	0.06762818	2.043291032	0.001343081	0.06573128	2.480135361	0.001155265	0.04658071
95	1.217369116	0.000792612	0.06510861	2.044576237	0.001281366	0.06267147	2.489060555	0.001737531	0.06980671
96	1.212736871	0.003327514	0.27438053	2.050086282	0.001007646	0.04915137	2.485289616	0.005800693	0.23340108
97	1.208096717	0.001167357	0.09662775	2.045837737	0.001722018	0.08417178	2.4713044	0.002218955	0.08978882
98	1.21621318	0.000724533	0.05957289	2.042139958	0.001263397	0.06186632	2.484173976	0.001205145	0.0485129
99	1.221336422	0.000855621	0.0700561	2.035288761	0.00142848	0.07018564	2.486353731	0.000555489	0.0223415
100	1.209011972	0.000265571	0.02196593	2.043757537	0.003362807	0.16454039	2.469037258	0.003547277	0.14367046

Appendix 2.4. The Pb stable isotope data

101	1.219432927	0.001100778	0.09026963	2.038837546	0.001725185	0.08461609	2.484310435	0.001697471	0.06832765
102	1.217108745	0.000506501	0.04161508	2.042708405	0.001009675	0.04942823	2.485879933	0.000884467	0.03557965
103	1.221539894	0.000551764	0.04516958	2.033918061	0.001180289	0.05803031	2.485207218	0.000979524	0.03941418
104	1.221824221	0.001600663	0.13100597	2.037293862	0.001590466	0.07806756	2.488958205	0.001961451	0.07880609
105	1.20402912	0.00096505	0.0801517	2.053570664	0.001194682	0.05817585	2.472533874	0.001408952	0.05698413
106	1.212148502	0.001112163	0.09175136	2.047299989	0.001754281	0.08568756	2.483320855	0.002013151	0.08106688
107	1.215768494	0.000498691	0.04101861	2.042263465	0.001069046	0.05234616	2.482920932	0.001012674	0.0407856
108	1.213997799	0.001143112	0.094161	2.045813536	0.00181645	0.08878862	2.48264937	0.002812738	0.11329584
109	1.210911747	0.000961239	0.07938145	2.044016894	0.001286885	0.06295864	2.474474058	0.00122443	0.04948243
110	1.214596718	0.001039528	0.08558628	2.039174735	0.001517633	0.07442388	2.478020521	0.001692155	0.06828658
111	1.209959817	0.00053228	0.04399153	2.048945949	0.001167466	0.05697888	2.478240531	0.000845219	0.03410561
112	1.204863604	0.001037782	0.0861327	2.047524488	0.001441546	0.07040432	2.466065109	0.001947129	0.0789569
113	1.209305117	0.000441143	0.03647902	2.048917531	0.000958097	0.04676115	2.477664327	0.000843205	0.03403226
114	1.215993833	0.001337041	0.10995459	2.045145905	0.001555563	0.07606125	2.486518951	0.002141812	0.08613696
115	1.211050327	0.001026624	0.08477139	2.04703635	0.001363974	0.06663165	2.477985477	0.001690878	0.06823599
116	1.215771336	0.001098881	0.09038548	2.047976762	0.001800715	0.08792652	2.48917915	0.002113967	0.08492628
117	1.214763501	0.000809949	0.06667548	2.044355653	0.001777879	0.08696523	2.48295242	0.001935762	0.0779621
118	1.210603374	0.000751005	0.06203558	2.044688608	0.00121237	0.05929365	2.474881771	0.00117937	0.0476536
119	1.214845208	0.00070589	0.05810538	2.04260155	0.00121049	0.05926219	2.481556524	0.000529438	0.02133492
120	1.215820785	0.000424243	0.03489356	2.042193335	0.001107502	0.05423103	2.482758022	0.00080168	0.03228989
121	1.216779851	0.000842246	0.0692193	2.037353425	0.001404551	0.06893996	2.477923696	0.001513044	0.06106094
122	1.218928065	0.001203648	0.0987464	2.039209275	0.001551768	0.07609654	2.4855707	0.001756794	0.0706797
123	1.211987368	0.000966588	0.0797523	2.041690948	0.00141746	0.06942577	2.474507328	0.001241766	0.05018237
124	1.216858385	0.00073692	0.06055922	2.040612152	0.001183981	0.05802086	2.483735783	0.001122583	0.04519737
125	1.213638257	0.000506243	0.04171281	2.043120848	0.001217794	0.05960462	2.479796389	0.000941817	0.0379796

126	1.21176506	0.000788363	0.0650591	2.044652265	0.001518183	0.07425142	2.478287231	0.00179979	0.07262232
127	1.196683127	0.000833596	0.06965891	2.053233849	0.001254958	0.06112106	2.456969315	0.001766751	0.07190772
128	1.216947879	0.001076199	0.08843425	2.041072279	0.00134246	0.0657723	2.48431807	0.001277474	0.05142152
129	1.224484598	0.002548459	0.20812504	2.03259898	0.003659417	0.18003635	2.484703386	0.003789714	0.15252181
130	1.212459081	0.001455729	0.12006418	2.045363859	0.000923736	0.04516244	2.480773908	0.000579138	0.02334504
131	1.20885602	0.000807089	0.06676468	2.04060632	0.001219881	0.05978033	2.46679091	0.001669387	0.06767446
132	1.209165035	0.000675999	0.05590623	2.051125001	0.001439705	0.07019099	2.480309092	0.001196536	0.04824141
133	1.203373427	0.000676967	0.05625581	2.050738608	0.001509787	0.0736216	2.467795738	0.001520039	0.06159502
134	1.205221896	0.000956473	0.07936078	2.048829109	0.001913626	0.09340095	2.472414411	0.001710394	0.06917909
135	1.207558118	0.001268139	0.10501683	2.049448539	0.001349034	0.06582426	2.474412267	0.002010556	0.08125388
136	1.212709872	0.000774867	0.0638955	2.047160966	0.001291082	0.06306695	2.482761956	0.001636989	0.06593418
137	1.204639044	0.000891143	0.07397592	2.053736875	0.001499917	0.07303355	2.47403487	0.001317568	0.05325584
138	1.203893363	0.000776429	0.06449315	2.056488796	0.001339391	0.06512997	2.476136971	0.00113195	0.04571435
139	1.200964653	0.000805634	0.06708227	2.058127772	0.001144966	0.05563146	2.471196753	0.000969122	0.03921672
140	1.2061834	0.000536524	0.04448111	2.054197501	0.001103003	0.05369508	2.47847724	0.000952375	0.0384258

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