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# LATE JURASSIC TO EARLY CRETACEOUS STABLE ISOTOPE AND GEOCHEMICAL RECORDS FROM THE NORTHERN HIGH LATITUDES: IMPLICATIONS FOR PALAEOCLIMATE

by

# **ELIZABETH VICTORIA NUNN**

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

# **DOCTOR OF PHILOSOPHY**

School of Earth Ocean & Environmental Sciences Faculty of Science

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# ABSTRACT

#### Elizabeth Nunn

#### Late Jurassic to Early Cretaceous Stable Isotope and Geochemical Records from the Northern High Latitudes: Implications for Palaeoclimate

The Jurassic and Cretaceous periods are widely accepted as being dominated by greenhouse conditions with elevated  $CO_2$  levels and warm polar regions. Although much compelling evidence to support this idea of global warmth exists, some recent studies propose that the greenhouse climate may at times have been punctuated by sub-freezing polar conditions and the presence of limited polar ice. The evidence, however, is somewhat equivocal and is both spatially and temporally limited with much of this research until now being concentrated in mid- to low latitudes, despite it being generally accepted that global climate is defined to a significant degree by prevailing conditions at the poles. Existing data are also often plagued by poor sampling resolutions and dubious diagenetic histories.

This research presents the first extensive stable isotope and geochemical investigation of well-preserved belemnite rostra from the Callovian-Hauterivian Boreal Realm. Belemnites of the genera *Cylindroteuthis, Pachyteuthis, Acroteuthis, Lagonibelus* and occasionally *Belemnopsis* were investigated. Preservation was assessed using Backscattered Scanning Electron Microscopy, Cathodoluminescence, carbonate staining and trace element techniques. Organic carbon isotope analysis of fossilised wood was also undertaken where possible. Material from Staffin Bay, Isle of Skye, and Helmsdale, Sutherland, Scotland; the Izhma River, Timan-Pechora Basin, Russia; the Boyarka River, Yenisei-Khatanga Basin, Siberia; and Festningen and Janusfjellet, Svalbard was analysed.

The carbon isotope data record relatively positive values in the Oxfordian, followed by a gradual shift towards more negative values through the Kimmeridgian and into the Volgian/Tithonian. A distinct Late Valanginian positive carbon isotope excursion is identified in both the marine carbonate and terrestrial organic carbon records from the Izhma and Boyarka rivers. The excursion occurs at a time of relatively low sea level in Russia and Siberia. The exposure and erosion of lowland areas and restricted ocean circulation (and therefore enhanced stratification) associated with a period of sea-level lowstand may account for increased rates of organic carbon burial. The Late Valanginian positive carbon isotope excursion is coeval with a distinct cooling in the Russian Izhma River succession. This could be explained by a fall in atmospheric  $CO_2$  concentration and a subsequent drop in temperature as the result of significant burial of sediments rich in organic carbon. Further evidence for cold conditions during the Valanginian interval comes from glendonites and dropstones, which were identified on Svalbard.

High latitude warmth is most likely the norm for the Late Jurassic and Early Cretaceous interval, although this warmth is likely to have been punctuated by cold conditions providing the opportunity for the development of at least a seasonal cover of polar ice. The oxygen isotope data record the occurrence of cold episodes during the Lower Oxfordian *Cordatum* Zone, the mid-Ryazanian *Kochi-Analogus* zones and the Upper Valanginian *Bidichotomus* Zone. Palaeotemperatures as low as 2°C were calculated, providing strong evidence for the existence of cold polar conditions at theses times. Ultimately, climatic instability is probably the key characteristic of this greenhouse interval.

# TABLE OF CONTENTS

4. METHODOLOGY	
3.4. Belemnites as Palaeoclimate Indicators	
3.3.3. Austral Realm	
3.3.1. Boreal Realm	
3.3. Belemnite Palaeobiogeography	
3.2.2. Belemnite Palaeoecology	
3.2. The Belemnite Animal	
3.1. Systematic Position	
3. BELEMNITES	
2.3.2. Evidence for Cold Polar Regions	
2.3. Palaeoclimate	
2.2. Palaeogeography	
2.1. Biostratigraphy 2.1.1. Boreal-Tethyan Correlation	8 Q
2. THE LATE JURASSIC AND EARLY CRETACEOUS	
1.4. Thesis Structure	7
1.3. Aims & Objectives	
1.2. Locations	
1.1. Rationale	
1. INTRODUCTION	
AUTHOR'S DECLARATION	x
ACKNOWLEDGEMENTS	IX
LIST OF PLATES	VII
LIST OF TABLES	VII
LIST OF FIGURES	V
TABLE OF CONTENTS	
ABSTRACT	

4.1. Selection of Sites	
4.2. Field Techniques	
4.2.1. Graphic Sedimentary Logs	
4.2.2. Sample Collection	
4.3. Laboratory Techniques	
4.3.1. Rationale	
4.3.2. Optical Techniques	
4.3.3. Trace Element Analysis	
4.3.4. Carbonate Stable Isotope Analysis	
4.3.5. Organic Carbon Analysis	ر د
4.3.6. Total Organic Carbon (TOC)	
4.3.7. Rock-Eval Pyrolysis	
4.3.8. Storage of Material	
5. STAFFIN BAY, ISLE OF SKYE, SCOTLAND	61
5.1. Location & Site Description	61
5.2. Geological Setting	
5.3. Sampling & Methodology	
5.4. Results	69
5.5. Discussion	
5.5.1. Stable Isotope, Geochemical & Taxonomic Records	
5.5.2. The Oxygen Isotope Record & Palaeotemperature Implications	
5.5.3. The Elemental Records & Palaeotemperature Implications	
5.5.4. The Terrestrial Carbon Isotope Record	
5.5.5. The Marine Carbon Isotope Record	
5.5.6. The Carbon Isotope Records & Ocean-Atmosphere Correlation	
5.5.7. Callovian-Kimmeridgian Marine & Terrestrial Isotopic Records	
5.6. Conclusions	
6. HELMSDALE, SUTHERLAND, SCOTLAND	08
6.1. Location & Site Description	
6.2. Geological Setting	
6.3. Sampling & Methodology	
	-
6.4. Results	
6.5. Discussion	
6.5.1. Stable Isotope, Geochemical & Taxonomic Records	
6.5.2. The Oxygen Isotope Record & Palaeotemperature Implications	
6.5.3. The Elemental Records & Palaeotemperature Implications	
6.5.4. The Carbon Isotope Record	
6.5.5. Kimmeridgian Stable Isotope Records	116
6.5.6. Correlation of the Helmsdale & Staffin Bay Isotope Records	119
6.6. Conclusions	
7. BOYARKA RIVER, YENISEI-KHATANGA BASIN, SIBERIA	
7.1. Location & Site Description	
7.2. Geological Setting	110
·····	

7.3. Sampling & Methodology	
7.4. Results	134
75 Discussion	
7.5. Discussion	
7.5.1. Stable Isotope, Geochemical & Taxonomic Records	
7.5.2. The Oxygen Isotope Record & Palaeotemperature Implications	
7.5.3. The Elemental Records & Palaeotemperature Implications	
7.5.4. The Terrestrial Carbon Isotope Record	145
7.5.5. The Marine Carbon Isotope Record	147
7.5.6. The Carbon Isotope Records & Ocean-Atmosphere Correlation	
7.5.7. Ryazanian-Hauterivian Marine & Terrestrial Isotopic Records	
7.6. Conclusions	
8. IZHMA RIVER, TIMAN-PECHORA BASIN, RUSSIA	161
8.1. Location & Site Description	
8.2. Geological Setting	
8.3. Sampling & Methodology	
8.4. Results	
8.5. Discussion	171
8.5.1. Stable Isotope, Geochemical & Taxonomic Records	
8.5.2. The Oxygen Isotope Record & Palaeotemperature Implications	
8.5.3. The Elemental Records & Palaeotemperature Implications	
8.5.4. The Carbon Isotope Record	
8.5.5. Volgian-Hauterivian Stable Isotope Records	
8.6. Conclusions	
9. FESTNINGEN & JANUSFJELLET, SVALBARD	
9.1. Location & Site Description	
9.2. Geological Setting	
9.3. Sampling & Methodology	
9.4. Results	
9.5. Discussion	
9.5. Discussion 9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites	<b>199</b> 199
<ul> <li>9.5. Discussion</li> <li>9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites</li> <li>9.5.2. Sedimentary Indicators of Palaeoclimate - Outsized Clasts</li> </ul>	
<ul> <li>9.5. Discussion</li></ul>	199 199 201 204 204 204 207 211 212
<ul> <li>9.5. Discussion</li></ul>	199 199 201 204 204 204 207 211 212 212 213
<ul> <li>9.5. Discussion</li> <li>9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites</li></ul>	199 199 201 204 204 204 207 211 212 212 213 213
9.5. Discussion         9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites         9.5.2. Sedimentary Indicators of Palaeoclimate - Outsized Clasts         9.5.3. Stable Isotope, Geochemical & Taxonomic Records         9.5.4. The Oxygen Isotope Record & Palaeotemperature Implications         9.5.5. The Elemental Records & Palaeotemperature Implications         9.5.6. The Carbon Isotope Record         9.5.7. Ryazanian-Valanginian Stable Isotope Records         9.6. Conclusions         10. DISCUSSION         10.1. Evaluating Belemnites as Palaeoenvironmental Indicators	199 199 201 204 204 204 207 211 212 213 213 218
<ul> <li>9.5. Discussion</li></ul>	199 199 201 204 204 204 207 211 212 213 213 218 218
9.5. Discussion         9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites         9.5.2. Sedimentary Indicators of Palaeoclimate - Outsized Clasts         9.5.3. Stable Isotope, Geochemical & Taxonomic Records         9.5.4. The Oxygen Isotope Record & Palaeotemperature Implications         9.5.5. The Elemental Records & Palaeotemperature Implications         9.5.6. The Carbon Isotope Record         9.5.7. Ryazanian-Valanginian Stable Isotope Records         9.6. Conclusions         10. DISCUSSION         10.1. Evaluating Belemnites as Palaeoenvironmental Indicators	

10.1.5. Carbon Isotopes	234
10.2. Late Jurassic - Early Cretaceous Global Palaeoenvironment	
10.2.1 Boreal Realm Data	
10.2.2. Global Palaeoenvironmental Studies	
11. CONCLUSIONS	
11.1. Summary of Site Specific Investigations	
11.1.1. Stattin Bay, Isle of Skye, Scotland	
11.1.2. Helmsdale, Sutherland, Scotland	
11.1.3. Boyarka River, Yenisei-Khatanga Basin, Siberia	
11.1.4. Izhma River, Timan-Pechora Basin, Russia	
11.1.5. Festningen & Janusfjellet, Svalbard	
11.2. Wider Implications of Research	
11.2.1. Belemnites as Palaeoenvironmental Indicators	
11.2.2. Late Jurassic - Early Cretaceous Global Palaeoenvironment	
11.3. Future Work	
REFERENCES	
APPENDIX 1. SYSTEMATIC PALAEONTOLOGY	
A1.1. Introduction	
A1.2. Systematic Descriptions	
APPENDIX 2. DATA TABLES : BELEMNITES	415
APPENDIX 3. DATA TABLES : ORGANICS	

# LIST OF FIGURES

Figure 1.1.	Atmospheric CO <sub>2</sub> through the Phanerozoic	1
Figure 1.2.	Distribution of potentially glacially derived sediments and glendonites through the Mesozoic	2
Figure 1.3.	Present day circumpolar view of the Northern hemisphere	4
Figure 1.4.	Temporal distribution of the locations investigated as part of this study.	5
Figure 2.1a	Tethyan-Boreal (British and Russian) correlation of the Middle-Upper Jurassic period	. 10
Figure 2.1t	. Tethyan-Boreal (British and Russian) correlation of the Lower Cretaceous period	. 11
Figure 2.2.	Callovian palaeogeography map	. 13
Figure 2.3.	Hauterivian palaeogeography map	. 14
Figure 2.4.	Late Jurassic palaeogeography of the Arctic region	15
Figure 3.1.	Belemnite morphology	30
Figure 3.2.	Hauterivian palaeobiogeography	.35
Figure 4.1.	Volgian circumpolar map	43
Figure 4.2.	Key to sedimentary log symbols used in this study	.44
Figure 5.1.	Location map of Staffin Bay	61
Figure 5.2.	Broad foreshore exposure typical of the Staffin Bay coast	62
Figure 5.3.	Mid-Jurassic (Bathonian) Scottish palaeogeography	63
Figure 5.4.	Stratigraphic chart of the Staffin Bay section	65
Figure 5.5.	Relatively abundant belemnites in a mudrock	68
Figure 5.6.	Cross-plot of $\delta^{18}$ O and $\delta^{13}$ C values from belemnites from Staffin Bay	70
Figure 5.7.	Cross-plots of $\delta^{18}$ O against Fe and Mn	71

Figure 5.8. Cross-plots of $\delta^{18}$ O against El/Ca.	72
Figure 5.9. El/Ca ratios from the Callovian-Lower Kimmeridgian at Staffin Bay Figure 5.10. $\delta^{13}C_{org}$ , $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ records from the Callovian-Lower Kimmeridgian succession at	
Staffin Bay	74
Figure 5.11. TOC record from the Callovian-Lower Kimmeridgian succession at Staffin Bay	75
Figure 5.12. Van Krevlan diagram showing the origin of organic matter analysed from the Callovian-Lowe	r
Kimmeridgian Staffin Bay succession	76
Figure 5.13. Palaeotemperatures calculated from Mg/Ca data	79
Figure 5.14. Temperature-salinity plot for the Staffin Bay data	81
Figure 5.15. Callovian-Lower Kimmeridgian $\delta^{13}C$ correlation between a composite Tethyan $\delta^{13}C_{carb}$ curve and the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ curves from Staffin Bay	<u></u>
and the or Cearb and or Corg curves nom startin Day	92
Figure 6.1. Location map of the Sutherland coastal region	00
Figure 6.2. Foreshore exposure typical of the area around the Helmsdale coast	70 00
Figure 6.3. Late Jurassic palaeogeography.	ምም በበ
Figure 6.4. Stratigraphic chart for the Middle-Upper Jurassic of the Brora-Helmsdale region	กา
Figure 6.5. Typical preservation of Helmsdale belemnites	05
Figure 6.6. Cross-plots of $\delta^{18}$ O against Fe and Mn	06
Figure 6.7. $\delta^{13}$ C and $\delta^{18}$ O records from the Kimmeridgian succession at Helmsdale and Eathie	08
Figure 6.8. Cross-plot of $\delta^{15}$ O and $\delta^{13}$ C values from belemnites from Helmsdale. Eathie and Brora	09
Figure 6.9. Cross-plots of δ <sup>18</sup> O against El/Ca	12
Figure 6.10. El/Ca ratios from the Kimmeridgian succession at Helmsdale and Eathie	14
Figure 6.11. Kimmeridgian palaeogeography map showing published belemnite derived palaeotemperature	S
for this time period	16
Figure 6.12. Kimmeridgian $\delta^{13}$ C correlation between a composite Tethyan $\delta^{13}$ C bulk curve and the $\delta^{13}$ C curve	e
from Heimsdale	18
Figure 6.13. Composite Callovian-Kimmeridgian $\delta^{13}$ C and $\delta^{18}$ O records from northern Scotland	21
Figure 7.1. Location map of the Boyarka River	27
Figure 7.2. River-side cliff, exposure typical of the Boyarka River	28
Figure 7.3. Simplified geological map of the Yenisei-Khatanga Basin and surrounding areas	29
Figure 7.4. Sedimentary log and photographs of the Boyarka River succession.	30
Figure 7.5. Photographs of belemnites and macroscopic wood from the Boyarka River succession	33
Figure 7.6. Cross-plots of $\delta^{18}$ O against Fe and Mn	54
Figure 7.7. δ <sup>13</sup> C <sub>org</sub> , δ <sup>13</sup> C <sub>carb</sub> , and δ <sup>18</sup> O <sub>carb</sub> records from the Ryazanian-Lower Hauterivian Boyarka River succession	~
Figure 7.8. Cross-plot of $\delta^{18}$ O and $\delta^{13}$ C values from belemnites from the Boyarka River succession	50 77
Figure 7.9. El/Ca ratios from the Ryazanian-Lower Hauterivian succession at the Boyarka River	>7 20
Figure 7.10. Close-up of the Ryazanian Kochi-Analogus zones, Boyarka River	20
Figure 7.11. Temperature-salinity plot for the Boyarka River data	17
Figure 7.12. Cross-plots of $\delta^{18}$ O against El/Ca for the Boyarka River belemnites. 14	14
Figure 7.13. Valanginian-Hauterivian $\delta^{13}$ C correlation between the Boyarka River succession $\delta^{13}C_{org}$ curve	-
and the Crimea, and the $\delta^{13}C_{carb}$ curve and a composite Tethyan bulk $\delta^{13}C$ curve	51
Figure 8.1. Location map of the Izhma River	51
Figure 8.2. River-side cliff, exposure typical of the Izhma River	52
Figure 8.3. Simplified map of the Timan-Pechora Basin and surrounding areas	53
Figure 8.4. Sedimentary log and photographs of the Izhma River succession	56
Figure 8.5. Photographs of belemnites from the Izhma River succession	58
Figure 8.6. Cross-plots of δ <sup>18</sup> O against Fe and Mn16	<b>i9</b>
Figure 8.7. Cross-plot of Mn and Fe	0
Figure 8.8. Cross-plot of $\delta^{18}$ O and $\delta^{13}$ C	0
Figure 8.9. $\delta^{13}$ C and $\delta^{18}$ O <sub>carb</sub> records from the Callovian-Lower Hauterivian Izhma River succession	2'2
Figure 8.10. El/Ca records from the Callovian-Lower Hauterivian Izhma River succession, Russia	13
Figure 8.11. Cross-plots of $\delta^{18}$ O against El/Ca	6
Figure 8.12. Ryazanian-Hauterivian $\delta^{13}$ C and $\delta^{18}$ O correlation between the Izhma River succession and the	
Boyarka River succession	1
Figure 9.1. Location map of Svalbard	7
Figure 9.2. Low coastal cliff typical of the Festningen exposure	2
Figure 9.3. Typical exposure at Janusfjellet	0  2
Figure 9.4. Simplified palaeogeographic map of the Arctic region	0
Figure 9.5. Summary of events and facies in the Late Jurassic and Early Cretaceous history of Svalbard 19	n n
Figure 9.6. Stratigraphic chart for principal lithostratigraphic units of the Middle Jurassic to Early	0
Cretaceous of Svalbard	2

Figure 9.7. Typical preservation of Svalbard belemnites	. 196
Figure 9.8. Cross-plot of Fe and Mn for belemnites from Svalbard.	. 197
Figure 9.9. Cross-plot of $\delta^{18}$ O and $\delta^{13}$ C	. 198
Figure 9.10. Glendonites from the Rurikfjellet Formation at Janusfjellet and Festningen	. 199
Figure 9.11. Outsized clast	. 202
Figure 9.12. $\delta^{13}$ C and $\delta^{18}$ O records from the Upper Valanginian succession at Festningen	. 205
Figure 9.13. δ <sup>13</sup> C and δ <sup>18</sup> O records from the Ryazanian-Upper Valanginian succession at Janusfjellet	. 206
Figure 9.14. Cross-plots of $\delta^{18}$ O and El/Ca.	. 208
Figure 9.15. El/Ca ratios from the Upper Valanginian succession at Festningen	
Figure 9.16. El/Ca ratios from the Ryazanian-Upper Valanginian succession at Janusfjellet	210
Figure 9.17. Valanginian palaeogeography map showing published belemnite derived palaeotemperature	
for this time period.	
Figure 10.1. Cross plots of $\delta^{18}$ O and $\delta^{13}$ C offsets observed from coeval belemnites	. 224
Figure 10.2. Calculated palaeotemperatures and relative $\delta^{18}O_{seawater}$ values for the Callovian-Hauterivian	
Izhma River succession, Russia.	. 233
Figure 10.3. Callovian-Hauterivian compilation of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data	. 238
Figure 10.4a. Callovian-Hauterivian compilation of $\delta^{13}C_{carb}$ data derived from this study and compared v	with
published data	. 239
Figure 10.4b. Callovian-Hauterivian compilation of $\delta^{18}O_{carb}$ data derived from this study and compared v	with
published data	. 240
Figure 10.5. Latitudinal changes in 8 <sup>18</sup> O <sub>seawater</sub> in warm climates	. 245
Figure 10.6. Calculated average palaeotemperatures for the Oxfordian and Valanginian periods	. 246
Figure A1.1. Morphological terms employed in the systematic descriptions of belemnite rostra	
Figure A1.2. Stratigraphical and geographical ranges of the belemnite species recorded in this study	. 374

# LIST OF TABLES

Table 10.1. Table showing genus-level differences in stable isotope and geochemical measurements coeval belemnites	
Table 10.2. Table showing ontogenetic differences in stable isotope and geochemical measurements coeval belemnites.	from
Table 10.3. Compilation of published Late Jurassic-Early Cretaceous $\delta^{18}O$ and palaeotemperature da	ta 243
Table A2. Data tables: Belemnites	415
Table A3. Data tables: Organics	

# LIST OF PLATES

Plate 1. Staffin Bay, Isle of Skye, Scotland. CL	95
Plate 2. Staffin Bay, Isle of Skye, Scotland. BSEM	
Plate 3. Staffin Bay, Isle of Skye, Scotland. Carbonate Staining	
Plate 4. Helmsdale, Sutherland, Scotland. CL	124
Plate 5. Helmsdale, Sutherland, Scotland. BSEM	
Plate 6. Helmsdale, Sutherland, Scotland. Carbonate Staining	
Plate 7. Boyarka River, Yenisei-Khatanga Basin, Siberia. CL	
Plate 8. Boyarka River, Yenisei-Khatanga Basin, Siberia. BSEM	
Plate 9. Boyarka River, Yenisei-Khatanga Basin, Siberia. Carbonate Staining	158
Plate 10. Boyarka River, Yenisei-Khatanga Basin, Siberia. Wood	
Plate 11. Boyarka River, Yenisei-Khatanga Basin, Siberia. Wood	
Plate 12. Izhma River, Timan-Pechora Basin, Russia. CL	
Plate 13. Izhma River, Timan-Pechora Basin, Russia. BSEM	
Plate 14. Izhma River, Timan-Pechora Basin, Russia. Carbonate Staining	
Plate 15. Festningen & Janusfjellet, Svalbard. CL	
Plate 16. Festningen & Janusfjellet, Svalbard. BSEM	
Plate 17. Festningen & Janusfjellet, Svalbard. Carbonat Staining	
Plates A1. Belemnite Taxonomy	
Plates A2. Belemnite Taxonomy	

Plates A3. Belemnite Taxonomy	
Plates A4. Belemnite Taxonomy	
Plates A5. Belemnite Taxonomy	
Plates A6. Belemnite Taxonomy	
Plates A7. Belemnite Taxonomy	
Plates A8. Belemnite Taxonomy	
Plates A9. Belemnite Taxonomy	
Plates A10. Belemnite Taxonomy	
Plates A11. Belemnite Taxonomy	
Plates A12. Belemnite Taxonomy	
Plates A13. Belemnite Taxonomy	
Plates A14. Belemnite Taxonomy	
Plates A15. Belemnite Taxonomy	
Plates A16. Belemnite Taxonomy	
Plates A17. Belemnite Taxonomy	

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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 prior agreement of the Graduate Committee.

This study was financed with the aid of a studentship from the University of Plymouth.

A programme of advanced study was undertaken, which included training in palaeontological, isotopic and geochemical analytical techniques.

Relevant scientific seminars and conferences, both national and international were regularly attended at which work was often presented and external institutions were visited for consultation purposes.

Publications (or presentation of other forms of creative and performing work):

- Price, G. D., & Nunn, E. V. A Sedimentological and Isotopic evaluation of a high latitude Jurassic Early Cretaceous succession from Svalbard. BSRG AGM, Aberdeen (Dec 2006).
- Price, G. D., & Nunn, E. V. Early Cretaceous Isotope Records from the Arctic. EGU General Assembly, Vienna, Austria (Apr 2006).
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#### **1. INTRODUCTION**

#### 1.1. Rationale

The Jurassic and Cretaceous periods are widely accepted as being a time of warm equable climates with a low global temperature gradient (e.g., Frakes, 1979; Barron, 1983; Huber *et al.*, 1995), elevated CO<sub>2</sub> levels (e.g., Barron *et al.*, 1983; Weissert & Lini, 1991; Francis & Frakes, 1993; Berner, 1994; Bice & Norris, 2002; Dromart *et al.*, 2003a; Royer *et al.*, 2004) and warm polar regions (e.g., Poulsen *et al.*, 1999; Spicer *et al.*, 2002; Tarduno *et al.*, 1998; Jenkyns *et al.*, 2004). The general assumption has been that this period of extreme warmth is primarily the result of elevated concentrations of atmospheric CO<sub>2</sub> (Fig. 1.1). This presents an interesting idea, namely that the Jurassic and Cretaceous 'greenhouse' period could be considered as a potential analogue for future climatic change providing it was better understood.

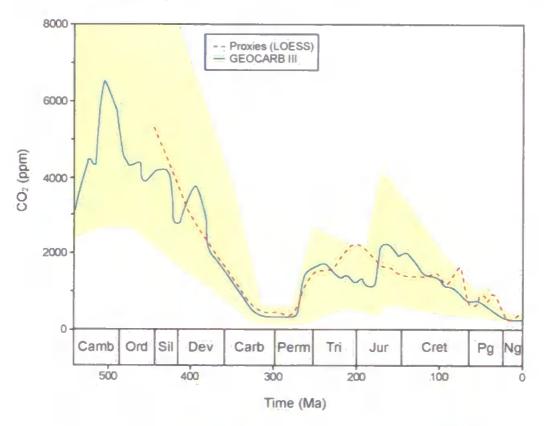


Figure 1.1 Atmospheric  $CO_2$  through the Phanerozoic. The LOESS record is a compilation of published proxies (e.g., palaeosols, stomata, phytoplankton, boron, liverworts) produced by Royer (2006). The GEOCARB III record is derived from a geochemical model (Berner & Kothavala, 2001). Diagram adapted after Royer (2006).

The assumption that warm equable climates existed throughout the Jurassic and Cretaceous has recently been contested by newer research suggesting that the greenhouse climate may at times have been punctuated by sub-freezing polar conditions and the presence of limited polar ice. Such evidence includes the presence of potentially glacially derived sediments and minerals (Fig. 1.2) (e.g., Woolfe & Francis, 1991; Frakes & Krassay, 1992; Francis & Frakes, 1993; De Lurio & Frakes, 1999; Price, 1999; Alley & Frakes, 2003), observations from global sea level curves (e.g., Stoll & Schrag, 1996, 2000; Dromart *et al.*, 2003a; Miller *et al.*, 2003, 2005) and isotopic studies (e.g., Pirrie & Marshall, 1990; Ditchfield *et al.*, 1994; Pirrie *et al.*, 1995; Ditchfield, 1997; van de Schootbrugge *et al.*, 2000; Pucéat *et al.*, 2003; Price & Mutterlose, 2004).

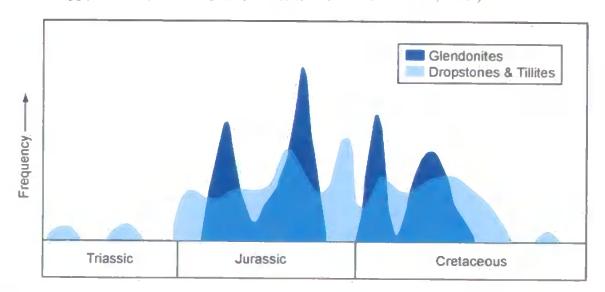


Figure 1.2 Distribution of potentially glacially derived sediments and glendonites through the Mesozoic. Diagram adapted after Price (1999).

The evidence for cool polar conditions, however, is still somewhat equivocal since much of the existing research has been carried out at a poor sampling resolution (in the high latitudes) or in the mid- to low latitudes or in the southern high latitudes of Antarctica, South America, Australia and New Zealand. There has been very little research undertaken in the Arctic region, which prevents a thorough understanding of this issue. It is generally accepted that global climate is defined to a significant degree by the prevailing conditions at the poles (e.g., Jenkyns *et al.*, 2004) and it is therefore essential to collect robust data from the northern high latitudes in order to accurately reconstruct palaeoclimatic conditions.

In September 2004, the first scientific drilling expedition to the central Arctic Ocean was completed. Integrated Ocean Drilling Program (IODP) Expedition 302, the Arctic Coring Expedition (ACEX) recovered sediment cores, of Late Cretaceous to Holocene age, from the Lomonosov Ridge, 250 km from the North Pole. In their IODP proposal Backman *et al.* (2002) highlighted the importance of the Arctic Ocean in driving climate change. They stated that:

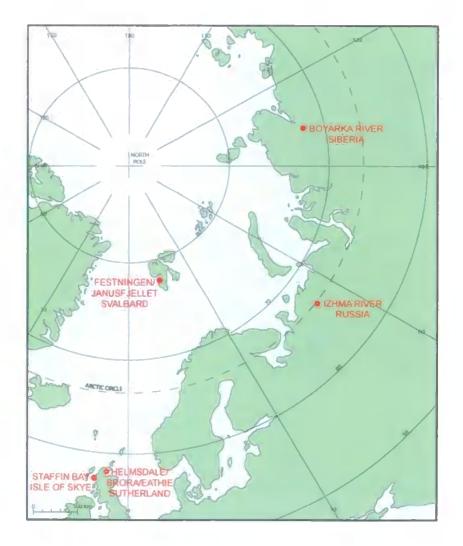
"The Arctic Ocean and its marginal seas play a fundamental role in the global ocean/climate system. The dense cold bottom waters of most of the world's oceans, which originate in the Nordic seas, strongly influence global thermohaline circulation, driving world climate. The permanent Arctic sea-ice cover has a tremendous influence on the Earth's albedo and the distribution of fresh water. It varies both seasonally and over longer time periods and thus has a direct influence on global heat distribution and climate. While understanding the history of the Arctic Ocean is critical for any climate, ocean-circulation or tectonic model that would be truly global, the logistical difficulties associated with the work in this remote and harsh region have prevented us from gathering the critical data needed to document the role of this key region in the development and maintenance of the global climate system."

Backman *et al.* (2002) ultimately recognised that a lack of knowledge about the influence of the Arctic Ocean on the development and maintenance of climatic extremes creates a fundamental gap in our ability to understand and model global environmental change.

This study will therefore investigate the Late Jurassic and Early Cretaceous northern high latitudes with regards to palaeoclimate. The Late Jurassic-Early Cretaceous

time interval has been chosen firstly, because only limited investigation has been carried out on this interval (most of the previously published palaeoclimate studies considering this issue prefer to concentrate on the Late Cretaceous) and secondly because several authors have indicated that sub-freezing polar conditions may be present throughout this interval, most notably during the Callovian-Oxfordian (e.g., Dromart *et al.*, 2003a, b; Lécuyer *et al.*, 2003), the Tithonian/Volgian (e.g., Price, 1999; Schudack, 1999) and the Valanginian (e.g., Price, 1999; Pucéat *et al.*, 2003; Kessels *et al.*, 2006) periods. Stable isotope and geochemical proxies (in conjunction with other observations) will be used to examine the Late Jurassic-Early Cretaceous Arctic palaeoclimate due to the high resolution data that these techniques can provide.







In order to contribute to the current debate about the existence of cold polar conditions during the Jurassic and Cretaceous greenhouse climate, five northern high latitude locations were considered (Fig. 1.3). The sites selected for this research ranged from Early Callovian to Early Hauterivian in age and were situated at Arctic or sub-Arctic palaeolatitudes during this time interval. There is a considerable degree of temporal overlap between the locations, which is essential for the accurate correlation of data between the different field sites (Fig. 1.4). Further information about each location is given in the respective chapters.

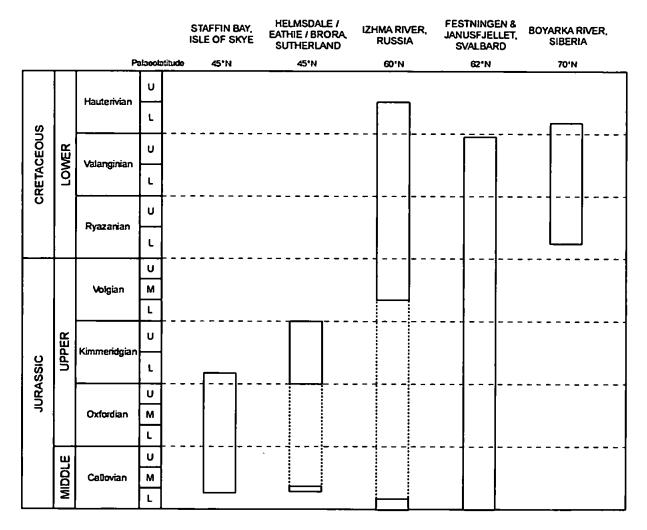


Figure 1.4 Temporal distribution of the locations investigated as part of this study. The timescale is illustrated is the Boreal (Russian) timescale.

#### 1.3. Aims & Objectives

The major aim of this research is to investigate the nature of Late Jurassic and Early Cretaceous northern high latitude climates, principally via stable isotope and geochemical proxies as derived from belemnites and fossilised wood.

In order to achieve this aim the following objectives must be accomplished:

- To undertake high resolution sedimentary logging and systematic bed-by-bed sampling of belemnites and, where possible, fossilised wood fragments/wood debris from five biostratigraphically constrained localities within the Upper Jurassic and Lower Cretaceous of the Boreal Realm (see Chapter 2).
- To assess the level of preservation and effects of diagenesis on belemnite specimens.
- To provide stable isotope (δ<sup>18</sup>O and δ<sup>13</sup>C) and trace element records (Fe, Mn, Ca, Mg, Sr, Na and Li) from belemnite rostra from each of the five locations.
- To produce palaeotemperature estimates for each of the localities based on  $\delta^{18}$ O data.
- To investigate ocean-atmosphere links using marine (belemnite carbonate) and terrestrial (wood) records from coeval successions (Isle of Skye, Scotland and Boyarka River, Siberia).
- To provide organic geochemical analysis of fossilised wood from the Isle of Skye and Boyarka River (e.g., δ<sup>13</sup>C<sub>org</sub>, TOC and Rock-Eval pyrolysis).
- To evaluate the use of belemnites, stable isotopes and elemental/Ca ratios as palaeoclimate indicators.
- To provide a critical analysis of palaeoenvironmental conditions in the Late Jurassic and Early Cretaceous northern high latitudes.

#### 1.4. Thesis Structure

Chapters 2 and 3 of this thesis present background information that is critical to the current study. An overview of Late Jurassic and Early Cretaceous biostratigraphy and palaeogeography is presented in Chapter 2 with particular reference to the Arctic region. Also discussed in Chapter 2 are the key elements of the aforementioned palaeoclimate debate. In Chapter 3, an introduction to belemnites is given. This chapter provides a summary of the current state of knowledge with regards to this extinct group of organisms and ultimately focuses on the use of belemnites as palaeoclimate indicators. Together these chapters present the context in which the current study should be considered. A comprehensive review of methodology is given in Chapter 4, where each of the techniques utilised in this study are examined.

Chapters 5-9 present the full range of data obtained from each of the field sites investigated as part of this study (Staffin Bay, Helmsdale, Boyarka River, Izhma River, Festningen/Janusfjellet). Stable isotope and geochemical data are presented alongside detailed sedimentological and biostratigraphical information. The data are then interpreted in terms of palaeoclimate, with an emphasis on palaeotemperature and carbon cycling.

Chapter 10 expands upon earlier discussions and examines a number of broader themes relating to this thesis. The nature of Late Jurassic-Early Cretaceous climates in the northern high latitudes is discussed and a number of issues arising from the methodologies utilised and results obtained are explored. Finally, Chapter 11 presents the conclusions drawn from this work, acknowledges the limitations of the work and makes recommendations for future investigation.

## 2. THE LATE JURASSIC AND EARLY CRETACEOUS

## 2.1. Biostratigraphy

The Jurassic and Cretaceous periods have traditionally been correlated and subdivided on the basis of ammonite zones (e.g., d'Orbigny, 1842-51; Oppel, 1856-8; Arkell, 1933, 1956; Cope *et al.*, 1980a, b; Cox, 2001a), with the bases of most stages corresponding to the base of an ammonite zone (Ogg, 2004a). This biostratigraphic system was adopted due to the abundance of ammonite fossils from these periods (Harland *et al.*, 1990) as well as historical precedence.

A number of additional fossil groups have also been used for Jurassic-Cretaceous biostratigraphical purposes. These include brachiopods (e.g., Prosorovskaya, 1993; Garcia & Dromart, 1997; Cresta *et al.*, 2001), bivalves (e.g., Sha & Fürsich, 1993; Cresta *et al.*, 2001), belemnites (e.g., Meledina *et al.*, 1998), foraminifera (e.g., Dave & Chaterjee, 1996; Moss & Finch, 1997; Kabal & Tasli, 2003; Nagy & Seidenkrantz, 2003), ostracods (e.g., Boomer, 1994; Cresta *et al.*, 2001; Coimbra *et al.*, 2002), calcareous nannofossils (e.g., Moss & Finch, 1997; Halasova, 1999; Marino *et al.*, 2004), dinoflagellates (e.g., Poulsen, 1992), charophytes (e.g., Feist *et al.*, 1995) and palynomorphs (e.g., Mahmoud *et al.*, 1999; Cresta *et al.*, 2001; Coimbra *et al.*, 2002), although many of these taxa are often used on a local rather than a global scale.

The use of ammonites to construct a global biostratigraphic system poses a significant problem however, due to the marked provinciality displayed by ammonites throughout the Mesozoic (e.g., Arkell, 1956; Imlay, 1965; Casey, 1971; Hallam, 1971, 1975; Fürsich & Sykes, 1997; Page, 1996). During the Jurassic and most of the Cretaceous ammonites occupied three distinct realms, the Boreal Realm, the Tethyan Realm and the Austral Realm, the boundaries and extent of which changed considerably through time (Page, 1996). Such provincialism prevents the development of a truly global biostratigraphic scheme for this time, since different ammonite zones will characterise

different palaeogeographical regions (most significantly the Boreal and Tethyan Realms) making high-resolution correlation between these different realms difficult, but by no means impossible (Ogg, 2004a).

The major method of correlation is a biostratigraphic one (since the global system is based on ammonite zones) although additional techniques have also been employed. These include, for example, magnetostratigraphy (e.g., Housa *et al.*, 1999; Llanos & Riccardi, 2000; Hoedemaeker & Herngreen, 2003; Hounslow *et al.*, 2004; Speranza *et al.*, 2005; Grabowski & Pszczolkowski, 2006), strontium isotope stratigraphy (e.g., Jones *et al.*, 1994a, b; Crame *et al.*, 1999; Jenkyns *et al.*, 2002; Waltham & Gröcke, 2006) and carbon isotope stratigraphy (e.g., Jenkyns *et al.*, 2002; Padden *et al.*, 2002; Rey & Delgado, 2002, 2005).

#### 2.1.1. Boreal-Tethyan Correlation

Many of the stratotypes for the Late Jurassic and Early Cretaceous stages and substages are situated within western European (Tethyan) basins (Zakharov, 1997; Ogg *et al.*, 2004). For example, the proposed Global Boundary Stratotype Sections and Points (GSSP's) recognised by the International Commission on Stratigraphy for the bases of the Oxfordian, Tithonian, Valanginian, Hauterivian, Barremian and Aptian stages, are all from the UK, France, Italy or Spain (Ogg, 2004b).

The differentiation of marine faunas has resulted in the development of a separate biostratigraphic scheme for the Boreal Realm that includes different stages and ammonite zones to those recognised in the Tethyan regions. In particular, the Jurassic-Cretaceous boundary has a plethora of regional terms and, for example, is represented by the Tithonian-Berriasian boundary in the Tethyan Realm and by the Portlandian-Ryazanian boundary or Volgian-Ryazanian boundary in the Boreal British or Boreal Russian Realms respectively (Sey & Kalacheva, 1999).

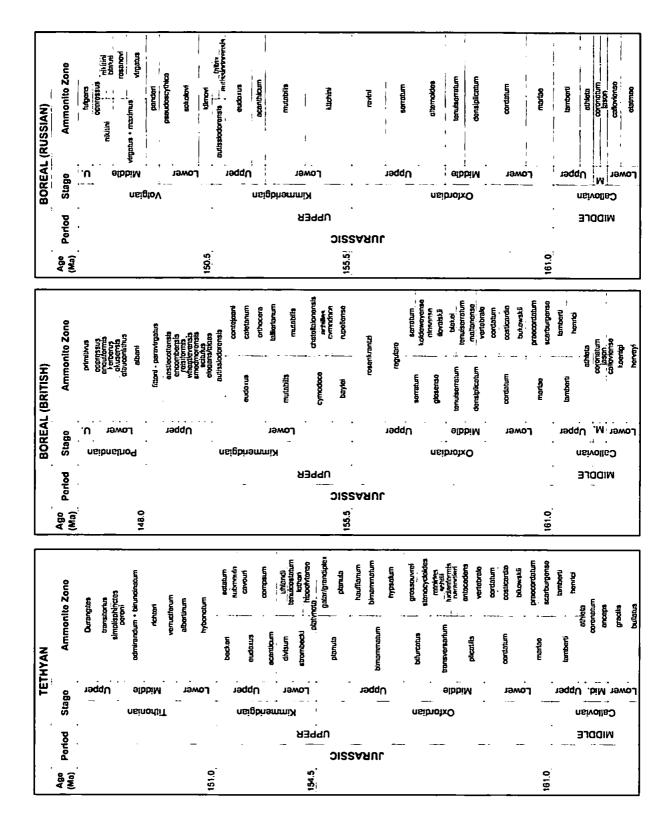


Figure 2.1a Tethyan-Boreal (British and Russian) correlation of the Middle-Upper Jurassic period (after Ogg, 2004a; Ogg et al., 2004, with additions from Sahagian et al., 1996; Baraboshkin, 2004; Pearce et al., 2005 (and references therein)).

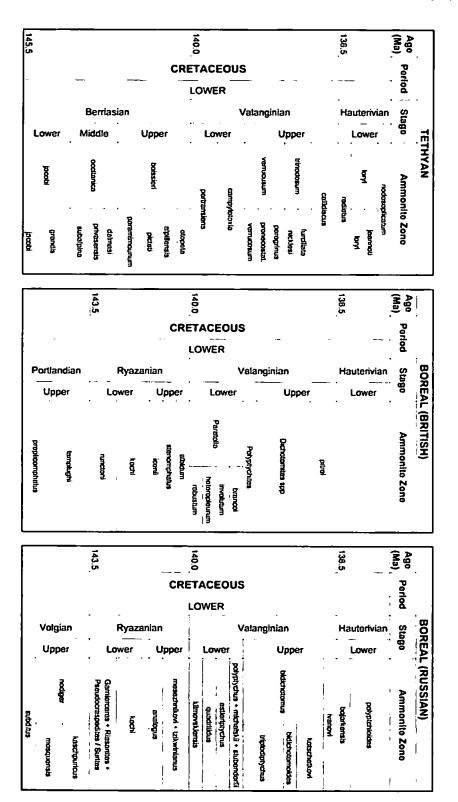
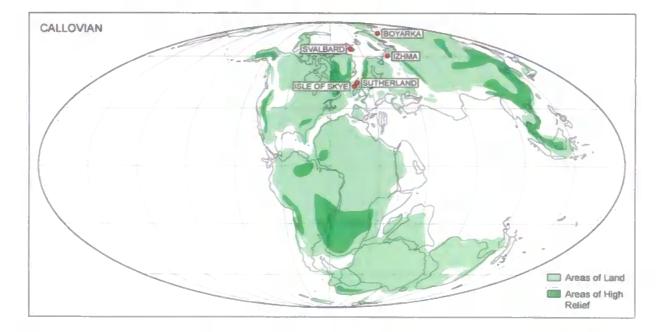


Figure 2.1b Tethyan-Boreal (British and Russian) correlation of the Lower Cretaceous period (after Ogg, 2004a; Ogg et al., 2004; with additions from Sahagian et al., 1996; Baraboshkin, 2004; Pearce et al., 2005 (and references therein)).

The Boreal-Tethyan correlation of zonal biostratigraphic scales is particularly important and has been attempted by several authors (e.g., Sey & Kalacheva, 1997, 1999; Zakharov *et al.*, 1997; Baraboshkin, 1999, 2002, 2004; Ogg *et al.*, 2004). In order to attempt such correlation, it is necessary to either employ for example, chemostratigraphic or magnetostratigraphic techniques or to identify localities with a mixed Tethyan-Boreal fauna (e.g., the Russian platform, northern Caucasus, Mangyshlak (western Kazakhstan), the Crimea and Poland) (Sey & Kalacheva, 1997, 1999). The presence of a mixed ammonite fauna is obviously desirable, however correlations have also been attempted where Tethyan ammonites are associated with the Boreal bivalve, *Buchia* (e.g., California, Oregon and western Canada) (Jeletzky, 1984; Zeiss, 1986; Hoedemacker, 1987; Sey & Kalacheva, 1997, 1999). It is also worth noting that there is some considerable variability, in terms of ammonite zonation, between different Boreal Zonal schemes. British, Russian Platform and Siberian schemes, for example, are not always consistent, although attempts to correlate these different schemes have been made (e.g., Zakharov *et al.*, 1997; Baraboshkin, 1999, 2002; Ogg *et al.*, 2004).

The Jurassic and Cretaceous Boreal-Tethyan correlations (Fig. 2.1a & b) used for this research were compiled primarily from the work of Ogg (2004a) and Ogg *et al.* (2004), with additions from Sahagian *et al.* (1996), Baraboshkin (2004) and Pearce *et al.* (2005) (and references therein). Wherever possible the most appropriate timescale was used for each of the sites investigated here. For example, the Boreal (Russian) timescale was used for the Izhma River and Boyarka River successions, whilst the Boreal (British) timescale was used for the Staffin Bay succession. At Helmsdale, the Boreal (British) timescale (as illustrated in Fig. 2.1a) was also used with the *autissioderensis-paravirgatus* ammonite zones regarded as belonging to the Upper Kimmeridgian (as per the BGS Helsmdale sheet S103EC). It should be noted however, that the use of the Upper Kimmeridgian in this sense is now commonly considered to be redundant, with this

interval generally renamed as the Tithonian following the Tethyan nomenclature, although other alternative stage names have also been proposed (e.g., the Bolonian (Ogg, 2004a)).



# 2.2. Palaeogeography

Figure 2.2 Callovian palaeogeography map. The sites investigated in this study are shown. Map adapted after Smith *et al.* (1994).

The break-up of the supercontinent Pangaea began in the Early to mid-Jurassic (Fig. 2.2) with the opening of the Central Atlantic Ocean and continued into the Early Cretaceous (Fig. 2.3) (Irving, 1983; Scotese, 1991; Golonka & Bocharova, 2000; Veevers, 2004; Page 2005). Two key mechanisms have been postulated as being the origin of this break-up, namely, mantle plume activity (e.g., Leitch *et al.*, 1998; Golonka & Bocharova, 2000; Janney & Castillo, 2001) and lithospheric stress (e.g., Scotese, 1991; McHone, 2000). It has been argued that the large volumes of melt associated with the Central Atlantic Magmatic Province (CAMP) and the geochemical signature of the earliest Atlantic crust could only be produced by plume activity, whilst advocates of a non-plume origin have argued that the geochemical diversity of CAMP magmas indicates a lithospheric origin (Beutel *et al.*, 2005).

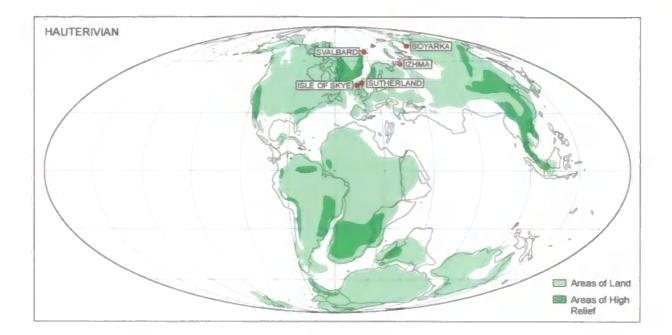
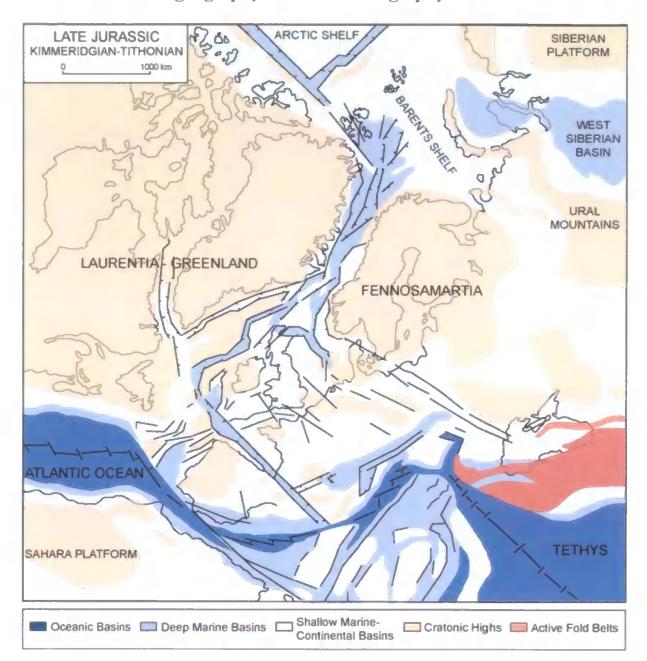


Figure 2.3 Hauterivian palaeogeography map. The sites investigated in this study are shown. Map adapted after Smith *et al.* (1994).

In the Middle Jurassic, Atlantic spreading continued and by the Late Jurassic, the North Atlantic and western Tethys had opened significantly (Irving, 1983), with the Central Atlantic Ocean reaching a width of ~500 km (Veevers, 2004). During this time, the Laurasian continents (North America, North China, Siberia and Eurasia) rifted away from the still intact Gondwana (Africa, South America, India, Australia, Antarctica) (MacLeod, 2005) and the two discrete supercontinents were separated by a continuous equatorial seaway through which surface ocean currents could flow (Skelton, 2003).

Rifting in the South Atlantic and the separation of India from Africa and from Antarctica/Australia, began in the Valanginian-Barremian (Irving, 1983; Veevers *et al.*, 1985; Scotese, 1991) splitting Gondwana first into two distinct parts (South America-Africa and India-Antarctica-Australia) (MacLeod, 2005) and by the Albian (at ~100 Ma) into five dispersed continents (Veevers, 2004). Connections between the newly developed oceans were generally narrow and shallow, which had significant implications for ocean circulation, poleward heat transport and global climate (Skelton, 2003). Continental fragmentation and drift continued throughout the Cretaceous, until the mid-Tertiary, when the main elements of modern physical geology emerged (Irving, 1983).



#### 2.2.1. Arctic Palaeogeography & Palaeoceanography

Figure 2.4 Late Jurassic palaeogeography of the Arctic region. Adapted after Ziegler (1990).

Throughout the Jurassic and earliest Cretaceous, Arctic palaeogeography and palaeoceanography were controlled principally by the break-up of Pangaea and the opening of the Arctic-North Atlantic rift (Fig. 2.4). From the earliest Jurassic a connection between the Tethys and Arctic seas was established via a series of major marine transgressions across the Arctic-North Atlantic rift system and by the end of the Early Jurassic, epi-continental seas covered much of Western and Central Europe (Ziegler, 1990; Doré, 1991). The development and uplift of the North Sea rift dome in the Middle Jurassic created a barrier between the Tethys and Arctic seas as a consequence of the silting-up and choking of the connecting seaways (Ziegler, 1990; Doré, 1991). This barrier was a major contributing factor to the pronounced provinciality displayed by marine faunas at this time (e.g., Arkell, 1956; Imlay, 1965; Stevens, 1967; Hallam, 1975; Doyle, 1987; Mutterlose, 1988, 1998). The North Sea rift dome collapsed during the Callovian to Volgian (Ziegler, 1990). At this time, a strong transgressive regime continued and crustal extension intensified throughout the Arctic-North Atlantic rift to re-open the Tethys-Arctic connection via a system of interconnected straits and seas (Ziegler, 1990; Doré, 1991; Bjerrum *et al.*, 2001). These conditions continued into the Early Cretaceous, although tectonic activity increased at the Jurassic-Cretaceous boundary (Ziegler, 1990) and a series of structural highs developed, which controlled faunal provinciality through the construction of land barriers in the European-Arctic seaway (Doré, 1991).

The deposition of organic-rich black shales is widespread in the Late Jurassic and Early Cretaceous, giving rise to extensive oil and gas accumulations across the circum-Arctic region (Ziegler, 1990; Doré, 1991; Langrock *et al.*, 2003; Mutterlose *et al.*, 2003; Langrock & Stein, 2004). Economically viable accumulations of such petroleum source rocks are known from West Siberia, the Barents Shelf, mid-Norway and the North Sea Basin (Doré, 1991). An increase in the preservation potential of organic carbon can be caused by several different mechanisms, such as anoxic bottom waters, high primary production, reduced clastic input and rapid burial (Demaison & Moore, 1980; Stein *et al.*, 1986; Meyers, 1997; Langrock *et al.*, 2003).

Late Jurassic and Early Cretaceous black shale formation in the Norwegian-Greenland seaway has been attributed to suboxic to anoxic bottom water conditions in restricted shallow marine basins as the result of a sea-level low stand (e.g., Ziegler, 1990; Mutterlose *et al.*, 2003; Langrock *et al.*, 2003). Langrock & Stein (2004) suggest that in addition to formation in anoxic or stagnant conditions, black shales from this region were

also deposited in highly-productive environments resulting from coastal upwelling. Macquaker & Keller (2005) consider organic-rich mudstone sedimentation from the Lower Cretaceous of Alaska to be attributed to high organic productivity related to episodic and rapid sedimentation rather than bottom water anoxia or upwelling. Doré (1991) concluded that organic-rich shale deposition was the result of multiple local mechanisms operating concurrently during the Late Jurassic and Early Cretaceous (e.g., a strong transgressive regime, extensional tectonics, reduced clastic input and the globally warm and equable climate), which together created an environment prone to stagnation and organic productivity in some basins. This trend was terminated post-Berriasian as the result of palaeoceanographic changes creating new ocean margins in the Canada Basin and Rockall Trough (Doré, 1991).

During the Early Cretaceous the Canadian Basin of the Arctic Ocean began to open (Ziegler, 1990; Hay et al., 1999) and the extensive rifting history of the Rockall Trough culminated in a spreading event (Doré, 1991). At the same time the narrow Greenland-Norwegian Seaway (at the north of the Arctic-North Atlantic rift) reached a length of 1500-2000 m and a width of ~300 km (Gradstein et al., 1999; Mutterlose et al., 2003). The rotational opening of the Canadian Basin may have provided a connection between the Arctic Basin and the Pacific Ocean, possibly along a narrow, deep passage to the South Anyui Basin (Hay et al., 1999; Mutterlose et al., 2003), although this passage may have been blocked by a land bridge so that there was no deep water connection between the Arctic Basin and the world ocean at this time (Mutterlose et al., 2003). In the mid-Cretaceous, tectonic activity gradually abated in Central and Western Europe (Ziegler, 1990). A major marine transgression in the Aptian-Albian submerged the structural highs created by Late Jurassic to Early Cretaceous tectonics and formed an open seaway from southern England to the Barents Sea, so that by the mid-Albian faunal connections from Svalbard to the Mediterranean had been fully established (Doré, 1991). Arctic-North Atlantic plate reorganisation continued from the Late Mesozoic until the Late EoceneNeogene post-Alpine plate reorganisation, which led to the present-day continent assembly and configuration of the Arctic Ocean (Ziegler, 1990).

#### 2.3. Palaeoclimate

As mentioned previously the Jurassic and Cretaceous periods are commonly considered as a time of warm, equable global climates (e.g., Frakes, 1979; Hallam, 1981, 1985, 1993). High mean annual temperatures, a low global temperature gradient (and subsequently weak climatic zonation) and warm polar regions are commonly hypothesised for this period (e.g., Frakes, 1979; Hallam, 1981; Barron, 1983).

A number of studies have, however, suggested that during this period a more variable climate with seasonally low ocean temperatures and limited polar ice caps would have been present (e.g., Francis & Frakes, 1993; Ditchfield, 1997; Price, 1999; Price & Mutterlose, 2004; Kessels *et al.*, 2006).

#### 2.3.1. Evidence for a Warm, Equable Climate

There is much compelling evidence to support the concept of a warm, equable, icefree climate during the Jurassic and Cretaceous periods. In the past, the reported absence of glacial deposits has been considered as sufficient evidence for a greenhouse world (e.g., Hallam, 1985). Some of the more convincing recent evidence is discussed below and includes information about CO<sub>2</sub> levels, polar forests and plant phenology, polar faunas, General Circulation Models (GCM's), stable isotopes and the new TEX<sub>86</sub> temperature proxy. It should be noted that much of this research has been conducted on the Cretaceous period.

The general assumption is that this greenhouse climate was related to high atmospheric concentrations of carbon dioxide (e.g., Barron *et al.*, 1993; Weissert & Lini, 1991; Francis & Frakes, 1993; Dromart *et al.*, 2003a; Royer *et al.*, 2004), with recent estimates for Jurassic and mid-Cretaceous CO<sub>2</sub> levels in the range of 1200 to 3000 ppm

(approximately 4-10 times modern pre-industrial values) (Dromart *et al.*, 2003a) and >4000 ppm (Bice & Norris, 2002) respectively. Additional factors of climatic significance may be the galactic cosmic ray flux (e.g., Shaviv & Veizer, 2003; Wallmann, 2004) and palaeogeography (e.g., Barron & Washington, 1982; Barron, 1983).

Perhaps the most compelling evidence of Jurassic and Cretaceous polar warmth is the abundance of fossil forest localities recorded from both poles (<85° palaeolatitude) throughout the Mesozoic (Spicer & Parish, 1986). The poleward limit of present day forest vegetation is 59°N - 72°N in the northern hemisphere and 55°S in the southern hemisphere (Falcon-Lang *et al.*, 2001). Cretaceous fossil forests have been recorded from high palaeolatitudes in Alaska (e.g., Herman & Spicer, 1997), Northern Russia (e.g., Spicer *et al.*, 2002), New Zealand (e.g., Kennedy *et al.*, 2002), Australia (e.g., Dettmann *et al.*, 1992) and Antarctica (e.g., Cantrill & Nichols, 1996; Falcon-Lang *et al.*, 2001; Falcon-Lang & Cantrill, 2001). In the northern hemisphere these forests tended to be dominated by deciduous vegetation and in the southern hemisphere by evergreen vegetation (Falcon-Lang & Cantrill, 2001; Brentnall *et al.*, 2005).

Plants are not mobile after germination and, therefore, strongly reflect the physical environment in which they lived (Spicer & Corfield, 1992). Analysis of fossil leaf phenology (e.g., Falcon-Lang & Cantrill, 2001), including physiognomy (e.g., Herman & Spicer, 1996, 1997; Spicer *et al.*, 2002), the analysis of growth rings or anatomical characters in trunk woods (e.g., Creber & Chaloner, 1985; Francis & Poole, 2002) and comparison with nearest living relatives (e.g., Chaloner & Creber, 1990) have yielded palaeotemperature information indicating that the Cretaceous poles were relatively warm. For example, Spicer *et al.* (2002) calculated a mean annual temperature of  $13.0 \pm 1.8^{\circ}$ C and a cold month mean temperature of  $5.5 \pm 3.3^{\circ}$ C for northeastern Russia during the mid-Cretaceous.

The extensive distribution of fossil fauna at high latitudes is also considered to be evidence for warmer polar climates in the past. The first record of polar dinosaurs is

believed to be that of Lapparent (1960) who discovered Iguanodon footprints on Svalbard. Since then, dinosaurs, mosasaurs, plesiosaurs, ichthyosaurs, champosaurs and crocodilians have all been recorded from Mesozoic polar regions (e.g., Huber, 1998; Markwick, 1998; Tarduno et al., 1998; Rich et al., 2002; Buffetaut, 2004; Kear, 2006). Many authors interpret such finds as providing confirmation that polar regions were warm rather than near freezing. Tarduno et al. (1998), for example, estimate a mean annual temperature of >14°C for the Late Cretaceous based on the presence of champosaurs in the Canadian Arctic. Poleward habitat expansion of marine thermophilic organisms (rudistid bivalves, gastropods, larger foraminifera and coral reefs) has also been observed and further supports the idea of Cretaceous polar warmth (Kauffman, 1973; Gordon, 1973; Habicht, 1979; Lloyd, 1982; Huber et al., 1995). It is worth noting, however, that Markwick (1998) considers the periodic absence of crocodilians from high latitudes in the Late Cretaceous as an indictor of cooling in these regions at these times and that Kear (2006) suggests that Early Cretaceous plesiosaur and ichthyosaur taxa may have possessed adaptations to enable them to cope with low temperatures (e.g., elevated metabolic levels or annual migration).

GCM's have been used to provide both qualitative and quantitative evaluation of Jurassic and Cretaceous climates. Such models have generally supported the concept of Mesozoic warmth in the mid- to low latitudes (e.g., Moore *et al.*, 1992; Barron *et al.*, 1995; Price *et al.*, 1997; Poulsen *et al.*, 1999) although the nature of high latitude climates is more equivocal. Barron *et al.* (1995) conducted a series of GCM simulations of mid-Cretaceous climate. Their model simulation, which best matched observations, recorded a globally averaged sea surface temperature of 6.2°C above present-day levels. Barron *et al.* (1995) suggest that this value is at the lowest end of estimates for Cretaceous warmth.

There is an abundance of stable isotope data consistent with a warm, equable greenhouse climate dominating the Jurassic and Cretaceous periods (e.g., Stevens & Clayton, 1971; Barron, 1983; Huber *et al.*, 1995; Clarke & Jenkyns, 1999; Poulsen *et al.*,

1999; Wilson & Norris, 2001; Norris *et al.*, 2002; Wilson *et al.*, 2002), although much of the available data concentrates on the mid- to Late Cretaceous. Barron (1983) estimated sea surface temperatures in the range of 27-32°C for equatorial regions in the Albian-Cenomanian based on planktonic foraminifera. This is consistent with the data of Wilson *et al.* (2002), who estimated equatorial sea surface temperatures of 30-33°C for the Turonian using glassy foraminiferal calcite and the data of Clarke & Jenkyns (1999), who estimated low-latitude temperatures of >33°C for the mid-Cretaceous generated from calcareous fine-fraction and bulk sediments from the Exmouth Plateau.

Huber *et al.* (1995) investigated foraminiferal data from the southern high latitudes to provide evidence of a reduced latitudinal temperature gradient for the mid- to Late Cretaceous. They record palaeotemperatures of 17-23°C from the Albian to Cenomanian and <33°C in the Turonian, although they acknowledge that such values seem "excessively warm" for palaeolatitudes of 56-60°S. Further evidence consistent with mid-Cretaceous high-latitude warmth was reported by Poulsen *et al.* (1999) who recorded palaeotemperatures of approximately 18-20°C in the southern high-latitudes (Falkland Plateau and southeast Indian Ocean at ~58-62°S). These values were derived from the  $\delta^{18}$ O ratios of foraminiferal calcite. The  $\delta^{18}$ O values however, were inconsistent with the model predictions of the same study (Poulsen *et al.*, 1999), which for the same sites predicted palaeotemperatures ranging from 7-11°C. It should be noted that for all of the above palaeotemperature estimates there is an estimate of  $\delta^{18}O_{seawater}$ . This can be highly variable and is a potential unknown that must be acknowledged (and is discussed later).

Shouten *et al.* (2002) developed a new organic palaeothermometer, TEX<sub>86</sub>, which is based on the composition of lipids in the membranes of crenarchaeota (floating marine micro-organisms) and is independent of salinity or nutrient availability (Schouten *et al.*, 2002). Using the TEX<sub>86</sub> proxy, low latitude palaeotemperatures of ~30-36°C for the mid-Cretaceous were calculated from the Shatsky Rise (Dumitrescu *et al.*, 2006). In addition, Jenkyns *et al.* (2004) calculated an average sea surface temperature of ~ 15°C for the Arctic Ocean in the Late Cretaceous and extrapolated a temperature in excess of 20°C for polar waters during the mid-Cretaceous. Such palaeotemperatures are however, significantly higher than many previous calculations and the technique has yet to be fully evaluated. Sluijs *et al.* (2006) applied the TEX<sub>86</sub> proxy to Arctic Ocean sediments deposited at the Paleocene/Eocene Thermal Maximum and recognised that the TEX<sub>86</sub> record was probably skewed towards summer temperatures, since the export of lipids to the sea floor coincides with high phytoplankton productivity and hence the Cretaceous estimates may represent extreme summer values.

#### 2.3.2. Evidence for Cold Polar Regions

The Mesozoic Era almost certainly represents the longest period of warmth during the Phanerozoic. Nevertheless, this period of warmth would have been punctuated by oscillations in climate, which may or may not have been of sufficient magnitude and duration to produce cooling and the formation of polar ice (Price, 1999). Whilst many authors argue that this is unlikely, or at the least highly equivocal (e.g., Rowley & Markwick, 1992), there is much compelling evidence to the contrary (e.g., Moore *et al.*, 1992; Sellwood *et al.*, 1994; Pirrie *et al.*, 1995; Stoll & Schrag, 1996; De Lurio & Frakes, 1999; Price, 1999; Gale *et al.*, 2002; Alley & Frakes, 2003; Dromart *et al.*, 2003a; Miller *et al.*, 2003, 2005). The evidence presented below includes data from stable isotopes, GCM's, sea-level curves and from glacially derived sediments and minerals.

Much of the isotopic evidence for warm, equable Jurassic and Cretaceous climates has been based on climatic data derived from the mid- to low palaeolatitudes (Ditchfield, 1997; Price & Mutterlose, 2004), introducing a potential bias when considering higher latitude conditions. Even in studies conducted in the mid to low latitudes however, cooling episodes have been observed during the Cretaceous greenhouse climate (e.g., Stoll & Schrag, 2000; Miller *et al.*, 2003, 2005). Pucéat *et al.* (2003) investigated Tethyan marine waters using the oxygen isotope composition of fish tooth enamel. They were able to

distinguish three major cooling events at the million-year scale: at the Berriasian-Valanginian boundary; during the earliest Late Valanginian; and during the earliest Aptian. Such data are supported by other studies, for example, van de Schootbrugge *et al.* (2000), which identifies progressively cooler temperatures from the late Valanginian to early Hauterivian in southeastern France.

Where studies of high latitude sites have been undertaken, the isotopic data often record palaeotemperature values that are significantly cooler than might be expected based on mid- to low latitude estimates (e.g., Barrera *et al.*, 1987; Pirrie & Marshall, 1990; Ditchfield *et al.*, 1994; Sellwood *et al.*, 1994; Pirrie *et al.*, 1995; Ditchfield, 1997; Price & Mutterlose, 2004). It is possible, that studies recording very warm temperatures for the high-latitude regions may be recording a diagenetic component, since partial recrystallisation will generally lower  $\delta^{18}$ O values and, therefore, generate overestimates of palaeotemperature (Schrag *et al.*, 1992). Price *et al.* (1996) argue that this may account for the "intuitively unlikely" temperatures proposed by Huber *et al.* (1995) for the mid- to Late Cretaceous southern high-latitudes (<33°C).

Ditchfield *et al.* (1994) conducted an oxygen isotope study of molluscan macrofossils in Antarctica. They concluded that mean temperatures of almost 0°C may have occurred at the South Pole from the mid-Cretaceous and that elevated high latitude terrains were probably glaciated. Price & Mutterlose (2004) calculated minimum palaeotemperatures of 2°C derived from belemnites from the late Valanginian to early Hauterivian in the Yatria River, Western Siberia. This is consistent with the data of Polyak *et al.* (2003) whose stable isotope measurements of modern benthic foraminifera in the Kara and Pechora seas record an annual range of temperatures from -1 to +12°C. Cretaceous isotopic data have also been derived from foraminifera, for example, Sellwood *et al.* (1994) produced a poleward extrapolation of planktonic foraminiferal data to give an estimate of mid-Cretaceous latitudinal variations in mean annual temperature. Their model

suggested that palaeotemperatures could reach sub-freezing values at both poles during this time.

Several GCM simulations have predicted the presence of sub-freezing conditions and limited polar ice at the Jurassic and Cretaceous poles. Moore *et al.* (1992) considered two simulations of the Kimmeridgian/Tithonian palaeoclimate with differing CO<sub>2</sub> levels (280 and 1200 ppm). Each simulation predicted the presence of sea-ice, although the amount of sea-ice was significantly reduced in the 1200 ppm simulation. Valdes *et al.* (1995) also used a GCM to predict the presence of ice during the Late Jurassic. Their data indicate the presence of a modest, but significant Antarctic ice-cap, which they suggest would have disappeared at times of maximum seasonal forcing. Mid-Cretaceous greenhouse and icehouse climates were modelled by Price *et al.* (1998). Their icehouse simulation predicts small permanent ice-caps at both poles during this time.

Further evidence for the presence of ice sheets during the Jurassic and Cretaceous can be found in records of rapid sea level change. Stoll & Schrag (1996) use strontium data from the Berriasian and Valanginian to suggest that global sea level fluctuated by ~50 m over 200,000 to 500,000 years and that such geologically rapid fluctuations indicated the existence of an Antarctic ice sheet at this time. This hypothesis is supported by the authors oxygen isotope measurements, which suggested that these rapid sea level changes were indeed caused by the growth of continental ice sheets. Dromart *et al.* (2003a) provide a detailed record of northern hemisphere sea surface temperatures for the Middle to Late Jurassic transition that record a severe cooling event coincident with an abrupt global-scale sea level fall. Such data could indicate a period of ice sheet formation, which the authors suggest may have developed over the mountainous regions of far-east Russia. A further sea level study of the Late Cretaceous shows large and rapid sea level changes occurring on a global scale, which are also interpreted as having a glacio-eustatic control (Miller *et al.*, 2003). Miller *et al.* (2003, 2005) comment that the only alternative to a glacio-eustatic mechanism would be something that is as yet undefined since other potential mechanisms

(e.g., water storage in lakes, groundwater, deepwater changes or sea ice) cannot explain such large and rapid sea level changes.

Tillites, dropstones and glendonites are often considered to be evidence of glacial conditions. Deposits with affinities to glacial tillites have been described from the Jurassic and Cretaceous of Russia, Siberia, Eastern Europe, Antarctica, South America and Australia (e.g., Epshteyn, 1978; Chumakov, 1981a, b; Woolfe & Francis, 1991; Price, 1999; Huber *et al.*, 2001; Alley & Frakes, 2003). However, the glacial nature of such deposits is often disputed and alternative mechanisms of origin are commonly proposed. For example, Oberbeck *et al.* (1993) and Rampino (1994) suggest that meteoric impacts could produce tillite-like deposits.

Potential dropstones have been described from the Jurassic and Cretaceous of Europe and Australia (e.g., Pickton, 1981; Jeans *et al.*, 1991; Frakes & Krassay, 1992; Francis & Frakes, 1993; Price, 1999). Such deposits are commonly considered to be the result of ice-rafting, although, it should be noted that Bennett & Doyle (1996) and Bennett *et al.* (1996) argue that caution should be exercised when interpreting dropstone evidence, because there are many agents besides icebergs by which dropstones may be transported (e.g., seaweed, kelp, driftwood).

Glendonites are star shaped calcite pseudomorphs after the metastable mineral ikaite that are commonly taken to reflect deposition in cold subaqueous conditions (Francis & Frakes, 1993; Sellwood & Price, 1994; De Lurio & Frakes, 1999). Cretaceous glendonites have been identified from Svalbard (Kemper, 1983), Australia (De Lurio & Frakes, 1999; Alley & Frakes, 2003) and Canada (Kemper & Schmitz, 1975, 1981). De Lurio & Frakes (1999) investigated glendonites from the Lower Cretaceous Bulldog Shale in Australia and concluded that the presence of glendonites at this site indicated a gradual warming of waters from near-freezing temperatures to temperatures above 5-8°C.

A well argued overview of this debate is presented by Price (1999). He evaluates published evidence for Mesozoic ice and cool temperatures from around the world. Based

on such evidence he suggests that several cold or sub-freezing periods can be identified in the polar regions, namely, during the (?)Pliensbachian, Bajocian-Bathonian, Tithonian/Volgian, Valanginian and Aptian. Price (1999) concludes that although high latitude warmth is the norm throughout the Mesozoic, the occurrence of limited polar ice at times is not a myth but a reality.

### **3. BELEMNITES**

## 3.1. Systematic Position

The Belemnoidea (Hyatt, 1884) are a superorder of the Coleoidea, a monophyletic group of cephalopod molluscs characterised primarily by their possession of an internal (endocochleate) shell (Doyle *et al.*, 1994; House, 1998). The Belemnoidea first appeared in the Early Devonian (Engeser & Bandel, 1988; Doyle, 1990a), possibly in response to the diversification of fish at the time (Young *et al.*, 1998) and finally became extinct at the Cretaceous/Tertiary boundary (Engeser & Bandel, 1988).

Autapomorphies (the characteristics defining a taxon) of the Belemnoidea are the closing organic membrane of the phragmocone, the 5-layered conotheca (the outer wall of the phragmocone), and the presence of arm hooks on ten subequal arms (Engeser & Bandel, 1988; Engeser, 1990). These characters are widely accepted, although some have yet to be demonstrated in certain groups.

The Belemnoidea can be subdivided into the orders Aulacocerida (Middle Carboniferous - Early Jurassic), Belemnitida (Early Jurassic - end-Cretaceous) and Diplobelida (Late Jurassic - mid-Cretaceous), based primarily on their body chamber characteristics (Doyle *et al.*, 1994; Doyle & Shakides, 2004). The Order Belemnitida (Zittel, 1895) is the one to which the true 'belemnites' belong. The classification of the Belemnitida shown below is based on that of Doyle *et al.* (1994). Information beyond family level is not given.

In addition to the suborders Belemnitina and Belemnopseina (as included here), other suborders have also been included in various Belemnitida classifications (e.g., Diplobelina (Jeletzky, 1966; Mutterlose, 1988) and Belemnotheutididina (Doyle *et al.*, 1994)), however the taxonomic positions of such suborders are often disputed, with some authors preferring to create new orders for such problematic groups. As such, only those

suborders universally recognised (Belemnitina and Belemnopseina) have been included here.

The major distinction between the Belemnitina and Belemnopseina is in the ventral groove. The Belemnitina display apical furrows, whilst the Belemnopseina possess alveolar grooves (Mutterlose, 1988).

Class CEPHALOPODA Cuvier, 1794

Subclass COLEOIDEA Bather, 1888

Superorder BELEMNOIDEA Hyatt, 1884

Order BELEMNITIDA Zittel, 1895

Suborder BELEMNITINA Zittel, 1895

Family PASSALOTEUTHIDIDAE Naef, 1922

Family SALPINGOTEUTHIDIDAE Doyle, 1992a

Family HASTITIDAE Naef, 1922

Family CYLINDROTEUTHIDIDAE Stolley, 1919

Family OXYTEUTHIDIDAE Stolley, 1919

Suborder BELEMNOPSEINA Jeletzky, 1965

Family BELEMNOPSEIDAE Naef, 1922

Family DICOELITIDAE Saks and Nal'nyaeva, 1967

Family PSEUDODICOELITIDAE Saks and Nal'nyaeva, 1967

Family DUVALIIDAE Pavlow, 1914

Family BELEMNITELLIDAE Pavlow, 1914

Family DIMITOBELIDAE Whitehouse, 1924

## 3.2. The Belemnite Animal

The discussion presented below provides a general overview of belemnite morphology, palaeoecology and palaeobiogeography, as well as an overview of the use of belemnites in palaeoclimate studies. It is worth considering, however, that with regards to belemnite morphology and palaeoecology one model may not fit all.

### 3.2.1. Belemnite Morphology

The belemnite animal can perhaps best be described as a marine squid-like cephalopod (e.g., Bandel & Spaeth, 1988; Cox & Doyle, 1996; Clarkson, 1998), similar in appearance to the extant squid *Loligo* (Bandel & Spaeth, 1988). Modern squids possess a flexible, unmineralised internal shell called a gladius, which is composed of chitin (Donovan & Toll, 1988). Unlike most modern squid however, belemnites possessed a hard (calcified) internal skeleton (Kear *et al.*, 1995; Cox & Doyle, 1996). The only extant coleoid families which also possess mineralised tissue are the Sepiidae and Spirulidae (Kear *et al.*, 1995), which have retained a primitive phragmocone (Young *et al.*, 1998). The Sepiidae and Spirulidae are, therefore, commonly considered to be the closest analogue for the extinct order Belemnitida.

The hard internal skeleton of the belemnite animal is known as a rostrum (and is also commonly referred to as a guard, although this has an invalid functional connotation (Doyle & Kelly, 1988; Doyle, 1990a)). The rostrum is composed of low-magnesium calcite (Hudson & Anderson, 1989; Sælen, 1989; Doyle & Bennett, 1995) and is consequently readily preserved in the fossil record (as discussed later).

Early belemnite studies interpreted concentric rings exhibited within the rostrum as primary seasonal growth bands (e.g., Bøggild, 1930; Müller-Stoll, 1936; Urey *et al.*, 1951; Spaeth *et al.*, 1971) and the observed variations in oxygen isotope ratios between the bands were, therefore, interpreted as seasonal variations in temperature (Urey *et al.*, 1951). Longinelli (1969) however, hypothesised that diagenetic processes may have simulated seasonal temperature variations, since it was apparent that radial variations in oxygen isotope composition could be observed in belemnites that had undergone considerable diagenetic alteration (whilst such oscillations, if a primary feature, should be obscured by

diagenesis). Modern studies suggest (although not conclusively) that this pattern of concentric rings was probably the result of organic matter decay (Rosales *et al.*, 2004a). It is believed that belemnite rostra were originally composed of radial crystals of low-magnesium calcite, which were porous and contained variable amounts of organic matter that would have decayed post-mortem to create void space that was later infilled by secondary calcite (e.g., Sælen, 1989; Sælen & Karstang, 1989; Podlaha *et al.*, 1998; Rosales *et al.*, 2004a).

The rostrum is the largest and most posterior section of the belemnite shell (Fig. 3.1). It is cylindriconical in form, tapers to a point posteriorly and is indented by a conical cavity (the alveolus) at the anterior end (Clarkson, 1998). The phragmocone is an aragonitic, thin-walled and chambered part of the shell situated within, and projecting out of the alveolus (Sælen, 1989; Clarkson, 1998). A slender siphuncle threads through the phragmocone septa at the ventral margin (Clarkson, 1998). The final (and most anterior) component of the belemnite shell is the pro-ostracum. This is a long, flat, tongue-shaped extension of the phragmocone, which projects forwards and presumably covered the anterior part of the body (Clarkson, 1998). These three major components of the belemnite shell with the complete structure surrounded by soft tissue.

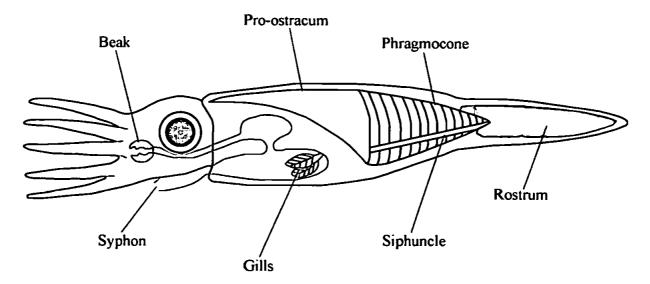


Figure 3.1 Belemnite morphology. A reconstruction of a living belemnite showing the internal skeleton. Adapted after Eyden (2003).

The preservation of belemnite soft body parts is extremely rare, although four belemnite specimens with soft parts, ink sacs and hooks preserved have been described from the Early Jurassic Posidonia Shale of South Germany (Reitner & Urlichs, 1983; Riegraf & Hauff, 1983; Engeser & Clarke, 1988). These specimens show the outline of the mantle and head, arms with double rows of hooks, but no fins (Hewitt *et al.*, 1999). No clear records of belemnite fins have ever been discovered, although fins are frequently included in reconstructions (Young *et al.*, 1998). For hydrodynamic reasons it seems likely that small manoeuvrable fins would have been present (probably attached at the sides, where lateral grooves can be seen in the rostrum), as in other coleoids (Monks *et al.*, 1996; Hewitt *et al.*, 1999).

Belemnites are believed to have had 10 subequal arms, each equipped with 30-50 pairs of normal sized hooks (Engeser & Bandel, 1988; Engeser & Clarke, 1988). Of the four belemnites described from the Posidonia Shale, one had a very large 'onychite' hook at the base of the arm crown, which has been interpreted as a sexual modification, probably of the male belemnite (Engeser & Clarke, 1988). The possibility of sexual dimorphism in belemnites was first proposed by d'Orbigny (1842) and has since been mentioned by numerous authors, for example Phillips (1867), Lissajous (1925), Roger (1952), Waterston (1952), Delattre (1956), Stevens (1965a), and Doyle (1985). The presence of dimorphic characters in ammonites (e.g., Makowski, 1963; Calloman, 1963; Palframan, 1966) and extant cephalopods (e.g., Westermann, 1969) has been widely accepted and it therefore seems reasonable to expect some degree of dimorphism in belemnites (Doyle, 1985).

### 3.2.2. Belemnite Palaeoecology

Belemnites, like modern squid, were nektonic organisms (Stevens, 1963; Spaeth *et al.*, 1971; Bandel & Spaeth, 1988; Anderson *et al.*, 1994; Doyle *et al.*, 1997; Rosales *et al.*, 2004a). Today, squid inhabit a diverse range of marine environments, including, the pelagic zones of shallow estuaries, continental shelves and open oceans, as well as the deep

sea, and polar oceans (Pörtner & Zielinski, 1998). This might suggest that belemnites also inhabited a comparable range of environments.

Hewitt et al. (1999) suggest that belemnites would have swum in a horizontal position similar to that of modern Loligo, although the method for achieving this horizontal poise is debated (e.g., Monks et al., 1996; Hewitt et al., 1999). Belemnites were presumably active pelagic swimmers, although there is also evidence to suggest that some may have been nektobenthic (Bandel & Spaeth, 1988; Anderson et al., 1994; Martill et al., 1994). A disparity in the oxygen isotope derived palaeotemperatures of belemnites and ammonites has long been recognised (e.g., Tan et al., 1970), and indicates that these nektonic organisms preferred to inhabit different positions in the water column. For example, Tan et al. (1970) observed a depletion of 1.0 to 1.6 ‰ in the oxygen isotope values of ammonites compared with associated belemnites, which they interpreted as ammonites inhabiting warmer, near-surface or near-shore waters than belemnites. Anderson et al. (1994) and Wierzbowski & Joachimski (2006) also record a lower range of palaeotemperatures for belemnites than for ammonites. These lower temperatures are often indistinguishable from those derived from benthic bivalves (Anderson et al., 1994) or oysters (Wierzbowski & Joachimski, 2006) of the same succession, which the authors interpret as belemnites inhabiting colder, deeper waters than the ammonites, which inhabited the warmer surface waters. This interpretation is supported by other authors (e.g., Martill et al., 1994; Price & Sellwood, 1994; van de Schootbrugge et al., 2000).

Analysis of concave septa in extant and fossil cephalopods can provide an estimate of the mechanical limits of coleoid shells to water depth. Westermann (1973) estimated that the Belemnitida would have inhabited rather shallow waters, with a maximum depth range of 50-200 m. The exception to this being *Cylindroteuthis*, which could potentially have descended to a maximum depth of 400 m. The notion that belemnites were restricted to shallow shelf waters is supported by the abundance of fossilised belemnite rostra in shallow marine deposits (e.g., Podlaha *et al.*, 1998).

It is now commonly accepted that belemnites lived in neritic (probably near-shore to mid-shelf) environments rather than in the open ocean (Christensen, 1976; Wignall & Hallam, 1991; Monks *et al.*, 1996; Rosales *et al.*, 2004a). The observed diversity in the habitats of modern squid however (e.g., Pörtner & Zielinski, 1998), may suggest that belemnites potentially inhabited different sub-habitats (which could be reflected in isotopic values). It has been hypothesised that although active swimmers, belemnites could have been restricted to shelf areas by their prey, which were themselves confined to the shelves (Stevens, 1963).

By analogy with extant squid it has been deduced that belemnites were carnivorous, hunting small fish and crustaceans (Bandel & Spaeth, 1988). Belemnites themselves were preyed upon by bony fish, sharks and marine reptiles (e.g., ichthyosaurs) (Cox & Doyle, 1996). Evidence for such predation has been identified in the form of tooth marks in belemnite rostra (Hölder, 1973; Hewitt, 1980) or healed rostra (Abel, 1916), as well as the presence of rostra (Bandel & Spaeth, 1988; Pollard, 1990; Cox & Doyle, 1996) and belemnite arm hooks (Martill, 1996) in the stomach contents of well preserved sharks and ichthyosaurs. Fossilised ichthyosaur vomit has even been discovered, with the regurgitated belemnites displaying signs of acid etching, presumably from the ichthyosaurs digestive juices (Doyle, 2002). The presence of an ink sac in exceptionally preserved specimens indicates that belemnites would have been able to expel a cloud of ink as a defensive mechanism when under attack (Bandel & Spaeth, 1988; Cox & Doyle, 1996).

Mass accumulations of belemnite rostra ('belemnite battlefields') are common in the Mesozoic fossil record (e.g., Quenstedt, 1856; Frebold, 1957; Taylor *et al.*, 1979; Jarvis, 1980; Ager, 1988; Doyle & Macdonald, 1993). This might suggest that like the majority of living coleoids, belemnites tended to form schools, particularly for feeding and spawning (Doyle & Macdonald, 1993). Post-spawning mortality has been recorded from almost all extant coleoid groups (Mangold, 1987) and has been extensively investigated in neritic squid populations (e.g., Fields, 1965; Mangold, 1987). Such a mechanism could

easily account for the occurrence of belemnite battlefields, where the population is composed only of adult individuals of a single species (e.g., Doyle & Macdonald, 1993).

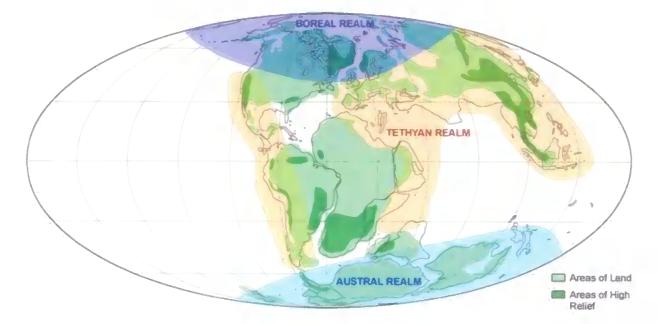
# 3.3. Belemnite Palaeobiogeography

Since the now classic study of Neumayr (1883) it has been recognised that many Jurassic marine faunas do not have a cosmopolitan distribution (Hallam, 1975; Fürsich & Sykes, 1977). Such provinciality has been well summarised by several authors (e.g., Arkell, 1956; Imlay, 1965; Stevens, 1967).

Belemnite provinciality developed in the Early Jurassic (Doyle, 1987) and from the Late Jurassic to Early Cretaceous belemnites occupied three distinct faunal realms (Fig. 3.2): the Boreal Realm (Russia, northern Europe, Greenland and North America) dominated by the suborder Belemnitina, which is often informally divided into the Boreal-Atlantic and Boreal-Arctic Provinces; the Tethyan Realm (southern and central Europe, East Africa, Madagascar, Antarctica, South America, Australasia and India) dominated by the suborder Belemnopseina and informally divided into the Mediterranean and Indo-Pacific Provinces; and the Austral Realm (Madagascar, Patagonia, New Zealand), dominated by the family Dimitobelidae (Stevens, 1963, 1971, 1973a, b; Doyle, 1987; Mutterlose, 1988, 1998). These realms persisted until the Aptian, when the Tethyan and Boreal Realms were homogenised by cosmopolitan taxa and a bipolar distribution of belemnites developed resulting in a Tethyan-Boreal Realm and an Austral Realm (Stevens, 1973b; Mutterlose, 1988, 1998; Doyle, 1992b).

The boundaries of these realms changed through time and migration between the realms was rare. The causes of this provinciality have been widely debated (e.g., Stevens, 1963, 1965b, 1973a, b; Fürsich & Sykes, 1977, Doyle, 1987) and include climate control, temperature or salinity gradients, environmental stability and physical or physiological barriers. The dominance of certain belemnite genera in the different realms has been

comprehensively described by a number of authors (e.g., Stevens, 1963, 1973a, b, Mutterlose *et al.*, 1983; Mutterlose, 1988, 1998; Doyle, 1987, 1992b).



**Figure 3.2** Hauterivian palaeobiogeography. The three distinct belemnite Realms are shown. Palaeogeographic map adapted after Smith *et al.* (1994) with additional palaeobiogeographic data from Stevens (1971, 1973b) and Doyle (1987).

#### 3.3.1. Boreal Realm

In the Pliensbachian, Boreal-Tethyan provinciality can be distinguished in certain ammonite families (Howarth, 1973; Hallam, 1975). It is not until the Toarcian, however, that such provinciality can be confirmed in belemnites (Doyle, 1987). In the Toarcian belemnites colonised Siberia, Svalbard and North America for the first time (Doyle *et al.*, 1997) with fauna dominated by endemic genera (Saks & Nal'nyaeva, 1970, 1975; Doyle *et al.*, 1997).

From the late mid-Jurassic the family Cylindroteuthidae became dominant in the Boreal Realm, after their first appearance in the Bajocian-Bathonian interval (Doyle, 1987). At this time the realm was characterised by the genera *Cylindroteuthis* and *Pachyteuthis. Pachyteuthis* evolved in the Arctic Basin from the Bajocian onwards and therefore dominated the Boreal-Arctic Province, whilst the Boreal-Atlantic Province was dominated by *Cylindroteuthis* (Mutterlose, 1988). Both genera were extremely common throughout the Boreal regions, with specimens found in sediments from Svalbard, North Russia and East Greenland (Doyle, 1987). However, in the Kimmeridgian *Cylindroteuthis* and *Lagonibelus* migrated into the Boreal-Arctic Province so that by the Early Cretaceous the Boreal-Atlantic Province was characterised by the cylindroteuthid genus *Acroteuthis* (which appeared in the Volgian), although *Cylindroteuthis* and *Pachyteuthis* were still common in places (e.g., Doyle, 1987; Mutterlose, 1988).

In the Late Berriasian (and into the Early Valanginian) *Acroteuthis* assumed dominance in both the Boreal-Atlantic and Boreal-Arctic Provinces (Stevens, 1973b). This dominance continued until the Early Hauterivian, when the Tethyan genus *Hibolithes* invaded the Boreal Realm and largely displaced *Acroteuthis* in the Boreal-Atlantic Province (Doyle, 1987). In the Barremian the differentiation of the Boreal Realm cannot be recognised and by the Albian, a distinct Boreal assemblage no longer exists (Mutterlose, 1988).

The Boreal family Cylindroteuthidae remained restricted to the Boreal Realm throughout the Late Jurassic and Early Cretaceous, despite the presence of conditions suitable for incursions of Tethyan taxa during parts of the Early Cretaceous (Mutterlose, 1998).

### 3.3.2. Tethyan Realm

During the Early Jurassic, belemnite evolution was centred in Europe, with migration somehow prevented until the Late Pliensbachian (Stevens, 1973a). Belemnites became widespread for the first time in the Toarcian, with diversity increasing significantly in the Late Toarcian (Doyle *et al.*, 1997).

From the mid-Jurassic the Tethyan Realm was characterised by the belemnopseid genera *Hibolithes* and *Belemnopsis* (Stevens, 1963; Doyle, 1987, 1992b; Mutterlose, 1988, 1998; Doyle *et al.*, 1997). *Belemnopsis* first appeared in the Mediterranean region during the Toarcian and in the Aalenian *Belemnopsis* migrated to the north and south (Mutterlose, 1988). *Hibolithes* gradually replaced *Belemnopsis* in the Mediterranean region throughout

the Callovian, to become the dominant Mediterranean genus by the Oxfordian (at which time European-type belemnites still dominated the Tethyan seaway) (Stevens, 1973a). From the Oxfordian, the Tethyan Realm faunas became differentiated into Mediterranean (with rare *Belemnopsis*) and Indo-Pacific Provinces (dominated by endemic *Belemnopsis* species) (Stevens, 1971, 1973a; Mutterlose, 1988).

The belemnopseid taxa continued their dominance of the Tethyan Realm into the Early Cretaceous. In the Valanginian of Europe, species of *Hibolithes*, *Duvalia* and *Conobelus* evolved and migrated along the Tethyan seaway, whilst the Indo-Pacific Province largely disappeared (Stevens, 1973b). During the Valanginian and Hauterivian, the Tethyan genus *Hibolithes* was able to penetrate the Boreal Realm and co-exist with cylindroteuthids, for example in the Pechora Basin, Svalbard and California (Doyle, 1987). The Aptian Tethyan Realm was characterised by *Mesohibolites*, *Neohibolites* and *Parahibolites* (Stevens, 1973b; Mutterlose, 1988).

The Tethyan Realm finally disappeared after the Early Cenomanian with the extinction of Belemnitidae genera *Neohibolites* and *Parahibolites* and for the remainder of the Cretaceous only Austral Realm and (homogenised) Tethyan-Boreal Realm faunas can be differentiated (Stevens, 1963, 1973b; Doyle, 1992b).

#### 3.3.3. Austral Realm

The anti-Boreal (Austral) Realm first developed during the Kimmeridgian-Tithonian in waters with earlier Jurassic Tethyan affinities and became firmly established after the Hauterivian (Stevens, 1973a, b). Throughout the Kimmeridgian and Tithonian, Indo-Pacific Province belemnites (*Belemnopsis, Hibolithes, Duvalia, Conobelus*) occupied much of the Southern hemisphere, extending to approximately 75°S. At this time an endemic form of *Belemnopsis* evolved in Madagascar and Patagonia that is believed to be the precursor of the Austral Realm genera (Stevens, 1973a).

The Dimitobelidae, which eventually dominated the Austral Realm, populated the Indo-Pacific and western Antarctic regions from the Aptian onwards, leading Stevens (1965) to differentiate them as part of an Indo-Pacific Realm, although Stevens (1973a, b) recognised that their later association with other Cretaceous Austral taxa, suggested that they should instead be assigned to an Austral Realm. From the Early Cenomanian the Austral Realm belemnites became restricted to Australasia and Antarctica (Stevens, 1973b; Doyle, 1992b).

## 3.4. Belemnites as Palaeoclimate Indicators

Urey (1947) was the first to hypothesise the correlation between temperature and  $\delta^{18}$ O variations as recorded in primary calcite. This was later confirmed by Epstein *et al.* (1953). Since that time belemnites have been considered to be one of the most eminently suitable fossil groups for palaeotemperature determinations (Spaeth *et al.*, 1971), because they have arguably the highest potential to preserve an original isotopic signal (Marshall, 1992). Belemnite rostra are constructed of low-magnesium calcite (Sælen, 1989), which is relatively insoluble in surface environments (compared with high-magnesium calcite or aragonite, which are metastable) and is therefore unlikely to undergo significant pervasive alteration (Marshall, 1992). It is worth noting that evidence for a belemnite species with an aragonitic rostrum has been presented (Bandel & Kulicki, 1988). There is also evidence for the incorporation of small amounts of phosphate in the carbonate rostrum (Longinelli *et al.*, 2002, 2003). Some modern marine organisms (e.g., *Sepia*) precipitate small amounts of phosphate (<0.5 %) in their carbonate shells, with such precipitation in isotopic equilibrium with the carbonate and ambient seawater (Bettencourt & Guerra, 1999; Longinelli *et al.*, 2003).

Belemnites are lergely facies independent and have a wide geographic range (from the Toarcian until their extinction at the end-Cretaceous) (Doyle and Bennett, 1995). Consequently belemnites are relatively abundant in the fossil record, and can therefore be used for accurate comparisons of palaeotemperatures on considerable spatial and temporal scales. This is important because different organisms can give different palaeotemperature results from the same locations, e.g., belemnites and ammonites (Tan *et al.*, 1970; Anderson *et al.*, 1994), and belemnites and planktonic foraminifera (Huber *et al.*, 1995; Price *et al.*, 1996; Huber & Hodell, 1996). Belemnites appear to record cooler palaeotemperatures than known shallow water taxa (Lowenstam & Epstein, 1954; Pirrie & Marshall, 1990; Ditchfield *et al.*, 1994), supporting the notion that belemnites inhabited intermediate to benthic water depths. Today, belemnite-derived palaeotemperatures are thought to potentially represent minimum estimates of sea-surface temperatures at high latitudes (Price *et al.*, 1996), as vertical ocean temperature gradients in shallow, high latitude regions will be minimal (Barrera *et al.*, 1987; Price *et al.*, 1996).

As an extinct group of organisms, belemnites provide several complicating factors when being considered for palaeoenvironmental analysis, since it is impossible to observe their life cycle and habitat. Being nektonic animals, it is possible that their habitat changed with ontogeny, perhaps as the result of migration, either laterally or vertically in the water column. Significant lateral migration appears unlikely, given the distinct provinciality exhibited by belemnites (e.g., Stevens, 1963, 1973a, b; Mutterlose *et al.*, 1983; Doyle, 1987, 1992b, 1997; Mutterlose, 1988, 1998). However, short-range lateral and vertical migration within a biogeographic province seems probable. Such behaviour would almost certainly produce an isotopic shift in shell composition, and shells can therefore be expected to preserve an average record of temperature for the areas in which the individual animal lived and secreted its shell (Spaeth *et al.*, 1971).

Another factor to be considered is that belemnite shell precipitation may involve a 'vital effect'. This occurs when an organism does not secrete its shell in equilibrium with its environment, a process that is known from several marine organisms, most notably echinoderms (Spaeth *et al.*, 1971) and corals (Hudson & Anderson, 1989). Modern cephalopods however, are known to secrete their shells very close to equilibrium with

seawater (Taylor & Ward, 1983; Morrison & Brand, 1986; Rosales *et al.*, 2004a; Rexfort & Mutterlose, 2006). More specifically, the oxygen isotope composition of extant molluscan shells appears to be in equilibrium with ambient seawater, whilst for the carbon isotope, disequilibrium precipitation often prevails, with shells being less enriched in <sup>13</sup>C than might be predicted (Wefer and Berger, 1991; Klein *et al.*, 1996; Bettencourt & Guerra, 1999; Geist *et al.*, 2005). Wefer & Berger (1991) attribute this to the presence of a larger pool of oxygen (i.e., water) compared with carbon (i.e., dissolved inorganic carbon, mostly bicarbonate) available for shell formation. The observed offset in the carbon isotope data is often attributed to a contribution from metabolic or kinetic carbon (e.g., Tanaka *et al.*, 1986; Klein *et al.*, 1996; Geist *et al.*, 2005).

Such isotopic disequilibrium has been observed in the cephalopod genera Sepia. Spirula, Argonauta and Nautilus (Rexfort & Mutterlose, 2006). Rexfort & Mutterlose (2006) studied stable isotope records from Sepia officinalis as an analogy for belemnites. They concluded that the oxygen isotope composition of Sepia was in equilibrium with the surrounding seawater and therefore, reflected ambient temperature. However, for the carbon isotope signal a biofractionation control was possible, although it was acknowledged that no direct conclusions could be drawn from their dataset. Wefer & Berger (1991) recorded lighter than expected carbon isotope values in the earliest portion of the calcareous shells. This, however, has been interpreted as the result of embryonic precipitation of the earliest septa within the egg (Eichler & Ristedt, 1966; Cochran et al., 1981; Taylor & Ward, 1983; Wefer & Berger, 1991). Belemnite rostra can, therefore, be considered to record both carbon and oxygen isotope changes in ambient seawater, and be used for palaeoclimatic analysis, providing care is taken with the use of juvenile specimens or early ontogenetic elements of the rostra. It is also important to note that no major seasonal or taxonomic differences in fractionation have yet been confirmed (Sælen et al., 1996; Podlaha et al., 1998; Rosales et al., 2004a), although McArthur et al. (2004) suggest that differences in fractionation or habitat may potentially produce a disparity in stable isotope values for different belemnite species.

Finally, it is important to ensure that the calcite being analysed has not been postdepositionally altered to corrupt the primary isotopic composition. Methods of identifying diagenesis are described and evaluated by Sælen (1989) and include scanning-electron microscopy, cathode-luminescence microscopy, blue-light fluorescence microscopy, staining of thin sections (using Dickson's (1955, 1966) methodology), and x-ray diffractometry. Furthermore, trace element geochemistry, in particular the analysis for Mn and Fe can be used to screen for diagenesis (see Chapter 4), as Fe and Mn are commonly associated with diagenetic cements (Veizer *et al.*, 1983). Once a belemnite has been ascertained to be unaltered (or only altered in easily removable sections of the specimen) it can be analysed with confidence.

## 4. METHODOLOGY

## 4.1. Selection of Sites

The purpose of this research is primarily to investigate northern high latitude climates during the Late Jurassic and Early Cretaceous. In order to explore this, it was necessary to consider a range of field locations. Those selected for this study were: Staffin Bay, Isle of Skye, Scotland; Helmsdale, Sutherland, Scotland; Izhma River, Timan-Pechora Basin, Russia; Boyarka River, Yenisei-Khatanga Basin, Northern Central Siberia; and Festningen and Janusfjellet, Svalbard. Each of the sites selected was situated within the Boreal Realm of the Late Jurassic - Early Cretaceous, with the sites deliberately chosen to provide a significant spatial and temporal distribution of data.

In terms of spatial distribution (Fig. 4.1), the sites ranged from palaeolatitudes of  $\sim$  45°N (Isle of Skye and Sutherland) at the periphery of the Boreal Realm to  $\sim$  70°N (Boyarka River), well within the palaeogeographic Arctic Circle (according to Smith *et al.*, 1994). The sites are also well distributed throughout the eastern circumpolar region.

The ages of the sections varied from Callovian (Middle Jurassic) in Staffin Bay, Brora (Sutherland), the Izhma River, Festningen and Janusfjellet to Hauterivian (Early Cretaceous) in the Izhma and Boyarka Rivers (Fig. 1.4). Whilst this distribution of age was important, it was also essential to ensure that there would be a considerable degree of temporal overlap between the different locations. This overlap is crucial for the correlation of data between the different field sites.

Additional factors that were considered when selecting these sites were faunal content, available biostratigraphic information and logistics. Most importantly, it was vital that the section was known to contain relatively abundant and well preserved belemnites. In addition, it had to be possible to date the section accurately (in terms of ammonite biostratigraphy). This was ensured by choosing sections where a detailed biostratigraphy already existed, or where a fairly accurate estimate of age was known by co-workers and

could be determined after a short period in the field. In this case the presence of abundant ammonites was also required, in order to constrain the section biostratigraphically.

The field sites selected for this study (Staffin Bay, Isle of Skye, Scotland; Helmsdale, Sutherland, Scotland; Boyarka River, Northern Central Siberia; and Festningen and Janusfjellet, Svalbard) were chosen using the criteria outlined above. An additional site that satisfied the aforementioned criteria was also included in this study but did not require fieldwork (Izhma River, Russia). The material obtained from this site was collected by Dr Gregory Price (University of Plymouth) in the summer of 2003.



Figure 4.1 Volgian circumpolar map. The extent of the Boreal (blue) and Tethyan (brown) belemnite Realms are shown and the sites investigated in this study are highlighted. Map adapted after Smith *et al.*, (1981) with additional data from Doyle (1987) and Stevens (1973a).

# 4.2. Field Techniques

Field data were collected during two major field seasons: in the spring/summer of 2004; and the spring/summer of 2005. UK based field work (e.g., Isle of Skye and

Sutherland) was conducted during the spring time, whilst Arctic field work (e.g., Siberia and Svalbard) was carried out during the summer months.

### 4.2.1. Graphic Sedimentary Logs

At each individual field location a sedimentary log was drawn. Features such as lithology, sedimentary characteristics and fossil content were noted, as well as the positions from which samples were obtained. It should be noted that the extent of the outcrops varied significantly between locations. For a guide to the log symbols used see Figure 4.2.

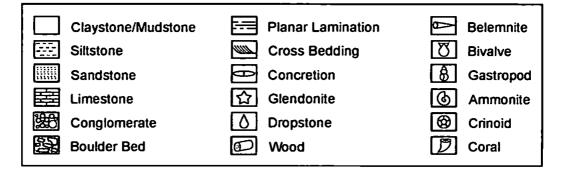


Figure 4.2 Key to sedimentary log symbols used in this study.

### 4.2.2. Sample Collection

The primary focus of the sample collection for this research was on belemnites. At each site, belemnite rostra were collected bed-by-bed from wherever possible. Multiple samples were taken from stratigraphic horizons where belemnites were abundant, with care being taken to select representative samples and, therefore, avoid any selection bias. Occasionally other elements of the faunal assemblages were collected either by myself or co-workers: e.g., ammonites were collected by Dr Kevin Page (University of Plymouth) from the Isle of Skye and Svalbard and Prof. Evgenij Baraboshkin (Moscow State University) from the Izhma River, Russia and Boyarka River, Siberia. Such samples were collected primarily for their use in biostratigraphy. In addition to the belemnite sampling, bulk sediment and fossil wood samples were also collected (from the Isle of Skye and Boyarka River respectively). The mudrock sediments of Staffin Bay, Isle of Skye are known to contain microscopic wood debris (Pearce *et al.*, 2005). The bulk sediment samples were collected frequently (although not regularly) at an average interval spacing of ~ 70 cm. The macrofossil wood samples were also collected frequently but irregularly (here, as a consequence of the limited presence of wood in certain sections of the outcrop). These samples were collected at intervals of ~ 1m.

# 4.3. Laboratory Techniques

#### 4.3.1. Rationale

The laboratory techniques outlined below were carefully selected for inclusion in this study. Each of the techniques has been repeatedly tested (in an appropriate context) through years of published, peer-reviewed research.

#### **Optical Techniques**

The photographic techniques employed either provided a record of representative specimens (prior to isotopic or geochemical analysis) or when used in combination with other techniques provided an assessment of sample preservation. Photography was undertaken principally on belemnite specimens, but also on wood samples.

Representative photographs of belemnite specimens were taken after the application of a thin coating of ammonium chloride (e.g., Doyle & Kelly, 1988). The use of such coating prevents preservational features obscuring morphological characteristics and therefore produces photographs that are suitable for taxonomic comparisons.

Additional optical techniques were employed on a number of belemnite rostra in order to identify areas of diagenetic alteration, for example, representative specimens were

photographed under cathodoluminescence (CL) and backscattered scanning electron microscopy (BSEM) conditions, and after carbonate staining (Dickson, 1965, 1966). Perhaps the most commonly used of these optical techniques (if used in isolation) is cathodoluminescence (e.g., McArthur *et al.*, 2000; O'Neill *et al.*, 2003; Rosales *et al.*, 2004a; Koleva-Rekalova & Metodiev, 2005). However, more often, a range of these techniques is used in combination in order to ensure that any and all alteration can be identified (e.g., Sælen, 1989; Podlaha *et al.*, 1998; Veizer *et al.*, 1999; Gröcke *et al.*, 2003; McArthur *et al.*, 2004; Price & Mutterlose, 2004).

Finally, photography was also performed on representative samples of well preserved macroscopic wood fragments. Photographs were taken using a scanning electron microscope (SEM), a technique which is popular for such samples as it permits an evaluation of preservation (e.g., Gröcke *et al.*, 2005; Pearce *et al.*, 2005).

#### Trace Element Techniques

Trace element analysis was undertaken for two primary reasons, firstly to identify the presence of diagenesis (undertaken in addition to the optical techniques) and secondly, to complement the stable isotope analysis of palaeoclimate. Investigations of extant molluscan species indicate that the concentrations of Fe and Mn incorporated into the mollusc shell are relatively low in recent populations. Milliman (1974) recorded values of Fe and Mn from recent *Sepia* (cuttlefish) shells (possibly the closest modern analogue of the extinct belemnite) as 32 ppm and 4 ppm respectively. These data are supported by more recent studies such as that of Miramand & Bentley (1992), which recorded average values of  $42 \pm 8$  ppm for Fe and  $2 \pm 0.4$  ppm for Mn from modern *Sepia* collected from the French coast of the English Channel. Miramand *et al.* (2006) also recorded Fe values from the cuttlebone of mature adults of the species *Sepia officinalis*. They recorded average values of  $25 \pm 2$  ppm for Fe but did not measure Mn. In a study of the extant limpet *Patella aspera*, Cravo *et al.* (2002) recorded Fe and Mn concentrations in shells collected

from Portugal. They recorded average values of 35.8 ppm and 29.9 ppm for Fe and Mn respectively, although the maximum Fe and Mn values were 70.5 and 130.5 ppm respectively. Such data suggest that relatively low Fe and Mn concentrations should be present in well-preserved belemnite rostra and authors commonly accept that values of <150 ppm Fe and <100 ppm Mn are representative of well preserved individuals (e.g., Pirrie & Marshall, 1990; Podlaha *et al.*, 1998; Price & Mutterlose, 2004).

Post-depositional repartitioning of trace elements during diagenesis typically causes the depletion of Sr, Mg, Na and Ba and the enrichment of Mn, Fe and Zn (among other elements) in low magnesium calcite (Veizer, 1983, 1999; Brand, 1989; Podlaha *et al.*, 1998). Diagenetic effects can normally be identified via trace element analysis (particularly of Fe and Mn), although it should be noted that alteration can take place in the absence of Fe and Mn, for instance, under oxidising conditions (Marshall, 1992; Jones *et al.*, 1994b). Nevertheless, trace element analysis is a technique that is commonly used to identify diagenetic alteration in belemnites and other carbonates since high concentrations of Fe and Mn virtually guarantee the presence of diagenetic calcite (e.g., Brand & Veizer, 1980; Ditchfield *et al.*, 1994; Jones *et al.*, 1994b; Price & Sellwood, 1997; Gröcke *et al.*, 2003; Price & Mutterlose, 2004). This technique was used here, together with the optical techniques outlined above, to ensure that the presence of any diagenetic alteration could be constrained.

Isotopic and trace element analysis of well preserved belemnite calcite have been used extensively to investigate (mainly Jurassic) seawater chemistry (e.g., Jenkyns *et al.*, 2002; Bailey *et al.*, 2003; McArthur *et al.*, 2004; Rosales *et al.*, 2004a). The trace element ratios Mg/Ca, Sr/Ca, Na/Ca and Li/Ca have been used here to assess changes in the environmental conditions of seawater (e.g., temperature and salinity). Mg/Ca and Sr/Ca ratios in biogenic calcite are commonly measured in order to investigate environmental conditions (e.g., Klein *et al.*, 1996, 1996; Bailey *et al.*, 2003; McArthur *et al.*, 2004; Rosales *et al.*, 2003; McArthur *et al.*, 2004; Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Rosales *et al.*, 2004a, b, 2006), although Na/Ca (e.g., Bailey *et al.*, 2003) and Li/Ca (e.g., Bailey *et al.*, 2004b, Ba

Hall & Chan, 2001; Bailey *et al.*, 2003) are less commonly utilised. Convention is followed here by expressing these values as mmol/mol (Mg/Ca, Sr/Ca, Na/Ca) or µmol/mol (Li/Ca) (e.g., McArthur *et al.* 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, 2004b). Arguably the most useful of these ratios is Mg/Ca, which has been shown to vary mainly with water temperature (e.g., Klein *et al.*, 1996; Wei *et al.*, 2000; Lear *et al.*, 2002; Steuber & Rauch, 2005) and to be affected only to an extremely limited degree by salinity (e.g., Yasamanov, 1981; Klein *et al.*, 1997; Rosales *et al.*, 2004a). It can therefore potentially be used as a salinity-independent (unlike  $\delta^{18}$ O) palaeotemperature proxy (Rosales *et al.*, 2004a).

McArthur *et al.* (2000) and Bailey *et al.* (2003) have recently investigated this relationship in belemnites, where they identified a marked correspondence between elemental composition (Mg/Ca, Sr/Ca, Na/Ca) and  $\delta^{18}$ O, suggesting that Mg/Ca (although, perhaps not Sr/Ca or Na/Ca) can be used as a palaeotemperature proxy. This technique (together with the  $\delta^{18}$ O technique) will be explored fully in this study, by using the Mg/Ca palaeotemperature equation of Klein *et al.* (1996), which was developed for extant bivalves. It remains impossible however to calculate absolute palaeotemperatures from Mg/Ca ratios (or  $\delta^{18}$ O values) as belemnites are an extinct group, and therefore the response of such proxies to water temperature cannot be observed experimentally (Rosales *et al.*, 2004a).

#### **Carbonate Stable Isotope Techniques**

Since the earliest days of isotope analysis when it was first observed that the precipitation of the <sup>18</sup>O-isotope in calcite was related to temperature (Urey, 1948) and that this provided the means to reconstruct palaeoclimates (Epstein *et al.*, 1953), belemnites have been considered as remarkably suitable organisms for such investigations (e.g., Urey *et al.*, 1951; Bowen, 1961a, b; Longinelli, 1969; Anderson *et al.*, 1994; Podlaha *et al.*, 1998; Bailey *et al.*, 2003; Voigt *et al.*, 2003; Wierzbowski, 2004). Plausible estimates of

palaeotemperature have been determined from belemnites, after taking into account the ecology, diagenesis and the isotopic composition of seawater (e.g., Pirrie & Marshall, 1990; Podlaha *et al.*, 1998; Price *et al.*, 2000; Hesselbo *et al.*, 2000). Belemnite derived oxygen isotope data were therefore produced for this research and palaeotemperatures were calculated using the equation of Anderson & Arthur (1983) for molluscan calcite.

There are however, limitations to using  $\delta^{18}$ O data to calculate palaeotemperatures. These are that the isotopic composition (which can be related to salinity) of the water from which the calcite was precipitated cannot be measured directly. The Anderson & Arthur (1983) formula requires an estimate of the isotopic composition of seawater to be made. In the Jurassic/Cretaceous greenhouse world this is generally assumed to be -1 ‰ SMOW (e.g., Pirrie & Marshall, 1990; Marshall, 1992; Sælen *et al.*, 1996; Price & Sellwood, 1997; Podlaha *et al.*, 1998; Price & Mutterlose, 2004; Rosales *et al.*, 2004a). This value however, is dependent on the amount of water stored as glacial ice (Rosales *et al.*, 2004a) and the  $\delta^{18}O_{seawater}$  composition can vary by as much as 1.5 ‰ between high and low latitudes in the modern open ocean (Broecker, 1989).

Local variation in  $\delta^{18}O_{seawater}$  (related to salinity) is also influenced by the input of fresh-water runoff (which is depleted in <sup>18</sup>O) into the system. This will produce more negative  $\delta^{18}O_{seawater}$  values than would otherwise be expected and the  $\delta^{18}O$  data will therefore overestimate palaeotemperatures (Klein *et al.*, 1996). The impact of salinity on seawater temperature however, can be determined by using Mg/Ca data (e.g., Klein *et al.*, 1996; Rosales *et al.*, 2004a; Immenhauser *et al.*, 2005). The use of Mg/Ca ratios is discussed above.

Carbon isotope data were simultaneously produced and provide additional information about carbon cycling, chemostratigraphy and palaeoclimatic change (although 'vital' effects (as mentioned earlier) also need to be considered). Carbon and oxygen isotope records are commonly considered together in order to provide a detailed assessment of palaeoclimate (e.g., Weissert, 1989; van de Schootbrugge *et al.*, 2000;

Wierzbowski, 2002; Gröcke *et al.*, 2003; Price & Mutterlose, 2004). Insights to be gained from the inclusion of carbon isotope data include information relating to palaeoceanography, palaeoatmospheres (e.g., atmospheric  $CO_2$  concentrations and methane release), weathering and carbon burial.

#### **Organic Carbon Techniques**

Carbon isotope values derived from terrestrial organic matter have been successfully used to investigate the coupling of marine and terrestrial carbon cycles throughout geological time (providing comparison is possible with marine curves), as well as providing palaeoenvironmental information (e.g., Bocherens *et al.*, 1993; Gröcke, 1998; Jahren *et al.*, 2001; Hesselbo *et al.*, 2003; Gröcke *et al.*, 2005). Gröcke *et al.* (1999) suggest that the magnitude of carbon isotope excursions as recorded in wood is considerably greater than in coeval pelagic carbonate. Detailed terrestrial carbon isotope records are virtually non-existent throughout much of the Mesozoic (Hesselbo *et al.*, 2003) and records from successions containing both marine carbonate and terrestrial organic carbon values have yet to be recorded, due to the rarity of suitable sedimentary successions in the geological record. Two such successions however, have been identified and investigated here. The terrestrial components are represented either by macroscopic fossilised wood fragments or by microscopic wood debris and the marine carbonate component by belemnites.

Modern terrestrial plants demonstrate considerable variability in  $\delta^{13}$ C values between different species, individuals of the same species and within an individual (Robinson & Hesselbo, 2004). Today plants can be divided into C<sub>3</sub>, C<sub>4</sub> and CAM groups based on their different photosynthetic systems (Bocherens *et al.*, 1993). Almost all Mesozoic plants can be classified as C<sub>3</sub> plants however, which are predominantly temperate shrubs, trees and some grasses (Bocherens *et al.*, 1993; Gröcke, 1998). Cretaceous floras, therefore, occupied one distinct photosynthetic pathway, which will

reduce the variability of carbon isotope values within the palaeo-ecosystem (Robinson & Hesselbo, 2004).

Modern C<sub>3</sub> plants demonstrate significant variability of carbon isotope composition (< ±4 ‰) between leaves, branches, twigs, and late and early wood (Leavitt & Long, 1991; Loader et al., 1995; Schleser, 1999). It is therefore important to restrict analyses to specific plant elements where possible. Carbon isotope ratios in modern plants may also be affected by environmental conditions such as varying salinity, temperature, light, water supply and local  $\rho CO_2$  (Gröcke, 1998). Diagenesis of fossil plant matter will also affect the  $\delta^{13}$ C values. The preservation potential of plant tissue varies between constituent parts of the plant, for example, lignin and lipids are the most resistant parts to diagenesis and carbohydrates, the least resistant (Gröcke, 1998; Robinson & Hesselbo, 2004). Lipids and lignin are therefore depleted in <sup>13</sup>C relative to the whole plant whilst carbohydrates are more enriched (Hedges et al., 1985; Bocherens et al., 1993; Gröcke, 1998). Fossil coal and plants are reported to be enriched in  ${}^{13}C$  by ~ 3 % compared to modern  $\delta^{13}C_{nlant}$  values (Gröcke, 1998; Robinson & Hesselbo, 2004), although the preservational state of fossil wood (e.g., coal or charcoal) does not appear to produce a systematic difference in  $\delta^{13}C$ values (Hesselbo et al., 2003; Robinson & Hesselbo, 2004; Gröcke et al., 2005; Pearce et al., 2005).

Similar problems are also inherent to the bulk-rock technique for analysing microscopic wood debris. Gröcke *et al.* (2005) describe the three key problems. These are that firstly, not every sample is assessed for the percentage of marine versus terrestrial organic matter (see Rock-Eval pyrolysis below), secondly, the terrestrial organic matter may be sourced from different floral components and finally, the terrestrial organic matter may be sourced from different environments (Gröcke *et al.*, 2005). Despite such potential for carbon isotope variability,  $\delta^{13}C_{org}$  values can be used to indicate long-term shifts in the composition of atmospheric carbon (e.g., Robinson & Hesselbo, 2004; Gröcke *et al.*, 2005).

Total Organic Carbon (TOC) analysis was performed on samples of microscopic wood debris to ensure that enough organic matter was present for  $\delta^{13}C_{org}$  analysis. TOC content can also provide additional information about palaeoproductivity, organic matter preservation and sediment dilution (e.g., Lallier-Vergès *et al.*, 1993; van Kaam-Peters *et al.*, 1998; Tribovillard *et al.*, 2001; Tyson, 2004).

Rock-Eval pyrolysis coupled with published palynology (e.g., Riding & Thomas, 1997; Hesketh & Underhill, 2002) was also performed in order to confirm the chemical composition of kerogen present in the microscopic wood samples and therefore, the source of organic matter (e.g., Espitalié *et al.*, 1985; Peters, 1986; Langford & Blanc-Valleron, 1990; Tyson, 2004). According to Espitalié *et al.*, (1985) Type I kerogen is predominantly lacustrine in origin, Type II kerogen is marine in origin and Type III, continental.

### 4.3.2. Optical Techniques

The optical techniques outlined below were undertaken on representative samples of either belemnites or wood. The techniques used to assess diagenesis in belemnites (CL, BSEM and carbonate staining) were carried out on 100 (approximately 1 in 5) of the samples measured for stable isotopes and trace element geochemistry. These samples were analysed in order to provide an independent check on the trace element results, which were conducted on all 586 of the belemnite samples.

The same 100 specimens were each analysed using CL, BSEM and carbonate staining, as all three techniques provide information at a different magnification and together, the limitations of each individual technique can be eliminated. For example, when using the CL technique on highly ferroan calcite, there will be limited or no luminescence (as  $Fe^{2+}$  is the main quencher of luminescence in calcite (Miller, 1988)). This absence of luminescence could be wrongly interpreted as indicating that there has been no diagenetic alteration in the sample. However, when the same sample is subjected to carbonate staining, it will display a purple-blue colouration, indicating that the sample

has a high Fe concentration (Dickson, 1966) and has in fact, been subject to very severe diagenetic alteration.

**.**...

#### Ammonium Chloride Technique

This technique was used to photograph representative examples of the belemnite species considered here. Prior to photographing, the specimens were cleaned, repaired (using a standard superglue) and taxonomically identified. The samples were then coated in a fine film of ammonium chloride. This was produced by putting ammonium chloride powder into a glass puffer and heating it over a Bunsen burner to produce a vapour that was then blown onto the specimens. The specimens were then photographed in black and white using a Nikon Coolpix 4500 digital camera. The ammonium chloride coating produced a smooth final image, where morphological details were not obscured by preservational features. After a short period of time the vapour evaporated from the specimens, leaving them uncontaminated for isotopic and geochemical investigation. In total, 99 belemnites were photographed using this technique, each from at least two different perspectives (ventral outline, right profile, and where suitable transverse/alveolar section).

#### Cathodoluminescence (CL)

Cathodoluminescence microscopy was used to evaluate if a belemnite had been diagenetically altered, as primary biogenic carbonate is thought to be non-luminescent (Czerniakowski *et al.*, 1984; Popp *et al.*, 1986; Sælen, 1989; Sælen & Karstang, 1989). Luminescence occurs where the diagenetic product Mn is present, as  $Mn^{2+}$  is the main activator of luminescence in calcite, whilst (as noted above)  $Fe^{2+}$  is the main quencher (Miller, 1988). Areas that have been diagenetically altered will, therefore, show luminescence, providing that the amount of Fe does not dramatically exceed the amount of Mn.

Polished thin-sections of the belemnite rostra were produced, with the crosssections cut horizontally through the rostrum (wherever possible this horizontal slice was taken from alongside the isotope/geochemical sample). Thin sections were made on a Logitech LP30 production lapping and optical polishing machine and then polished on a Buehler Petropol polishing system with a 12" lapping plate using Buehler aluminium oxide powder (0.3 micron) on a Texmet 1000 polishing cloth.

The CL analysis was performed using a CITL CL MK3A Luminoscope at the Camborne School of Mines (CSM), University of Exeter, in Cornwall. The thin sections were placed in a vacuum sealed specimen chamber, under an electron gun emitting a cathode ray (with a gun current of ~ 450  $\mu$ A and a gun voltage of ~10 kV). The specimens were viewed through an attached petrographic microscope and photographed. In total, 100 belemnites were analysed in this way.

#### Backscattered Scanning Electron Microscopy (BSEM)

Backscattered scanning electron microscopy (BSEM) was also used to assess the presence of diagenesis in the belemnite rostra. The efficiency of backscattered electrons reflected from the flat surface of a specimen is dependant on the chemistry of that surface (Trewin, 1988). The reflection coefficient increases as the atomic number increases, causing a brighter image where the atomic number is higher (Thornton, 1968). The presence of diagenetic products in calcite can therefore be identified, as calcite containing the common diagenetic products Fe and Mn will have a higher atomic number than unaltered calcite, and will therefore show as brighter areas in a BSEM image.

The rostra were sliced and polished (first with a lapping wheel, then with decreasing sizes of carborundum powder (starting at 600 microns) and finally aluminium oxide powder (0.3 microns)) to produce a smooth and highly polished surface. The belemnite slice was then washed in a sonic bath, mounted on a SEM stub and placed, uncoated in a JEOL 5600 scanning electron microscope housed at the University of

Plymouth. The samples were then photographed under low vacuum conditions using a back scattered electron detector (accelerating voltage 15kV, spot size 38) to show the atomic number contrast on the polished surface. This method of analysis was conducted on the same belemnites that were subject to CL microscopy (100 belemnites in total). Whilst both techniques identify diagenetically altered regions in the rostrum, they do so at significantly different magnifications.

#### Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to examine fossil plant material from the Ryazanian-Hauterivian of the Boyarka River, Siberia. All 184 samples were identified as charcoal, charcoal-coal or coal using a binocular microscope. Approximately 20 representative samples (e.g., of charcoal, charcoal-coal and coal) were then mounted on stubs and sputter coated with gold for SEM analysis. The University of Plymouth's JEOL 5600 SEM was used (in high vacuum mode with an accelerating voltage of 15kV and a spot size of 25).

#### **Carbonate Staining**

Carbonate staining was undertaken on 100 belemnites in order to identify the areas of the rostrum prone to diagenetic alteration. The technique used follows that described by Dickson (1965, 1966) for use on thin sections, where the section surface is first etched with dilute hydrochloric acid (HCl), then stained with an alizarin red-S and potassium ferricyanide mixture (3 parts : 2 parts), and finally stained with alizarin red-S to intensify the colour differentiation. This is a highly selective technique, with colouration confined sharply to crystal boundaries (Allman & Lawrence, 1972). Calcites stained using this method will display a very pale pink-red colouration, whilst ferroan calcites, show mauvepurple-royal blue colouration (Dickson, 1965). The polished thin sections of belemnite rostra made for CL microscopy were first photographed under the CL microscope, and then stained by emersion of the section in the following sequence: dilute HCl (15 seconds), deionised water (10 seconds), alizarin red-S and potassium ferricyanide mixture (45 seconds), alizarin red-S (15 seconds), deionised water (10 seconds). The thin sections were then quickly dried before being photographed under a low-powered binocular microscope using a Nikon Coolpix 4500 digital camera.

### 4.3.3. Trace Element Analysis

In total 586 samples were analysed (with duplicate samples taken from approximately 1 in 6 belemnite specimens to evaluate the consistency of both trace elements and stable isotope values within the rostrum). Trace element analysis of every sample was undertaken prior to stable isotope analysis. This provided screening for diagenesis, so that severely altered specimens could be excluded from further analysis. This technique was performed on every sample to ensure that there was a constant and accurate, quantitative measure of preservation for every belemnite sample. The trace element work was complimented by optical techniques (conducted on representative samples) that were used to double-check the trace element data.

The carbonate subsamples were digested in 20% nitric acid (HNO<sub>3</sub>) (~100 mg in 10 ml) and analysed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the NERC ICP facility, Department of Geology at Royal Holloway, University of London. Each sample was analysed for Ca, Na, Mg, K, Fe, Al, B, Ba, Li, Mn, Pb, Sr, Ti and Zn, with values given in ppm.

#### 4.3.4. Carbonate Stable Isotope Analysis

Prior to isotopic analysis the areas of the belemnite rostrum most susceptible to diagenesis were removed. These areas were identified using several of the techniques described in this chapter: Cathodoluminescence (CL), Backscattered Scanning Electron Microscopy (BSEM) and carbonate staining (following the technique of Dickson (1965, 1966)). Those areas most prone to diagenetic alteration are the rostrum margin, the apical line and any cracks or prominent growth bands. Such areas were removed using a circular saw and lapping wheel. The remains were then washed in de-ionised water and fragmented, before being picked under a binocular microscope to ensure that only the most well preserved fragments were selected for analysis. The selected fragments were ground into a fine homogenous powder using an agate pestle and mortar, and a subsample was removed for trace element analysis. A similar method of preparation has been used by several authors in an attempt to homogenise any intra-specimen geochemical variation (e.g., McArthur *et al.*, 2000, 2004; Bailey *et al.*, 2003).

Stable isotope data were generated using a Multiflow (GV Instruments, UK) automated carbonate preparation module with Gilson 222XL autosampler, interfaced with an Isoprime isotope ratio mass spectrometer (GV Instruments, UK), at the University of Plymouth, UK and on a VG Optima mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), Keyworth, UK. A small set of representative samples were analysed on both instruments to ensure reproducibility (and to allow correlation of data from the different institutions). The mean difference in values from replicate analysis was 0.28‰ and 0.09‰ for oxygen and carbon respectively. For oxygen, this value is outside of the reproducibility of each instrument (see below), however, such variability is to be expected as a belemnite sample will never be completely homogenous due to the variability occurring across a belemnite rostrum.

The Isoprime isotope ratio mass spectrometer analysed triplicate injections from each vile, with liberated  $CO_2$  (from carbonate reaction with phosphoric acid) measured

against reference  $CO_2$  (research grade, BOC Special Gases). The VG Optima mass spectrometer measured  $CO_2$  liberated from water vapour under vacuum, after the carbonate had reacted with anhydrous phosphoric acid *in vacuo* overnight at a constant 25°C.

The measurements from both institutions were standardised using within-run laboratory standards and calibrated with the internationally recognised NBS19 standard using the daily correction method. Values were expressed using the standard delta ( $\delta$ ) notation as a per mil (‰) deviation from the Vienna Peedee Belemnite (V-PDB) standard. Replicate analyses for each instrument gave a reproducibility of <± 0.1‰ for both oxygen and carbon isotope ratios.

### 4.3.5. Organic Carbon Analysis

#### Bulk Sediment Samples (Microscopic Wood Debris)

Carbon isotope measurements were made on a total of 207 bulk sediment samples from Staffin Bay, Isle of Skye. For each sample approximately 1-2 g of powdered sediment was covered with 200 ml of 5% hydrochloric acid (HCl). The samples were left overnight until all the carbonate had reacted and then rinsed thoroughly with de-ionised water (3 overnight 500 ml washes). Samples were then oven dried at 40-50 °C until a constant weight. The resulting samples were then re-powdered, weighed (between 10-30 mg) and placed in tin capsules for combustion. Analyses were performed by combustion in a Carlo Erba NA1500 (series 1) elemental analyser at NIGL, Keyworth. The resulting gas samples were subsequently measured for carbon isotope ratios by an on-line VG TripleTrap and Optima dual-inlet mass spectrometer. Carbon isotope ratios were measured using within-run laboratory standards (BROC 1) and calibrated against NBS-19 and NBS-22. Values were expressed in delta ( $\delta$ ) notation against the international, V-PDB standard. All results were accurate to within  $\pm 0.3$ %.

#### Macrofossil Wood Samples

A total of 184 individual wood samples were analysed for carbon isotope ratios from the Boyarka River, Siberia. Samples were divided (where enough material was present) to allow a portion of the sample to be archived. The rest of the sample was prepared for analysis using a preparation technique similar to that described previously. Samples were treated with 5% HCl to remove any carbonate material and then washed with de-ionised water. The samples were then oven dried at 40-50 °C before being powdered with an agate pestle and mortar.

The samples were analysed by Dr Darren Gröcke at McMaster University, Ontario, Canada, where samples were weighed, combusted in an elemental analyser and the resulting gas purified and passed through a SIRA II Series 2 dual-inlet isotope-ratio massspectrometer for isotopic analysis. Carbon isotope ratios were measured against an international standard (NBS-21). Analytical reproducibility using this method was better than  $\pm 0.1\%$ .

### 4.3.6. Total Organic Carbon (TOC)

In total 103 bulk sediment samples from Staffin Bay, Isle of Skye were analysed for Total Organic Carbon (TOC). Sediment samples were crushed, oven dried at 40-50 °C (until a constant weight) and ground to produce a fine homogenised powder.

TOC was then measured using two different techniques (to ensure accuracy a selection of samples were analysed using both methods). The first technique (which was used to analyse approximately 3 out of 4 of the samples) was the industry standard, high-temperature catalytic oxidation (HTCO) technique. This was conducted on a Primacs SLC Carbon Analyzer at the University of Plymouth. Samples were weighed (~ 100 mg) into a small crucible and covered with quartz wool before being combusted at a high temperature to release carbon, giving a measurable Total Carbon (TC) value. A separate sample was weighed (~ 100 mg) into a glass test tube and mixed with a small amount of deionised

water. This was combusted at a low temperature with acid to release the Inorganic Carbon (IC). The Total Organic Carbon was then calculated as TOC = TC - IC. The second technique (which was used to measure 50 sediment samples) is described below, as TOC was also measured as a component of Rock-Eval pyrolosis. All TOC values are given as wt % TOC.

#### 4.3.7. Rock-Eval Pyrolysis

Rock-Eval pyrolosis was performed on 50 bulk sediment samples from the Isle of Skye in order to determine the source of organic matter within the sediments. The samples selected for analysis were distributed fairly evenly throughout the Staffin Bay succession, although particular attention was paid to sections of the  $\delta^{13}C_{org}$  curve where minor fluctuations could have been caused by changes in the source of organic carbon. Samples were prepared according to the same technique described above for TOC analysis. The samples were then analysed with a Rock-Eval 6, at the University of Neuchâtel, Switzerland. Values for TOC, Hydrogen Index (HI) and Oxygen Index (OI) were obtained.

#### 4.3.8. Storage of Material

All of the materials used during this research are currently stored in the School of Earth, Ocean and Environmental Sciences at the University of Plymouth, UK.

# 5. STAFFIN BAY, ISLE OF SKYE, SCOTLAND

## 5.1. Location & Site Description

The Isle of Skye lies to the northwest of the Scottish mainland at a latitude of approximately 57°N. Staffin Bay is situated on the northeast coast of Skye, on the Trotternish peninsula, approximately 30 km north of the main town of Portree.

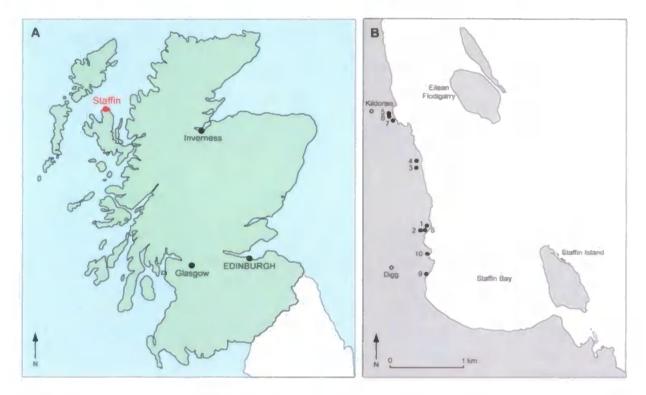


Figure 5.1 Location map of Staffin Bay, Isle of Skye, Scotland. (A) Location of Staffin Bay. (B) Relative positions of each of the sites visited on the Staffin Bay coast.

Ten different sites were examined along a ~2.5 km stretch of the Staffin Bay coast between Digg and Kildorais (Fig. 5.1). These sites were predominantly broad foreshore exposures (Fig. 5.2), often accessible only at low tide and intermittently covered with boulders and seaweed, with such cover varying seasonally as the result of weather conditions and beach processes. Occasional low cliff exposures located near to the shore line were also studied. The Staffin Bay composite section extends from the Middle Callovian (*Koenigi* Zone) to the Early Kimmeridgian (*Cymodoce* Zone) and provides an almost complete record of sedimentation during this time.



**Figure 5.2** Broad foreshore exposure typical of the Staffin Bay coast, Isle of Skye, Scotland. Dunans Clay Member of the Staffin Shale Formation (location SK1 - see Fig. 5.1).

# 5.2. Geological Setting

During the Jurassic period, Scotland was situated at a palaeolatitude of approximately 45°N (Smith *et al.*, 1994). The Jurassic rocks of the Hebrides occur in tilted fault blocks within a major half graben, probably formed during the early extensional phases of the evolution of the Central and North Atlantic Oceans (Morton & Hudson, 1995). The Hebrides Basin (Fig. 5.3) is itself a complex half-graben that was gently subsiding throughout Jurassic time (Riding & Thomas, 1997; Hesselbo & Coe, 2000; Hudson & Trewin, 2002) and was just one of a system of basins on the North Atlantic margins that extended as far north as Greenland and Svalbard (Tankard & Balkwill, 1989; Ziegler, 1990; Morton & Hudson, 1995). The basin is bounded to the west by the Minch Fault Zone, just east of the Outer Hebrides (Brewer & Smythe, 1984; Stein, 1988; Hudson & Trewin, 2002), whilst to the east, the margin is unfaulted (Morton & Hudson, 1995; Hudson & Trewin, 2002). The basin is commonly subdivided into two; the Hebrides (Little Minch) sub-basin and the Inner Hebrides sub-basin (Riding & Thomas, 1997; Hesselbo & Coe, 2000; Hudson & Trewin, 2002). It has been proposed that activity along major onshore faults linked the development of the Hebrides Basin with coeval development in the Moray Firth Basin in the northeastern North Sea (see Chapter 6) (Underhill, 1991; Wignall & Pickering, 1993; Hesselbo & Coe, 2000).

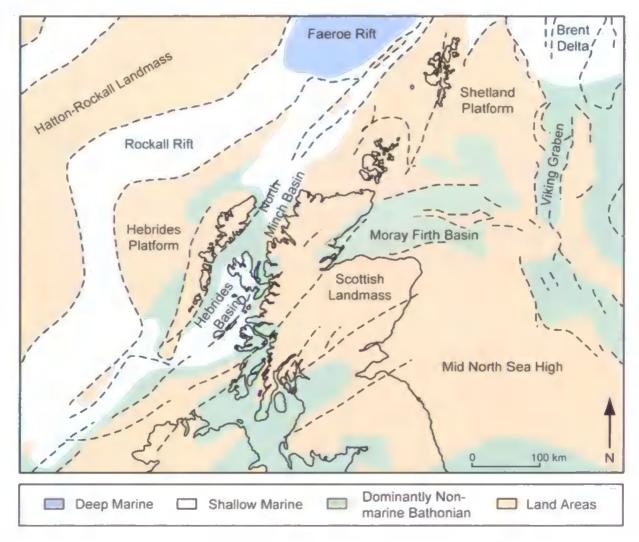


Figure 5.3 Mid-Jurassic (Bathonian) Scottish palaeogeography. Adapted after Hudson & Trewin (2002).

The Jurassic period is characterised by an overall eustatic rise in sea level (Haq et al., 1987), causing widespread transgression in the Early and Late Jurassic, although, the

Middle Jurassic was marked by a relative sea level fall (Fyfe *et al.*, 1993). During the transgressive phases of the Early and Late Jurassic, deposition in the Hebrides Basin occurred predominantly in shallow-marine environments (Fyfe *et al.*, 1993).

The Mesozoic sediments of the Hebrides Basin thicken westwards as a result of faulting of the Precambrian/Palaeozoic basement (Riding & Thomas, 1997). The Jurassic succession reaches a maximum thickness of ~1000 m and is commonly overlain by basaltic lava flows from the Palaeogene Thulean Igneous Province (Morton & Parson, 1988; Riding & Thomas, 1997). Many of the successions in the Hebrides Basin have been affected by thermal alteration, although, this is not the case near Staffin (Thrasher, 1992; Bishop & Abbott, 1995; Morton & Hudson, 1995; Pearce *et al.*, 2005).

The Staffin Bay section on the Isle of Skye is one of the most stratigraphically complete Oxfordian sections in Europe (Sykes & Callomon, 1979; Morton & Hudson, 1995; Matyja *et al.*, 2004; Pearce *et al.*, 2005). It is of great importance for Upper Jurassic stratigraphy in the Boreal Realm because it contains the type localities for several of the Boreal Middle and Upper Oxfordian Zones and Subzones established by Sykes and Callomon (1979). It is also a proposed GSSP for the Oxfordian-Kimmeridgian boundary (Wierzbowski *et al.*, 2006).

The sedimentation at Staffin appears to have been continuous from the Callovian and through into the Kimmeridgian (Wright, 2001). The strata are comprised of the Staffin Bay Formation (Hudson, 1962) and the Staffin Shale Formation (Turner, 1966) (Fig. 5.4). The Staffin Bay Formation is Lower Callovian in age (*Herveyi* to *Koenigi* zones) and the Staffin Shale Formation is Middle Callovian to Lower Kimmeridgian (*Jason* to *Cymodoce* zones). The outcrops at Staffin Bay are the most accessible, extensive and fossiliferous outcrops of these formations (Morton & Hudson, 1995).

Comprehensive descriptions of the Staffin Bay and Staffin Shale Formations are given by Morton & Hudson (1995). The Staffin Bay Formation is divided into the Upper Ostrea Member (*Herveyi* Zone) and the Belemnite Sands Member (*Koenigi* Zone). The

Upper Ostrea Member is composed of dark grey shales with shell beds. The shell beds are generally of low but fluctuating diversity and are dominated by bivalves (Anderson & Cox, 1948; Morton & Hudson, 1995). Deposition occurred in a non-fully marine environment, most likely a coastal lagoon (Morton & Hudson, 1995). Such an interpretation is supported by palynological evidence, which is consistent with a restricted, inshore and brackish depositional environment (Riding & Thomas, 1997).

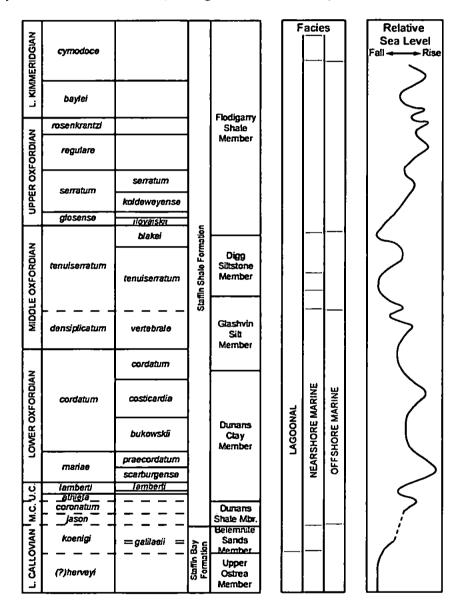


Figure 5. 4 Stratigraphic chart of the Staffin Bay section. Facies association and relative sea level are also shown. Figure adapted after Hesselbo & Coe (2000).

The Belemnite Sands Member is made up principally of siltstones and sandstones with a more varied and more marine fauna of bivalves and belemnites (Anderson & Cox, 1948; Anderson & Dunham, 1966; Morton & Hudson, 1995; Riding & Thomas, 1997).

Belemnites are common in the glauconitic beds towards the top of the member (Riding & Thomas, 1997). Morton & Hudson (1995) interpret this member as an offshore sandy bar migrating across the coastal lagoons.

The Staffin Shale Formation is dominated by mudrocks deposited in a generally offshore marine environment (Pearce *et al.*, 2005) and is broadly equivalent to the better known English Jurassic, Oxford Clay Formation, Corallian Group and Kimmeridge Clay Formation (Hesselbo & Coe, 2000). The Dunans Shale Member (*Jason to Coronatum* zones), Dunans Clay Member (*Athleta to Cordatum* zones), Glashvin Silt Member (*Cordatum to Tenuiserratum* zones), Digg Siltstone Member (*Tenuiserratum* Zone) and Flodigarry Shale Member (*Tenuiserratum* to *Cymodoce* zones) make up the Staffin Shale Formation (Fig. 5.4).

The dark, laminated, bituminous shales of the Dunans Shale Member are very distinct from the coarse sandstones of the Belemnite Sands Member beneath (Morton & Hudson, 1995). The bituminous shales are interspersed with thin, silty, glauconitic layers (Sykes, 1975) and belemnites are common throughout. The lack of benthos suggests a period of anoxic sea floor deposition (Fisher & Hudson, 1987), with silty, glauconitic layers layers representing occasional oxic perturbations (Morton & Hudson, 1995).

Sykes (1975) described the Dunans Clay Member (Fig. 5.2) as being dominated by grey-green clays with some siltstones (occassionaly with visible woody debris). Both ammonites and belemnites are often abundant but the bivalve fauna is limited. Deposition probably occurred in dominantly well-oxygenated conditions (Morton & Hudson, 1995).

A gradual coarsening upwards trend, from the Dunans Clay to Digg Siltstone Member, coupled with an increase in carbonate content from the Glashvin Silt Member is described by Pearce *et al.* (2005). The Glashvin Silt Member is dominated by dark grey carbonaceous silts, with a diverse bivalve fauna (with large bivalves (*Pinna, Cucullaea, Pleuromya* and *Pholadomya*) often in life position) and some sandstones with lignite debris (Morton & Hudson, 1995; Wright, 2001). The depositional environment was probably

similar to that of the Dunans Clay Member but somewhat shallower (Morton & Hudson, 1995).

The Digg Siltstone Member is composed predominantly of light grey sandy silts with some fine sandstone beds and darker grey silts (Wright, 2001). The lithologies are coarser and lighter than those of the Glashvin Silt Member and probably represent a shallowing sequence, with deposition of this member occurring near to the fair-weather wave base (Morton & Hudson, 1995).

Dark grey, slightly bituminous, shaly clays are the principal lithology of the Flodigarry Shale Member (Wright, 1989, 2001; Morton & Hudson, 1995) (Fig. 5.5). Glauconitic silts and muds are present at the base and mark a major change of facies from the Digg Siltstone Member (Morton & Hudson, 1995; Pearce *et al.*, 2005). The Flodigarry Shale Member is particularly fossiliferous, with abundant belemnites, ammonites and bivalves (Morton & Hudson, 1995). Pearce *et al.* (2005) interpret the occurrence of glauconitic mudstones at the base of the member as representing a return to higher sea levels from the upper *Tenuiserratum* Zone.

## 5.3. Sampling & Methodology

The ten different sites examined in the Staffin Bay area provided an almost complete succession from the Upper Callovian - Lower Kimmeridgian. In total, 241 horizons were sampled from the Staffin Bay section. This included 174 belemnite horizons (each horizon often containing multiple specimens) and 216 sediment horizons (with such sediment containing microscopic wood debris). Wherever possible both belemnite and sediment samples were collected from the same horizon (Fig. 5.5).

The preservation of belemnite rostra was evaluated through trace element and stable isotopic analysis, backscattered scanning electron microscopy (BSEM), cathodoluminescence (CL) and carbonate staining (following the technique of Dickson (1965, 1966)). The areas most susceptible to diagenesis were removed prior to isotopic

and geochemical analysis. Samples were analysed for carbon and oxygen isotopes, with subsamples taken for trace element analysis (Fe, Mn, Ca, Sr, Mg, Na and Li). The stable isotope data was compared with a small amount of data generated by Wierzbowski (2004) for the upper part of the Staffin section. This helped ensure the reproducibility of the data.



Figure 5.5 Relatively abundant belemnites in a mudrock (suitable for sampling) containing microscopic wood debris. Flodigarry Shale Member of the Staffin Shale Formation (location SK6).

Stable isotope data were generated on a VG Optima mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), Keyworth, UK. Samples for trace element data were digested in 20% nitric acid (HNO<sub>3</sub>) and analysed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the NERC ICP facility, Department of Geology, Royal Holloway, University of London.

Bulk sediment samples (containing microscopic wood debris) were covered with 5% hydrochloric acid (HCl) then rinsed with deionised water, oven dried and powdered with an agate pestle and mortar. Carbon isotope analysis was performed by combustion in

a Carlo Erba NA1500 (series 1) elemental analyser at NIGL, Keyworth. The resulting gas samples were subsequently measured for carbon isotope ratios by an on-line VG TripleTrap and Optima dual-inlet mass spectrometer. A representative selection of samples (67 in total) were also analysed for Total Organic Carbon (TOC) on a Primacs SLC Carbon Analyzer at the University of Plymouth. An additional 50 samples were also analysed by Rock-Eval Pyrolysis (which includes a measurement for TOC) on a Rock-Eval 6, at the University of Neuchâtel, Switzerland. For a full description of the methodology used see Chapter 4.

### 5.4. Results

The isotopic compositions derived from belemnite carbonate were determined using well-preserved rostra of the genera *Cylindroteuthis*, *Pachyteuthis* (Boreal Realm genera) and occasionally *Belemnopsis* (a typically Tethyan genus). There appears to be no major discrepancy between the isotope values derived from the different belemnite genera (Fig. 5.6). The belemnites sampled from this region were predominantly composed of honey-coloured translucent calcite. Several specimens displayed areas of intense endolithic borings on the margins, which were removed prior to analysis. Carbonate staining, CL and BSEM analysis (Plates 1-3) was conducted on 40 out of 206 specimens and indicated that the belemnite margins were often Fe-rich, with some pyrite replacement and sparite infilling of borings. Such features were identified by mauve-blue colouration after carbonate staining, pale grey to white colouration under BSEM and luminescence under CL conditions. Such areas were removed prior to subsampling because even subtle diagenetic alteration can have an isotopic effect.

The determined elemental abundances of the belemnite rostra were as follows: Fe 0-2134 ppm, mean 68 ppm; Mn 1-305 ppm, mean 24 ppm; Mg 539-4220 ppm, mean 1045 ppm; Sr 766-1232 ppm, mean 953 ppm and Ca 28 % - 33 %, mean 30 %. Low Mn (<100 ppm) and Fe (<150 ppm) values were recorded for most of the belemnites. Relatively low

Mn and Fe concentrations can be assumed to reflect well preserved shell material, since such concentrations have been measured from modern molluscs (e.g., Pirrie & Marshall, 1990; Podlaha *et al.*, 1998; Price & Mutterlose, 2004). Trace element data (Fe and Mn) were plotted against  $\delta^{18}$ O to constrain any diagenetic alteration (Fig. 5.7). The higher amounts of Fe and Mn and occasional negative  $\delta^{18}$ O outliers are regarded as an artefact of diagenesis. The lack of correlation between the values, however, suggests minimal postdepositional alteration. Those samples with higher concentrations were considered likely to have undergone diagenetic alteration and were excluded from any further analysis (24 samples in total).

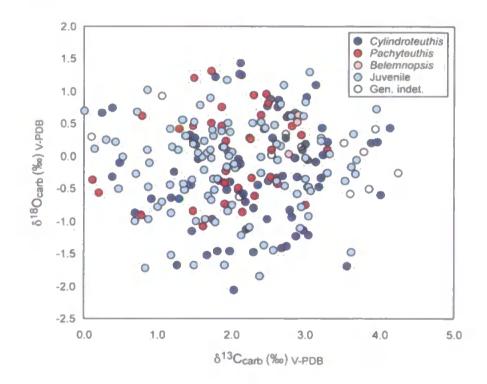
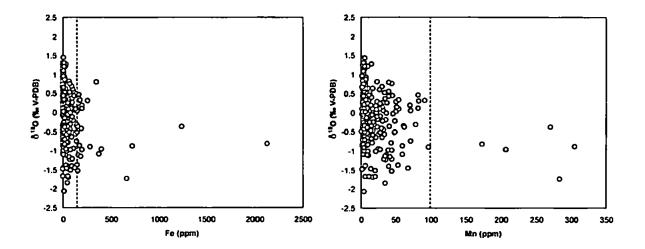


Figure 5.6. Cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C values derived from belemnites from Staffin Bay, Isle of Skye, Scotland.

The Mg/Ca ratios vary from 3.08 to 14.22 mmol/mol. A plot of  $\delta^{18}$ O vs. Mg/Ca shows no significant correlation (Fig. 5.8). The Mg/Ca trend (Fig. 5.9) shows minimum values in the Middle Oxfordian *Densiplicatum* Zone (as low as 3.14 mmol/mol) and in the Lower Kimmeridgian *Cymodoce* Zone (as low as 3.08 mmol/mol). The Sr/Ca ratios range from 1.13 to 1.80 mmol/mol. The Sr/Ca trend (Fig. 5.9) shows a general increase in values

from the Lower Oxfordian to the Lower Kimmeridgian. A cross-plot of  $\delta^{18}$ O vs. Sr/Ca reveals a negative correlation, although covariance is poor (Fig. 5.8). Neither the Na/Ca nor Li/Ca ratios show a significant covariance with  $\delta^{18}$ O (Fig. 5.8). Na/Ca ratios range from 4.01 to 11.00 mmol/mol and Li/Ca ratios from 7.08 to 113.24 µmol/mol.



**Figure 5.7** Cross-plots of  $\delta^{18}$ O against Fe (left) and Mn (right). The dashed line illustrates the cut off values for well preserved samples.

The oxygen and carbon isotope values derived from well preserved belemnite rostra range from -2.07 to 1.43 ‰ and from 0.01 to 4.26 ‰ respectively (Fig. 5.10). Both the oxygen and carbon isotope values show a considerable degree of scatter, although, long-term trends can still be recognised. The oxygen isotope ratios decrease very gradually throughout the succession from values of between -0.76 to 1.43 ‰ in the Middle Callovian to Lower Oxfordian to values of -1.85 to 0.73 ‰ in the Lower Kimmeridgian.

The carbon isotope ratios also decrease gradually throughout the succession. The Middle Callovian values are in the range of c. 2.0-3.0 ‰, compared with values in the range of c. 0.5-1.5 ‰ in the Lower Kimmeridgian. There is a brief, but distinct negative carbon isotope excursion at the *Cordatum-Densiplicatum* Zone boundary (with a peak negative value of 0.01 ‰). This excursion is followed by a return to pre-excursion values, which is followed by drop in values from c. 3.0 ‰ to c. 0.5 ‰ at the *Tenuiserratum-Glosense* Zone (Middle-Upper Oxfordian) boundary. The Upper Oxfordian and Lower Kimmeridgian carbon isotope record generally fluctuates between c. 0.0 and 2.0 ‰,

although, a brief, indistinct positive fluctuation is identified at the *Baylei-Cymodoce* boundary, with values reaching 3.57 ‰. A plot of the  $\delta^{18}$ O vs.  $\delta^{13}$ C data (Figs 5.6) reveals no significant correlation.

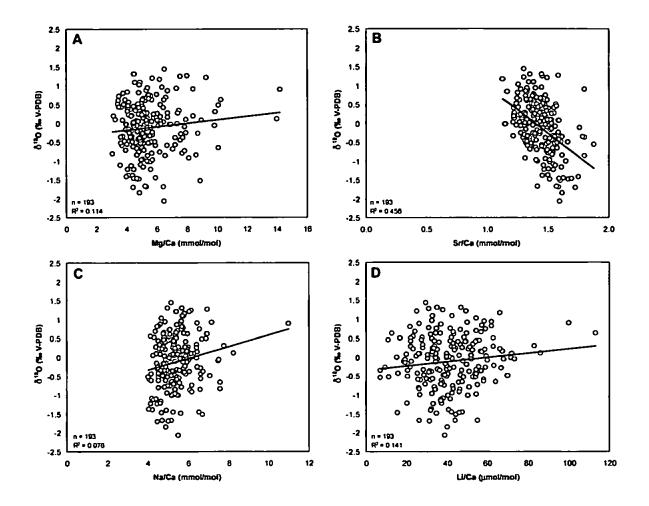


Figure 5.8 Cross-plots of  $\delta^{18}$ O against (A) Mg/Ca, (B) Sr/Ca, (C) Na/Ca and (D) Li/Ca.

Total Organic Carbon (TOC) values derived from the organic wood debris range from 0.18 to 9.22 %, with values gradually increasing up the sequence, despite significant scatter (Fig. 5.11). TOC values in the Dunans Clay and Glashvin Silt members are highly variable, whilst values in the Flodigarry Shale Member are more consistent (between ~ 1 and 3 wt %). Rock-Eval pyrolysis (Fig. 5.12) indicated that the analysed material was predominantly Type III kerogen (organic matter derived from higher plants), although a small amount of Type II kerogen (derived from the marine environment) was also present. The hydrogen indices ranged from 23 to 396 HC/g TOC and from 21 to 317 CO<sub>2</sub>/g TOC.

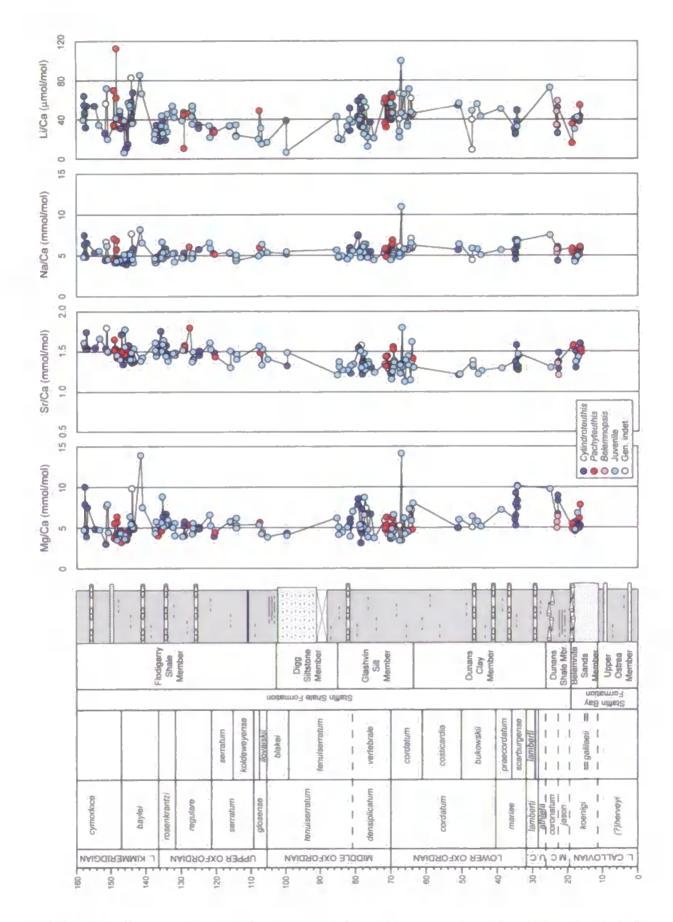
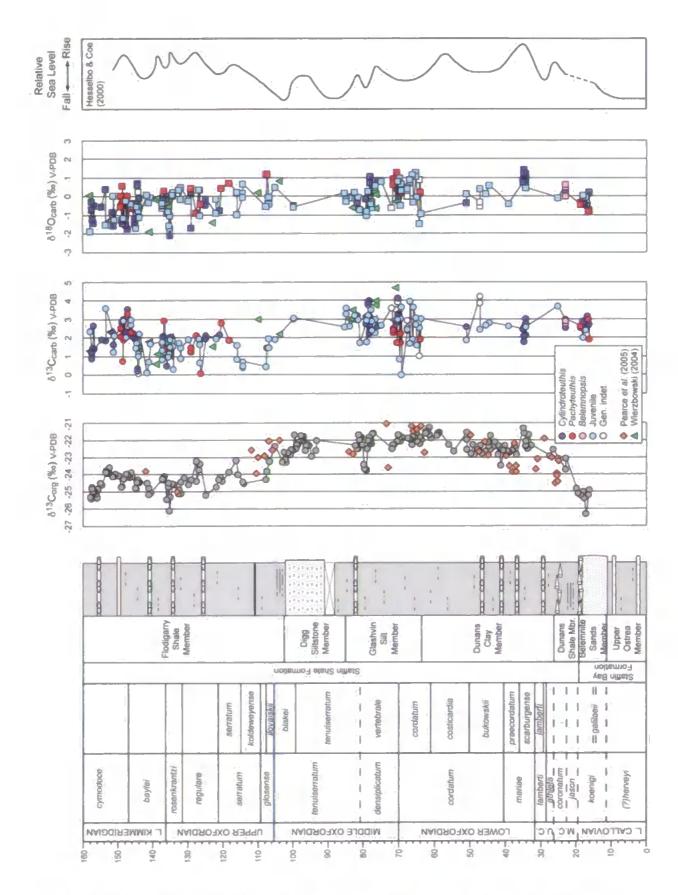


Figure 5.9. El/Ca ratios from the Callovian-Lower Kimmeridgian succession at Staffin Bay, Isle of Skye, Scotland. Boreal (British) ammonite zones and subzones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.



**Figure 5.10**  $\delta^{13}C_{org}$ ,  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  records from the Callovian-Lower Kimmeridgian succession at Staffin Bay, Isle of Skye, Scotland. Boreal (British) ammonite zones and subzones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

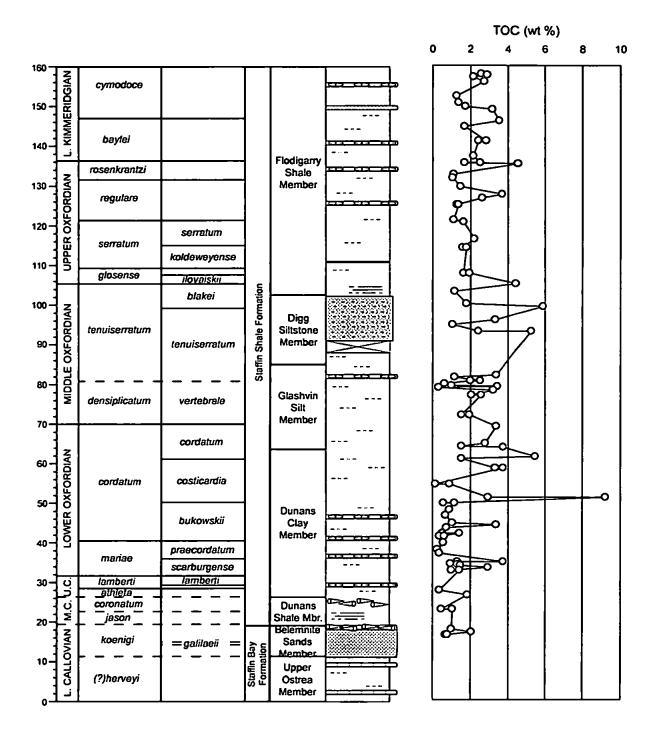


Figure 5.11 TOC record from the Callovian-Lower Kimmeridgian succession at Staffin Bay, Isle of Skye, Scotland. Boreal (British) ammonite zones and subzones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

The fossil wood samples have an average  $\delta^{13}C_{org}$  value of -23.2 ‰, with a range of -26.2 to 21.2 ‰. The organic carbon isotope data show a broad Lower to Middle Oxfordian positive carbon isotope excursion from the *Mariae* to *Tenuiserratum* Zone, with maximum values occurring in the *Cordatum* Zone (c. 21.0 ‰). This is followed by a

return to pre-excursion values continuing into the Lower Kimmeridgian *Cymodoce* Zone. There is a brief positive fluctuation in the *Cymodoce* Zone where  $\delta^{13}C_{org}$  values reach -23.54 ‰). This fluctuation occurs slightly later than a similar fluctuation observed in the  $\delta^{13}C_{carb}$  record, although, this is not easily identifiable given the scatter of the data. A brief negative excursion (of ~2.0 ‰) is also identified near the *Densiplicatum-Tenuiserratum* boundary. This brief negative excursion occurs approximately one ammonite zone later than negative excursion observed in the  $\delta^{13}C_{carb}$  record. The  $\delta^{13}C_{org}$  negative excursion was examined by Rock-Eval Pyrolysis. Five samples from the peak and shoulders of the excursion were analysed. The hydrogen indices for these samples ranged from 45 to 89 HC/g TOC and from 23 to 113 CO<sub>2</sub>/g TOC, with each sample demonstrating a Type III origin of kerogen. This excursion is therefore not the result of a change in the source of organic matter (*cf.* Foster *et al.*, 1997).

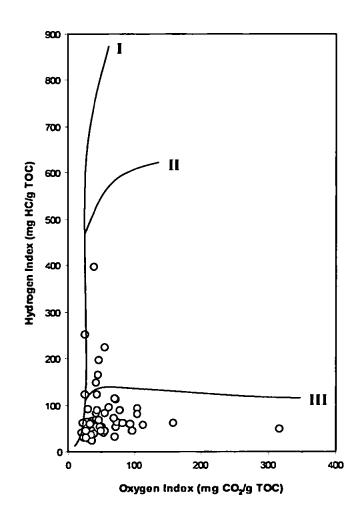


Figure 5.12 Van Krevlan diagram showing the origin of organic matter analysed from the Callovian-Lower Kimmeridgian Staffin Bay succession.

## 5.5. Discussion

#### 5.5.1. Stable Isotope, Geochemical & Taxonomic Records

The stable isotope (Fig. 5.10) and *El/Ca* (Fig. 5.9) records presented here highlight the different belemnite genera from which the data were derived. This was done in order to assess the impact (if any) of genus-specific differences in isotope or trace element fractionation. The greatest degree of scatter observed from the isotope ratios was found in the genus *Cylindroteuthis* and in the juvenile specimens. This, however, could be the result of the predominance of these groups. Those groups displaying less scatter are those which are less common in the succession (e.g., *Pachyteuthis* and *Belemnopsis*), with *Pachyteuthis* displaying less scatter than the other groups in the oxygen isotope record in particular. *Belemnopsis* exhibits very little scatter in the isotope or *El/Ca* records because it was collected from only one horizon.

The El/Ca ratios display similar generic patterns to those observed in the stable isotope records with the juvenile group of specimens once again exhibiting the greatest scatter. In neither the isotope nor El/Ca records does one genus appear to be consistently more positive or negative than the others. If taxonomic differences in fractionation do exist, these data suggest that they are likely to be minor here. It is therefore highly unlikely that the trends observed here are caused solely by genus-specific effects.

### 5.5.2. The Oxygen Isotope Record & Palaeotemperature Implications

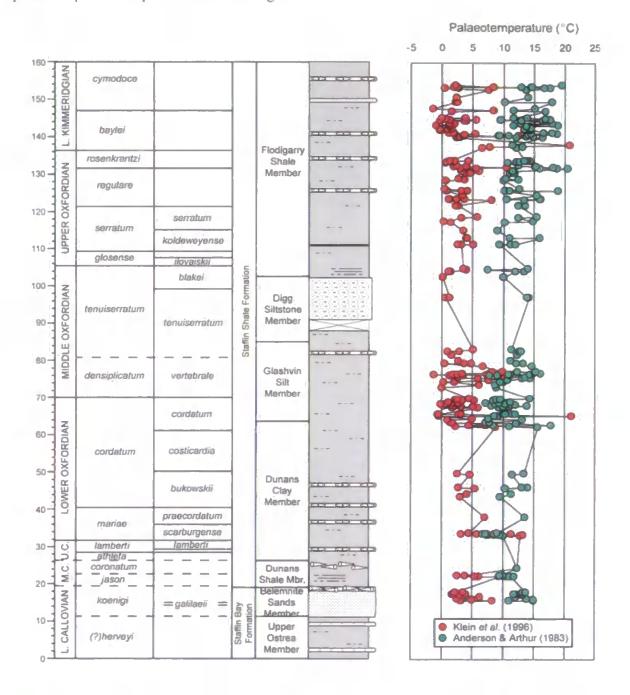
A long-term trend of gradually decreasing oxygen isotope values (and potentially increasing palaeotemperatures) is recorded from the Staffin Bay section. The oxygen isotope values presented here are consistent with those published by Wierzbowski (2004) from the Middle Oxfordian (*Densiplicatum* Zone) to Lower Kimmeridgian (*Cymodoce* Zone) of Staffin Bay (Fig 5.10). Wierzbowski (2004) analysed 23 belemnite specimens of the genera *Cylindroteuthis* and *Pachyteuthis* and recorded oxygen isotope values of -1.88

to 0.81 ‰ (compared with values of -2.07 to 1.20 ‰ recorded from the same time interval in this research).

There is some degree of scatter in the  $\delta^{18}$ O values (<2.38 ‰, mean 0.73 ‰) recorded here from coeval belemnites. This scatter could be the result of diagenetic alteration, salinity fluctuations, generic vital effects or generic palaeoecological variability. The effect of taxonomic differences in fractionation appears to be limited here, since no major isotopic trends can be identified at the generic level (as discussed previously). Major diagenetic alteration of the specimens has also been ruled out by extensive screening. However, it is possible that subtle alteration escaped detection, although since the specimens were collected from the same location, were exposed to the same postdepositional processes and passed the same selection criteria, any such effect on the scatter of data would be very limited, as it is likely that the whole data set would have been affected and therefore the temporal trend would still be preserved even if absolute values were not.

As discussed previously (in Chapter 3) modern cephalopods are known to secrete their calcite very close to isotopic equilibrium with surrounding seawater (e.g., Taylor & Ward, 1983; Morrison & Brand, 1986; Rosales *et al.*, 2004a; Rexfort & Mutterlose, 2006) and at present no major seasonal or taxonomic differences in fractionation have been confirmed (Sælen *et al.*, 1996; Podlaha *et al.*, 1998; Rosales *et al.*, 2004a). McArthur *et al.* (2004) suggest that differences in fractionation or habitat may potentially produce a disparity in isotope values for different belemnite species, although such disparity is not observed here. The Staffin Bay oxygen isotope record is therefore considered to primarily reflect changes in environmental conditions (temperature and salinity) rather than taxonomic or diagenetic processes. It should be noted however, that since belemnites are extinct organisms it is impossible to calibrate the temperature response of  $\delta^{18}$ O within the skeleton and it is therefore probably unrealistic to calculate absolute palaeotemperatures (McArthur *et al.*, 2000) from the oxygen isotope data, although the likely magnitude of

temperature change can be estimated (Bailey *et al.*, 2003). Nevertheless palaeotemperatures have been calculated here and should be considered as a guide to the potential palaeotemperatures for the region.



**Figure 5.13** Palaeotemperatures calculated from Mg/Ca data (using the Klein *et al.*, 1996 equation) and  $\delta^{18}$ O data (using the Anderson & Arthur, 1983 equation). Boreal (British) ammonite zones and subzones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

Figure 5.13 shows seawater palaeotemperatures calculated from the  $\delta^{18}$ O equation of Anderson & Arthur (1983). The isotopic composition of the water was assumed to be that of non-glacial seawater at -1 ‰ SMOW. This is consistent with previously published literature on the Jurassic period (e.g., Marshall, 1992; Sælen *et al.*, 1996; Price &

Sellwood, 1997; Podlaha *et al.*, 1998; Price & Mutterlose, 2004; Rosales *et al.*, 2004a, 2004b). The average palaeotemperature derived from the Staffin Bay belemnites was 12.4°C and the palaeotemperature range was 6.7°C to 20.6°C for the Callovian-Kimmeridgian interval. The lowest palaeotemperatures were recorded from the Lower Oxfordian *Mariae* Zone and the highest palaeotemperatures from the *Baylei* Zone of the Lower Kimmeridgian. Such values are broadly comparable with other published Oxfordian records. For example, Price & Gröcke (2002) record temperatures of 14.5 to 21.2°C from the Oxfordian-Kimmeridgian of the Falkland Plateau, Wierzbowski (2002) records values of 10.5 to 18.5°C during the Oxfordian in Central Poland and Riboulleau *et al.*, (1998) record values of 7 to 18°C from the Oxfordian of the Russian Platform.

As stated previously the Staffin Bay palacotemperatures were calculated using a value of -1 ‰ SMOW for non-glacial seawater (following convention). Broecker *et al.* (1989) however, suggest that seawater oxygen isotope compositions can vary by as much as 1.5 ‰ between high and low latitudes as a result of evaporation, precipitation and atmospheric vapour transport. High latitude  $\delta^{18}O_{scawater}$  values are lower that those of the low latitudes and have a lower salinity due primarily to the transport of isotopically depleted water vapour towards the poles. In addition, seasonal ice-melt and the proximity to landmass (and therefore the potential for riverine runoff) provide further opportunities for the input of isotopically light and low salinity waters into the high latitude system (Price & Mutterlose, 2004). Roche *et al.* (2006) modelled this phenomenon of  $\delta^{18}O_{scawater}$  values of higher than today in the equatorial region and lower than today in the high latitudes, with more pronounced differences occurring as the average climate becomes warmer. They conclude that neglecting these changes has led to an underestimation of temperature in the low latitudes and an overestimation of temperature at the poles.

The temperature-salinity plot shown in Figure 5.14 illustrates the effect that salinity can have on calculated temperature. This model was constructed by Railsback *et al.* 

(1989) and Woo *et al.* (1992) with modification by Price & Mutterlose (2004). Each isopleth represents the potential range of temperature (calculated using the Anderson & Arthur (1983) equation) and salinity combinations for calcite of a known isotopic value. For example, within the model, a  $\delta^{18}$ O value of 1.4 ‰ (the highest value recorded from Staffin Bay) corresponds to a palaeotemperature range of between 2.9°C (at 30 ‰ salinity) and 6.7°C (at 34 ‰ salinity) as shown by the dashed lines. The palaeotemperatures calculated using a 'normal' marine salinity of 34 ‰ correspond to those calculated by the Anderson & Arthur (1983) equation and a  $\delta^{18}$ O<sub>seawater</sub> value of -1 ‰.

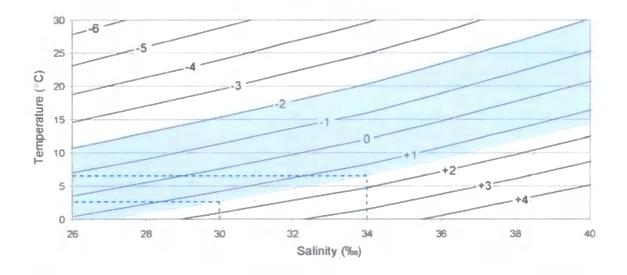


Figure 5.14 Temperature-salinity plot for the Staffin Bay data. The continuous diagonal lines are isopleths of  $\delta^{18}$ O values and show the possible combination of temperature and salinity that corresponds to calcite of a given isotopic composition of seawater (-1 %). The shaded area shows the range of isotope values recorded from belemnite rostra from the Callovian-Lower Kimmeridgian succession at Staffin Bay. The dashed lines represent the values discussed in the text above.

### 5.5.3. The Elemental Records & Palaeotemperature Implications

Several authors have recently investigated the use of elemental ratios (e.g., Mg/Ca, Sr/Ca, Na/Ca and Li/Ca) from biogenic calcite (e.g., belemnites, foraminifera, ostracods and corals) as palaeotemperature proxies (e.g., Dwyer *et al.*, 1995; Klein *et al.*, 1996; Mitsuguchi *et al.*, 1996; Lear *et al.*, 2000, 2002; McArthur *et al.*, 2000; Wei *et al.*, 2000; Hall & Chan, 2001; Bailey *et al.*, 2003; Billups & Schrag, 2003; Rosales *et al.*, 2004a, b; Immenhauser *et al.*, 2005). It has been suggested that elemental/Ca values in belemnites may reflect only temperature, whilst  $\delta^{18}$ O ratios reflect both temperature and variations in

ice-volume or salinity (McArthur *et al.*, 2000). McArthur *et al.* (2000) record a significant correlation between Sr/Ca, Na/Ca and Mg/Ca ratios with  $\delta^{18}$ O and they suggest that Sr/Ca values may be the most robust elemental ratio with which to estimate palaeotemperatures. Bailey *et al.* (2003) however, concluded that their belemnite Sr/Ca records were unlikely to reflect temperature alone and that physiological factors (e.g., growth rate or metabolic effects) may also significantly influence the Sr/Ca record. As such, they suggested that Mg/Ca would provide a better palaeotemperature proxy.

Both McArthur *et al.* (2000) and Bailey *et al.* (2003) observed inverse correlations between Mg/Ca, Sr/Ca, Na/Ca and  $\delta^{18}$ O, with R<sup>2</sup> values between 0.16 and 0.69, 0.19 and 0.56, and 0.0004 and 0.45 respectively. Cross-plots of *El/Ca* against  $\delta^{18}$ O for the Staffin Bay belemnites generally recorded less significant correlations, with R<sup>2</sup> values of 0.11 (Mg/Ca), 0.46 (Sr/Ca) and 0.18 (Na/Ca) (Fig. 5.8). Interestingly, only Sr/Ca shows a statistically significant (at the 99% confidence level) negative correlation with  $\delta^{18}$ O for the Staffin Bay data, whilst neither Mg/Ca nor Na/Ca show a statistically significant correlation with  $\delta^{18}$ O.

Mn/Ca values were calculated for each sample and only those samples with values below 100 µmol/mol are included here, as this is the lower limit for samples that are believed to have been altered under reducing conditions (McArthur, 1994). The elemental ratios presented here (Mg/Ca, Sr/Ca, Na/Ca and Li/Ca) show little long-term variability (Fig. 5.9), although this is also the case for the  $\delta^{18}$ O record, which becomes only slightly more negative up sequence. The Mg/Ca values decrease slightly up sequence, whilst Sr/Ca values increase. The Na/Ca and Li/Ca values show no discernible long-term trend. It is difficult to fully assess the relationship between  $\delta^{18}$ O and *El/Ca* ratios for the Staffin Bay section because the Callovian to Kimmeridgian interval is isotopically quite static. If instead, a major isotopic event occurred during this time the relationship between  $\delta^{18}$ O and *El/Ca* would be more readily observable.

The only statistically significant correlation observed from the Staffin Bay belemnites is that between Sr/Ca and  $\delta^{18}$ O, where the lowest Sr/Ca values correspond with the highest  $\delta^{18}$ O values. McArthur *et al.* (2000) also observed a stronger correlation between Sr/Ca and  $\delta^{18}$ O than between Mg/Ca and  $\delta^{18}$ O, although Bailey *et al.* (2003) recorded the opposite for the same Pliensbachian-Toarcian Yorkshire succession. Studies based on extant coccoliths (Stoll *et al.*, 2002) and foraminifera (Lea *et al.*, 1999) indicate that the temperature sensitivity of Sr/Ca is approximately 10 times greater than that of Mg/Ca. However, this is not consistent with the relative changes observed here between Sr/Ca and Mg/Ca, which would indicate that these belemnite records may not reflect temperature alone. Klein *et al.* (1996) suggest that for the marine mussel *Mytilus trossulus* Sr/Ca appears to be strongly influenced by physiological factors and it is therefore possible that the Sr/Ca temperature response in belemnites is exaggerated by physiological effects.

The Mg/Ca proxy is generally considered to be the most appropriate elemental ratio with which to investigate palaeotemperature (e.g., Klein *et al.*, 1996; Lear *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b; Immenhauser *et al.*, 2005). The Mg content of seawater is primarily controlled by the balance between fluvial supply rates and removal into biogenic carbonates and hot basalt at ocean spreading ridges (Wilkinson & Algeo, 1989). At short time scales (ammonite zones or subzones) temperature change is the most likely control on Mg/Ca ratios in biogenic carbonates (Jenkyns *et al.*, 2002). In general, low Mg/Ca ratios have been associated with cooler seawater temperatures, whilst high values are associated with warmer conditions (Rosales *et al.*, 2004b). Several authors have suggested that unlike  $\delta^{18}$ O, the Mg/Ca proxy is largely independent of salinity effects (e.g., Klein *et al.*, 1996; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b; Immenhauser *et al.*, 2005). This idea is supported by experimental data indicating that even a salinity decrease of 18 ‰ is only weakly reflected in Mg/Ca ratios (e.g., Naydin & Teys, 1976; Yasamanov, 1981; Klein *et al.*, 1997; Rosales *et al.*, 2004b).

For the belemnites from Staffin Bay there is no statistical correlation between Mg/Ca and  $\delta^{18}$ O, although the linear regression line suggests a weak positive relationship between the two values. This positive relationship is contrary to the correlation observed in modern skeletal calcite (Steuber & Rauch, 2005) and in previous belemnite studies (as The absence of correlation observed here could be due to mentioned previously). interspecies offset (as different genera were sampled), ontogenetic variations (as different regions of the rostra were sampled), metabolic activity, salinity or temperature depending on the influence of each variable on each proxy. Assuming however, that temperature is the major control on Mg/Ca ratios and that belemnites have a similar temperature sensitivity to modern biogenic calcites (as has been concluded by several of the recent studies of *El/Ca* ratios in belemnites: e.g., Bailey et al. (2003) and Rosales et al. (2004a)) it seems likely that salinity has had an effect on the  $\delta^{18}$ O record. The palaeotemperatures calculated from the  $\delta^{18}$ O and Mg/Ca proxies show only slight long-term variation. The  $\delta^{18}$ O derived temperatures indicate a slight warming up sequence, whilst the Mg/Ca derived temperatures remain relatively static. The  $\delta^{18}$ O and Mg/Ca palaeotemperatures (calculated using the Anderson & Arthur (1983) and Klein et al. (1996) equations respectively) show a considerable offset (Fig. 5.13), with ranges of  $\delta^{18}$ O and Mg/Ca from 6.7 to 20.6 °C (average 12.4 °C) and -1.3 to 21.2 °C (average 3.8 °C) respectively. This offset is consistent with data from Klein et al. (1997) that recorded lower temperatures from Mg/Ca values compared with  $\delta^{18}$ O values for *Mytilus trossulus*. The average discrepancy between the palaeotemperature proxies is 8.6 °C. If this temperature difference was interpreted solely as the result of salinity it would require a change in salinity from, for example, 34 to 25.2 ‰. However, a change of this magnitude seems unlikely, since it would be occurring in a shallow marine succession with an abundance of marine fauna (ammonites and belemnites) throughout as well as a diverse palynoflora indicting open marine conditions (Morton & Hudson, 1995; Riding & Thomas, 1997; Wierzbowski, 2004). An average palaeotemperature of 3.8 °C for this palaeolatitude is

intuitively unlikely, which together with the salinity changes required to achieve this suggests that the use of Mg/Ca palaeotemperature equations on belemnites (after Klein *et al.* (1996) and based on an extant bivalve species) may not be entirely appropriate. Ultimately, the use of Mg/Ca as a palaeotemperature proxy requires further evaluation.

The covariance of both Na/Ca and Li/Ca with  $\delta^{18}$ O as observed here is statistically insignificant. Bailey *et al.* (2003) report weak covariance between these variables and suggest that the lack of correlation indicates that these elemental ratios are unlikely to reflect temperature variations in belemnites. This is supported by experiments on modern foraminifera (e.g., Delaney *et al.*, 1985). Hall & Chan (2001) demonstrated that for recent foraminifera Li/Ca ratios were temperature sensitive and responded in the opposite sense to Mg/Ca (with Mg/Ca ratios decreasing with falling temperatures whilst Li/Ca ratios increased). Bailey *et al.* (2003) could not confirm these observations for belemnites and suggested that Li/Ca signals were not recorded, probably as the consequence of the small size of the Li ion, which makes it likely to be quickly lost from the calcite lattice after burial.

The difficulty in interpreting the *El/Ca* ratios in terms of environmental conditions is exacerbated at Staffin Bay by the static nature of the oxygen isotope record during this time period. By considering a more dynamic time period containing more significant isotope shifts (e.g., the Valanginian - see Chapters 7 and 8) it should be possible to produce more useful data with which to assess the nature of the relationships between temperature,  $\delta^{18}$ O and *El/Ca* ratios.

### 5.5.4. The Terrestrial Carbon Isotope Record

The organic carbon isotope ratios presented here are considered to primarily reflect changes in the terrestrial carbon isotope reservoir. The limitations and reliability of fossil wood data were discussed in Chapter 4, where it was concluded that  $\delta^{13}C_{org}$  values could be used to confidently identify long-term shifts in the composition of atmospheric carbon.

The  $\delta^{13}C_{ore}$  data from Staffin Bay reveal a rapid change towards more positive carbon isotope values from the Lower-Middle Callovian boundary and into the Lower Oxfordian. The positive excursion has a magnitude of  $\sim 5$  % (from approximately -26.5 to -21.5 %). This excursion is coincident with a change of depositional conditions from a coastal lagoon-type environment in the Callovian to more fully marine conditions from the earliest Oxfordian. The observed shift towards more positive values in the Lower Oxfordian however, cannot be attributed to a change in the source of organic matter. This is contrary to the work of Foster et al. (1997), which concluded that although secular variations in  $\delta^{13}C_{org}$  were present, they were often overprinted by changes in organic source or facies. The Rock-Eval data (Fig. 5.12) presented here confirm that the organic matter analysed from the Isle of Skye was predominantly derived from a terrestrial source (Type III kerogen). This is consistent with published palynological data for Staffin Bay, which record abundant palynomorphs that are dominated by gymnospermous pollen grains and associated with pteridophytic spores (Riding & Thomas, 1997). More specifically, the conifer pollen Classopollis and the wood genus Cupressinoxylon (Pearce et al., 2005) have been recognised. The Rock-Eval pyrolysis identified several samples with relatively high hydrogen indices, which would suggest that a marine component is occasionally incorporated within the organic matter. Marine microplankton, most notably dinoflagellate cysts, have been recorded from throughout the Staffin Bay section (Riding & Thomas, 1997; Hesketh & Underhill, 2002). These data however, do not consistently correspond with heavier carbon isotope ratios. It is therefore assumed that the organic matter source has not significantly influenced the carbon isotope trend recorded here.

From the Lower Oxfordian the  $\delta^{13}$ C values remain fairly constant, fluctuating between approximately -21 and -23 ‰ (values typical of terrestrial organic matter) until the Middle-Upper Oxfordian boundary, after which the carbon isotope values decrease reaching ~ -25.5 ‰ in the Lower Kimmeridgian *Cymodoce* Zone. The timing and duration of the observed  $\delta^{13}C_{org}$  trend is consistent with data published by Pearce *et al.* (2005). Pearce *et al.* (2005) analysed 37 Upper Callovian (*Athleta* Zone) to Lower Kimmeridgian (*Baylei* Zone) samples of microscopic wood debris from the Staffin Shale Formation. Microscopic wood fragments were separated from the mud matrix and crudely categorised as coal, charcoal or a combination of both, although no relationship between the state of preservation and isotope ratio was discernable. The  $\delta^{13}C_{org}$  values presented here are consistent with those of Pearce *et al.* (2005) and are similar to the range expected for Cretaceous C<sub>3</sub> plants (-23 to -34 ‰) (Bocherens *et al.*, 1993; Gröcke, 1998; Robinson & Hesselbo, 2004; Pearce *et al.*, 2005). The coeval marine carbonate samples are offset by between 21 and 30 ‰.

### 5.5.5. The Marine Carbon Isotope Record

The marine  $\delta^{13}C_{carb}$  record shows a distinct change from more positive values in the Lower and Middle Oxfordian (typically ~2 to 4 ‰), to more negative values from the Upper Oxfordian and into the Lower Kimmeridgian (typically ~0 to 2 ‰). This trend can be observed despite a considerable degree of scatter in the marine carbonate data. Such scatter however, is consistent with published belemnite data from other sections (e.g., Bailey *et al.*, 2003; McArthur *et al.*, 2004; Price & Mutterlose, 2004; Wierzbowski, 2004) and is most likely the result of real and natural variation. By comparison, bulk records tend to produce smoother, less noisy curves. This is the result of time averaging, which dampens natural variability and homogenisation of the constituent components. For example, a 1 mm bulk sediment sample could represent anything in the range of 100-1000 years or more, whilst a 1 mm sample of belemnite calcite probably only represents a period of months.

The belemnite derived carbon isotope values presented here are compatible with those recorded by Wierzbowski (2004) from the Middle Oxfordian (*Densiplicatum* Zone) to Lower Kimmeridgian (*Cymodoce* Zone) of Staffin Bay (Fig. 5.10). Wierzbowski (2004) recorded carbon isotope values between 0.62 and 4.69 ‰ (compared with values of 0.11 to 4.02 ‰ recorded here for the same interval).

### 5.5.6. The Carbon Isotope Records & Ocean-Atmosphere Correlation

The comparison of marine with terrestrial carbon isotope stratigraphy is essential to confirm that isotopic patterns are of global origin rather than the result of local or diagenetic factors (Hesselbo *et al.*, 2003). There have been a number of recent studies that have compared marine and terrestrial carbon isotope records (e.g., Ando *et al.*, 2002, 2003; Hesselbo *et al.*, 2003; Robinson & Hesselbo, 2004; Gröcke *et al.*, 2005; Pearce *et al.*, 2005), however these studies almost always compare carbon isotope data from geographically different successions. Geological successions containing both a marine and terrestrial record suitable for isotope work are extremely rare and data from such a succession have never been published, where data were collected simultaneously. This study presents the first coeval marine and terrestrial record of this kind.

The observed offset between the Staffin Bay  $\delta^{13}C_{earb}$  and  $\delta^{13}C_{org}$  data is approximately ~25.5 ‰ on average, which is consistent with the observed offset of ~25 ‰ recorded by Pearce *et al.* (2005) for the same succession (their value was calculated using the carbonate data of Wierzbowski (2004)). The  $\delta^{13}C_{earb}$  curve corresponds well with the  $\delta^{13}C_{org}$  curve from the Lower Oxfordian and into the Kimmeridgian, which indicates a strong coupling of the ocean-atmosphere system at this time. The most positive  $\delta^{13}C$ values occur during the Lower and Middle Oxfordian (*Mariae* to *Glosense* zones) where values are consistently high in both the marine and terrestrial records. A change to increasingly negative values occurs during the Upper Oxfordian *Glosense* Zone until the occurrence of a brief positive fluctuation in the Early Kimmeridgian *Cymodoce* Zone. This trend is observed in both records, which suggests that the total exchangeable carbon reservoir would have been affected. It is worth noting that the  $\delta^{13}C_{org}$  data show a greater amplitude of change than the coeval  $\delta^{13}C_{earb}$  data, which is in agreement with other published Mesozoic  $\delta^{13}C_{wood}$  data (e.g., Gröcke *et al.*, 1999; Robinson & Hesselbo, 2004; Pearce *et al.*, 2005).

The Callovian  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$  curves, however, do not correspond. A rapid positive excursion of approximately 4 ‰ is observed in the  $\delta^{13}C_{org}$  record, whilst the  $\delta^{13}C_{carb}$  values remain relatively constant. This decoupling is probably the result of a small, local event which is only recorded in either the marine or terrestrial realm, although the nature of such an event remains unclear.

### 5.5.7. Callovian-Kimmeridgian Marine & Terrestrial Isotopic Records

The isotopic offset between the Staffin Bay  $\delta^{13}C_{org}$  and  $\delta^{13}C_{carb}$  records (~25.5 ‰) is greater than that observed between  $\delta^{13}C_{org}$  and  $\delta^{13}C_{carb}$  values in the Oxfordian of Poland and Germany (~23 ‰) as recorded and discussed by Wierzbowski (2002, 2004) and Pearce *et al.* (2005). Wierzbowski (2004) attributes this difference in offset to isotopically heavier belemnite values as a result of <sup>13</sup>C enrichment in the Boreal Realm due to high organic matter productivity in the partly isolated Boreal seas. Since no enrichment is observed here in the  $\delta^{13}C_{org}$  data (which are consistent with the sub-Tethyan Oxfordian  $\delta^{13}C_{wood}$  values from Dorset (Pearce *et al.* 2005)) the observed offset must be the result of localised changes of isotopic composition in the marine carbon reservoir. This lends support to the idea that  $\delta^{13}C_{org}$  data reflect a global signal influenced primarily by perturbations in the total exchangeable carbon reservoir (Pearce *et al.*, 2005).

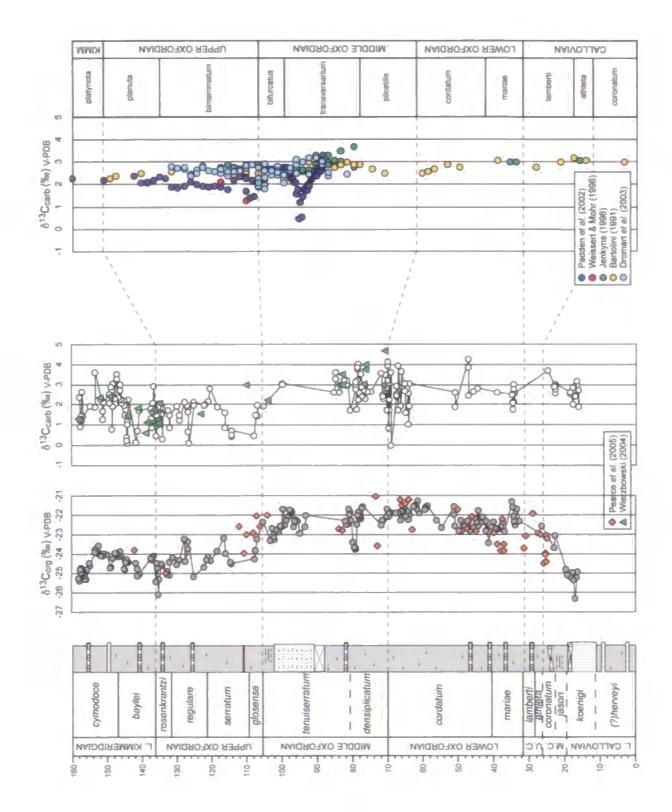
The timing of the positive  $\delta^{13}$ C excursion recorded here is similar to that recorded in previously published Callovian to Kimmeridgian  $\delta^{13}$ C marine and terrestrial data. The duration of the Staffin Bay excursion is from the *Mariae* to *Tenuiserratum* zones, with the maximum occurring across the *Cordatum-Vertebrale* Subzonal boundary (using the Boreal British ammonite zonation) in both the organic and carbonate records. Pearce *et al.* (2005) also record a broad positive  $\delta^{13}C_{wood}$  excursion at this time from the Staffin Bay succession, although their maximum occurs slightly later, across the *Vertabrale*- *Tenuiserratum* Subzonal boundary. A broad positive  $\delta^{13}C_{carb}$  excursion has also been recorded in the sub-Alpine basin of southeast France, with a maximum during the *Parandieri* Subzone (Tethyan ammonite zonation, equivalent to the Boreal British Upper *Tenuiserratum* Subzone) (Beat Louis-Schmid pers. comm.). Middle Oxfordian positive  $\delta^{13}C$  excursions have also been recorded by Jenkyns (1996), Weissert & Mohr (1996), Bartolini *et al.* (1999), Wierzbowski (2002), Dromart *et al.* (2003b).

It is worth noting that although the excursion maximum observed here in the Staffin Bay data occurs earlier than in the other comparable successions, the  $\delta^{13}$ C values remain relatively positive until the end of the *Tenuiserratum* Zone. Much of the discrepancy between the timing and duration of the positive excursion may be accounted for by factors such as poor sampling resolution, limited biostratigraphical data, condensed sections and missing strata in the previously published sections. The Staffin Bay data is very well constrained biostratigraphically and of a high sampling resolution, which may contribute to the elimination of some of this uncertainty.

Jenkyns (1996), Weissert & Mohr (1996) and Wierzbowski (2002) have interpreted the mid-Oxfordian positive carbon isotope excursion as the result of organic carbon burial during a eustatic sea-level rise. However, Hesselbo & Coe (2000) presented a sea level curve covering the complete Callovian to Kimmeridgian Staffin Bay succession, which led Pearce *et al.* (2005) to conclude that sea-level rise was not the primary factor to influence this  $\delta^{13}$ C excursion because, according to their investigation, increasing  $\delta^{13}$ C values corresponded to a relative sea-level fall. Instead, Pearce *et al.* (2005) proposed an increase in global organic carbon burial rates or an as-yet un-established mechanism to account for the excursion. Evidence for Oxfordian organic carbon burial in the form of high TOC values or organic rich deposits has been reported from Canada (Stewart *et al.*, 1992) the Arabian Peninsula and the U.S. Gulf Coast (Dromart *et al.*, 2003b). The TOC data presented here (Fig. 5.11) is relatively low (with an average value of ~2.0 wt % *cf.* ~11 wt % as reported from Canada (Stewart *et al.*, 1992)), however, this may be because the depositional environment at this location was not favourable to organic matter preservation. The TOC data may still support the idea of increased organic carbon burial however, as a slight increase in values is seen during the Oxfordian.

Middle Oxfordian (Transversarium and Bifurcatus zones) negative carbon isotope excursions have been identified by Padden et al. (2001, 2002) in the Tethyan region (Switzerland and France) (Fig. 5.15). The observed excursions are relatively brief and of a high magnitude (2 ‰ in marine carbonates) leading to the suggestion that they may be associated with episodes of methane release as the excursions are of a similar magnitude and duration to the Toarcian, Aptian and Palaeocene events, which have been more firmly attributed to the dissociation of oceanic methane hydrates (Padden et al., 2001). These negative excursions are not identified in the Staffin Bay data however. Small and brief negative excursions are observed in both the organic and carbonate records (~1.5 ‰), although these occur much earlier than those observed in the Tethys (in the Vertebrale Subzone and Cordatum Subzone respectively). These somewhat indistinct excursions could easily be explained by a slight fluctuation in the organic matter source (wood record) or natural variability in the data (carbonate record). It should be further noted that the negative excursion recorded in the organic carbon isotope data occurs almost immediately after the Middle Oxfordian positive  $\delta^{13}$ C excursion maximum. Pearce *et al.* (2005) suggest that this relationship is compatible with the theory that a relative sea-level rise associated with the reopening of Boreal-Tethyan oceanic connections changed oceanic circulation and released methane.

Pearce *et al.* (2005) did not observe the negative carbon isotope excursions in either their Staffin Bay or Dorset datasets. They suggested that this may have been the result of an insufficient sampling resolution. However, the greatly improved sampling resolution employed here, indicates that the negative excursions observed in the Tethyan region are not occurring in this part of the Sub-Boreal Realm. This would suggest that the negative excursions identified by Padden *et al.* (2001, 2002) may not be the result of fluctuations in



**Figure 5.15** Callovian-Lower Kimmeridgian  $\delta^{13}$ C correlation between a composite Tethyan  $\delta^{13}C_{carb}$  curve and the  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$  curves from Staffin Bay, Isle of Skye, Scotland. The Tethyan data was collected from the following locations: Bartolini (1991) - Italy; Jenkyns (1996) - Italy, Weissert & Mohr (1996) - E. Switzerland; Padden *et al.* (2002) - S. Alps, S. Switzerland; Dromart *et al.* (2003b) - France. For Staffin Bay curve Boreal (British) ammonite zonation is illustrated and scale is in metres. See Figure 4.2 for key to log symbols. For Tethyan curve Tethyan ammonite zonation is illustrated.

the total exchangeable carbon reservoir and that perhaps the global scenario needs to be revisited.

### 5.6. Conclusions

- The data presented here comprise the first combined high-resolution isotope investigation of  $\delta^{13}C_{org}$ ,  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  from Staffin Bay, Isle of Skye. It is also the first ever investigation of a coeval  $\delta^{13}C_{org}$  and  $\delta^{13}C_{carb}$  record (together with the data presented in Chapter 7), the development of which is essential to understanding oceanatmosphere interactions.
- The average palaeotemperature derived from the Staffin Bay δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) was 12.4°C and the palaeotemperature range was 6.7°C to 20.6°C for the Callovian-Kimmeridgian interval.
- The average palaeotemperature derived from the Staffin Bay Mg/Ca record (using the Klein *et al.* (1996) equation) was 3.8°C and the palaeotemperature range was -1.3°C to 21.2°C for the Callovian-Kimmeridgian interval. This average palaeotemperature is intuitively unlikely, suggesting that the use of belemnite Mg/Ca as a palaeotemperature proxy may require further investigation.
- The  $\delta^{13}C_{org}$  data record a broad Lower-Middle Oxfordian positive carbon isotope excursion of ~5 ‰. A return to pre-excursion values occurs from the Upper Oxfordian and into the Lower Kimmeridgian, although, a brief positive fluctuation is observed during the Lower Kimmeridgian *Cymodoce* Zone. This long-term trend is also observed in the  $\delta^{13}C_{earb}$  data, although the magnitude of the trend is approximately half that of the  $\delta^{13}C_{org}$  record (this is typical of other records). This correlation indicates a strong coupling of the ocean-atmosphere system at this time and suggests that the total exchangeable carbon reservoir was affected. Such a relationship has never before been observed from a coeval marine and terrestrial record.

- There is a possible decoupling of the ocean-atmosphere system during the Callovian. At this time a large shift of  $\delta^{13}C_{org}$  values occurs, whilst  $\delta^{13}C_{carb}$  values remain fairly constant. This indicates that there may have been a local influence on the marine or terrestrial realm during the Callovian period, although the nature of this influence in unclear.
- The Middle Oxfordian positive δ<sup>13</sup>C excursion maximum occurs earlier in the Staffin Bay record (*Cordatum-Vertebrale* Subzonal boundary) than it does in the Tethyan records (*Tenuiserratum* Subzone). However, consistently high values are observed at Staffin Bay until the end of the *Tenuiserratum* Zone. This positive excursion is believed to be the result of an increase in global organic carbon burial rates.
- The mid-Oxfordian negative carbon isotope excursions previously identified in the Tethyan regions are not recorded in the Staffin Bay data despite the relatively high sampling resolution and good biostratigraphic control. These negative excursions have previously been attributed to methane release, however, this new data indicates that the Tethyan excursions may not represent fluctuations in the total exchangeable carbon reservoir and therefore the fidelity of the methane hypothesis should be re-evaluated.

### PLATE 1

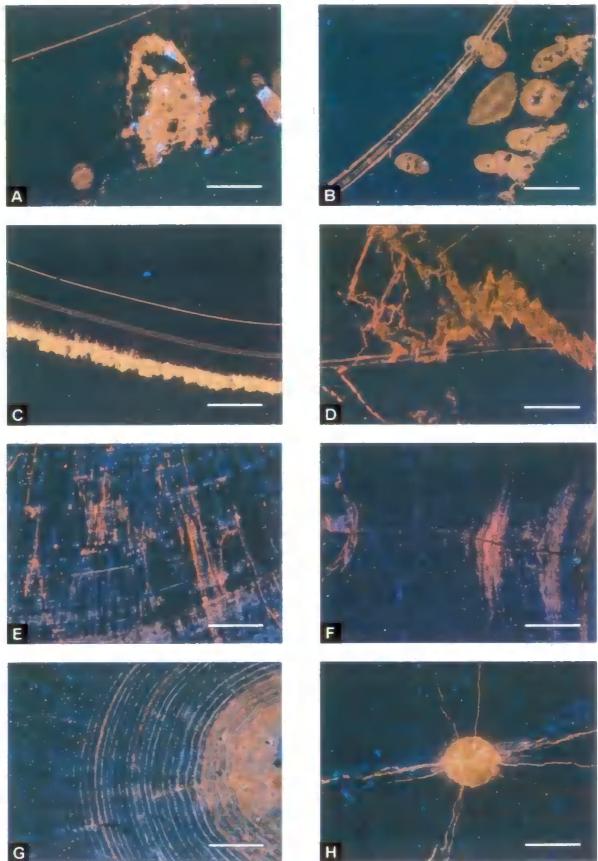
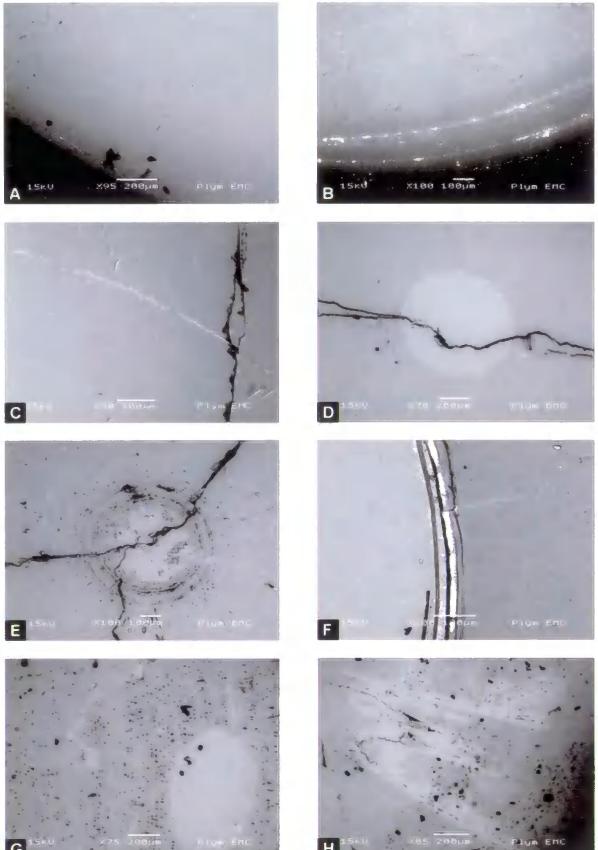


Plate 4. Cathodoluminescence images showing the state of preservation of belemnite rostra from Staffin Bay, Isle of Skye, Scotland. All scale bars represent 1 mm. (A) Borings in rostrum margin infilled with diagenetic cement. (B) Borings in rostrum margin infilled by diagenetic cement. (C) Rostrum margin and growth bands showing alteration. (D) Fractures displaying alteration. (E) Fractures and growth lines displaying alteration. (G) Apical canal with sedimem infilling and growth bands displaying alteration. (H) Diagenetically altered fractures eminating from the apical canal.

## PLATE 2



**Plate 2.** Backscattered SEM images showing the state of preservation of beleminte rostra from Staffin Bay. Isle of Skye. All scale bars represent lengths stated on images. (A) Well preserved calcite with some slight alteration at rostrum margin. (B) Generally well preserved calcite but with some pyrite growth along growth lines towards the rostrum margin. (C) Pyrite growth along fracture. (D) Fracture running through diagenetically altered apical canal. (E) Apical canal and surrounding growth lines displaying alteration. (F) Edge of apical canal with presence of pyrite. (G) Area of altered calcite. (H) Area of altered calcite around fractures.

### PLATE 3

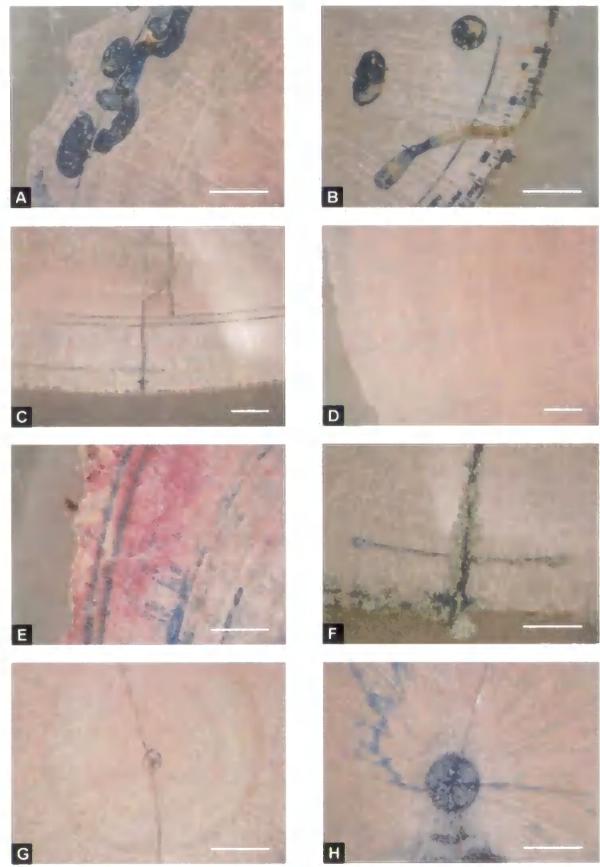


Plate 3. Carbonate stained images showing the state of preservation of belemnite rostra from Staffin Bay, Isle of Skye. All scale bars represent 1 mm. (A) Rostrum margin with borings infilled with diagenetic cement. (B) Rostrum margin with borings infilled with diagenetic cement. (C) Fractures and sections of growth lines displaying alteration, although otherwise well preserved. (D) Very well preserved calcite. No alteration present. (E) Rostrum margin showing alteration particularly along growth lines. (F) Fracture infilled with diagenetic cement and displaying pyritisation. (G) Faint fracture running through apical canal. (H) Apical canal with quartz replacement and fractures displaying alteration.

# 6. HELMSDALE, SUTHERLAND, SCOTLAND

### 6.1. Location & Site Description

Helmsdale is located on the eastern coast of Sutherland (at ~58°N), on the northeast coast of the Scottish mainland near Wick (Fig. 6.1). Five sites were examined along the coastline near Helmsdale between Kintradwell and Dùn Glas. In addition a further two sites were examined; Brora, approximately 15 km south of Helmsdale and Eathie Haven, 55 km south of Helmsdale near Cromarty on the northeast tip of the Black Isle.

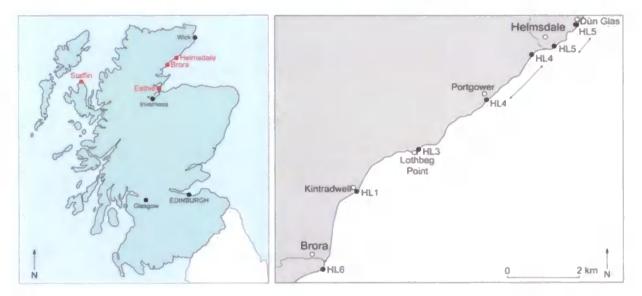


Figure 6.1 Location map of the Sutherland coastal region. The relative positions of Helmsdale, Brora, Eathie and Staffin (Isle of Skye) are shown (left). Also shown are the locations of the sites examined along the coast between Brora and Dùn Glas (right).

The Sutherland outcrops comprise predominantly of intermittent foreshore exposures of boulder beds, mudstones, siltstones and sandstones (Fig. 6.2). Several of the outcrops were accessible only at low tide and were covered by a mobile boulder beach and seaweed.

The Helmsdale succession provides an almost complete record of the Kimmeridgian (*sensu anglico* – see Chapter 2) *Cymodoce* to *Fittoni* ammonite zones. The Eathie section is Early Kimmeridgian (*Mutabilis* Zone) in age and the Brora section is Middle/Late Callovian in age.



Figure 6.2 Foreshore exposure typical of the area around the Helmsdale coast, Sutherland, Scotland. This photograph shows the exposure near Helmsdale Harbour (location HL5), which is part of the Portgower Boulder Beds Member.

# 6.2. Geological Setting

During the Jurassic Period, Scotland was situated at a palaeolatitude of approximately 45°N (Smith *et al.*, 1994). The coastal onshore Jurassic strata of northeast Scotland (e.g., at Brora, Helmsdale and Eathie) outcrop on the faulted western margin of the Inner Moray Firth Basin (Wignall & Pickering, 1993; Riding, 2005), which is part of the North Sea Basin system (Underhill, 1991) (Fig. 5.3). The Inner Moray Firth Basin was initiated in the Permian (Trewin *et al.*, 1990) and during the Mesozoic was controlled principally by two major extensional events (pre-Jurassic and Late Jurassic) (Underhill, 1991).

The basin is bounded on the north, northwest and south margins by the Wick, Helmsdale and Banff fault systems respectively (Trewin *et al.*, 1990; Underhill, 1991) and the Helmsdale and Great Glen faults separate the Helmsdale Terrace from the rest of the basin (Wignall & Pickering, 1993) (Fig. 6.3). The Helmsdale fault was active during the Jurassic and fault controlled Kimmeridgian deposition occurred on a proximal slope to deep marine system on the downthrow side (southeast) of the fault (Pickering, 1984; Trewin *et al.*, 1990).

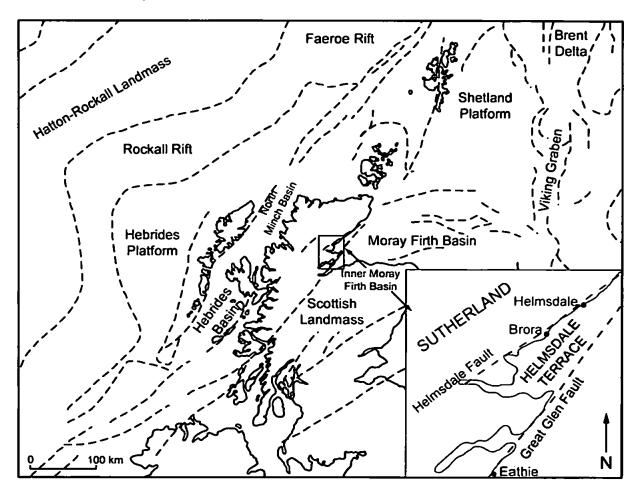


Figure 6.3 Late Jurassic palaeogeography. Inset is a locality map of the study area showing the Helmsdale Terrace and onshore outcrops of Jurassic strata. Palaeogeography map adapted after Hudson & Trewin (2002). Inset adapted after Wignall & Pickering (1993).

The basement of the Moray Firth Basin is composed of Moinian metasediments, intruded by the late Caledonian Helmsdale Granite and is unconformably overlain by Devonian Old Red Sandstone strata (Trewin *et al.*, 1990; Riding, 2005). The centre of Moray Firth deposition was situated offshore, 25 km east of Helmsdale, where the Jurassic succession reaches a thickness of ~ 2300 m (Chesher & Lawson, 1983; Riding, 2005). The most extensive and complete onshore outcrops are located on the Brora, Golspie and Dùn Glas foreshores (Riding, 2005) providing a narrow coastal strip of Jurassic outcrop bordering the margin of the Moray Firth Basin (Trewin *et al.*, 1990). The narrow outcrop

of Kimmeridgian strata in Helmsdale is the most extensive Kimmeridgian outcrop in Britain, excluding that of the Dorset coast (Cox, 2001b).

Three major formations make up the Bathonian to Upper Kimmeridgian (*sensu anglico*) strata of the Brora-Helmsdale region. These are the Bathonian-Callovian Brora Shale Formation; the Callovian-Oxfordian Clynekirkton Sandstone Formation; and the Kimmeridgian Helmsdale Boulder Beds Formation (BGS sheet S103EC, 1998) (Fig. 6.4).

UPPER JURASSIC	KIMMERIDGIAN	cymodoce - fittoni	HELMSDALE BOULDER BEDS FORMATION	~500m	Portgower Boulder Beds Mbr.
					Lothbeg Shale Mbr.
					Kintradwell Boulder Beds Mbr. / Allt na Cuile Sandstone Mbr.
MIDDLE JURASSIC	OXFORDIAN	athleta - baylei	CLYNEKIRKTON SANDSTONE FORMATION	~450m	Ardassie Limestone
					Brora-Clynelish Quarry-Fascally Ssts.
					Fascally Siltstone
	BATHONIAN - CALLOVIAN	? - coronatum	BRORA SHALE FORMATION	~150m	Brora Brick Clay
					Glauconitic Sandstone
					Brora Shale
					Brora Coal
					Inverbrora Shale
					Doll Sandstone

Figure 6.4 Stratigraphic chart for the Middle-Upper Jurassic of the Brora-Helmsdale region. Data from BGS sheet \$103EC, 1998.

The Brora Shale Formation (Bathonian to Middle Callovian, *Coronatum* Zone) is composed of the following units: Doll Sandstone (oldest), Inverbrora Shale, Brora Coal, Brora Shale, a Glauconitic Sandstone and the Brora Brick Clay (youngest) (BGS sheet S103EC, 1998). The formation is exposed on the foreshore south of Brora and on the banks of the Brora River (Sykes, 1975; Trewin *et al.*, 1990; BGS sheet S103EC, 1998). It is dominated by silty to shaly mudstones, with some bioturbation (Neves & Selley, 1975; Sykes, 1975; Trewin *et al.*, 1990). The Bathonian Doll Sandstone Member at the base of the formation is a cross-bedded sandstone containing plants and rootlets, which has been interpreted as fluvial or deltaic in origin (Hurst, 1981; Trewin *et al.*, 1990). The other units represent lagoonal conditions (the Inverbrora Shale) followed by a transgressive event (at the base of the Brora Shale Member) and subsequent marine regression (Trewin *et al.*, 1990). Belemnites are common in this formation, particularly within the Brora Shale, Glauconitic Sandstone and Brora Brick Clay members, which have a greater marine influence (Lee, 1925; Sykes, 1975; MacLennan & Trewin, 1989; Trewin *et al.*, 1990).

The Fascally Siltstone, Brora-Clynelish Quarry-Fascally Sandstone and Ardassie Limestone make up the Clynekirkton Sandstone Formation (Athleta to Baylei zones) (BGS sheet S103EC, 1998). This formation coarsens upwards slightly from bioturbated siltstones at the base (Fascally Siltstone), to fine-grained sandstones, with some rounded pebbles and trough cross-bedding towards the top of the Brora-Clynelish Ouarry-Fascally Sandstone Member (Sykes, 1975; Trewin et al., 1990). The ~12 m thick, Ardassie Limestone is composed of alternating calcareous sandstones and limestones, with the limestones reportedly comprised almost entirely of Rhaxella sponge spicules that have been replaced by calcite (Sykes, 1975; Trewin et al., 1990). The sandstone facies of this formation were deposited on a coastal marine shelf during a period of marine regression, whilst the Ardassie Limestone, was deposited under transgressive conditions (Trewin et al., 1990). The Clynekirkton Sandstone Formation is exposed on the foreshore near the mouth of the Brora River and along the rivers banks (Lee, 1925; Trewin et al., 1990; BGS sheet S103EC, 1998). It is also exposed at Ardassie Point, just north of Brora (Lee, 1925; Trewin et al., 1990; BGS sheet S103EC, 1998). Belemnites have been observed throughout the Clynekirkton Sandstone Formation (Lee, 1925; Trewin et al., 1990).

The Helmsdale Boulder Beds (*Cymodoce* to *Albani* zones) include the Kintradwell Boulder Beds Member, the Allt na Cuile Sandstone Member, the Lothbeg Shale Member and the Portgower Boulder Beds Member (youngest) (BGS sheet S103EC, 1998). The Allt na Cuile Sandstone Member and the Kintradwell Boulder Beds Member are believed to be lateral equivalents of each other, demonstrating the sedimentological variability occurring along an active fault (Trewin *et al.*, 1990). The Allt na Cuile Sandstones are medium to fine-grained and are often planar-laminated (Brookfield, 1976; Pickering, 1984; Trewin *et al.*, 1990; Wignall & Pickering, 1993). In places they are extensively veined due to their proximity to the active Helmsdale Fault (Trewin *et al.*, 1990). By comparison, the Kintradwell Boulder Beds are dominated by finely-laminated and fissile siltstones that contain rounded clasts, presumably derived from earlier Jurassic formations (Roberts, 1989; Tyson, 1989; Wignall & Pickering, 1993). Wignall & Pickering (1993) remark that perhaps the most spectacular feature of the Kintradwell Boulder Beds is the abundant evidence for synsedimentary deformation. These facies are exposed on the coastal foreshore between Kintradwell and Lothbeg Point (Trewin *et al.*, 1990), although exposure is often limited by an extensive cover of seaweed. Small, isolated outcrops of the Kintradwell Boulder Beds are distributed along the coastline. The boulder beds were observed to contain relatively abundant sandstone clasts, wood debris, occasional belemnites and rare partial ammonite clasts.

Also exposed at Lothbeg point is the Lothbeg Shale Member, which overlies the Allt na Cuile Sandstone and Kintradwell Boulder Beds. It is composed of interbedded shaly mudstones, siltstones and sandstones (Trewin *et al.*, 1990; Wignall & Pickering, 1993). Again the outcrop is extensively covered by seaweed, although interbedded mudstones, siltstones and sandstones were observed, some containing slumps and folds resulting from wet sediment deformation. This unit is overlain by the Portgower Boulder Beds Member, which is exposed on the coast from Lothbeg Point to Dùn Glas, northeast of Helmsdale (Trewin *et al.*, 1990; BGS sheet S103EC, 1998). These boulder beds have been described in detail by Pickering (1984) and Wignall & Pickering (1993). The boulder beds are supported by a sandstone matrix and separated by interbedded sandstones and siltstones, some of which have been described as 'tiger-strip' facies (Pickering, 1984; Trewin *et al.*, 1990; Wignall & Pickering, 1993). The boulder bed clasts are mostly

103

subrounded to subangular and are typically derived from Devonian and Jurassic lithologies (Pickering, 1984; Trewin *et al.*, 1990; Wignall & Pickering, 1993). Synsedimentary wetsediment deformation structures are common in these boulder beds (Wignall & Pickering, 1993). The exposure of the Portgower Boulder Beds Member north of Helmsdale Harbour is particularly good. The clasts within the boulder beds become more angular and chaotic up sequence and bedding becomes more difficult to discern. Belemnites are relatively abundant components in parts of the boulder bed succession and corals, gastropods, crinoids, bivalves and occasionally ammonites were also observed.

In the earliest Kimmeridgian, onset of activity along the Helmsdale Fault changed the environment of deposition from a broad, shallow marine shelf (on which the Clynekirkton Sandstone Formation was predominantly deposited) to a rapidly subsiding palaeoslope on which debris flow, rock slide and turbidity current deposition alternated with poorly oxygenated hemipelagic deposition (Pickering, 1984; Wignall & Pickering, 1993). Wignall & Pickering (1993) concluded that the deepest waters were located immediately next to the Helmsdale fault scarp, which would account for the more diverse benthic fauna observed in the lithologies at the Eathie location, representing shallower water conditions (Fig. 6.3).

# 6.3. Sampling & Methodology

The five main sites examined in the Helmsdale region provided samples from the Early Kimmeridgian (*Cymodoce* Zone) to latest Kimmeridgian (*Fittoni* Zone). These key sites provided an extension of the Early Kimmeridgian samples collected at Staffin Bay, Isle of Skye. In addition, the site visited in Brora (at which only 1 belemnite horizon was sampled) was Callovian in age (*Koenigi* Zone) and the site at Eathie (from which 9 belemnite horizons were sampled) was Early Kimmeridgian (*Mutabilis* Zone). In total, 58 belemnite horizons were sampled from the Sutherland region. Complete specimens were very rare from the Helmsdale region because the belemnites were generally well cemented

within the rock so that only fragments could be collected (Fig. 6.5). This was not the case at Brora or Eathie however, where more complete samples were collected from mudstones/siltstones. No sediment samples were collected from this region. Wherever possible multiple specimens were collected from the belemnite horizons. All samples were collected in June 2005.

The preservation of belemnite rostra was evaluated through trace element and stable isotopic analysis, backscattered scanning electron microscopy (BSEM), cathodoluminescence (CL) and carbonate staining (following the technique of Dickson (1965) and (1966)). The areas most susceptible to diagenesis were removed prior to isotopic and geochemical analysis. Samples were analysed for carbon and oxygen isotopes, with subsamples taken for trace element analysis (Fe, Mn, Ca, Sr, Mg, Na, Li).

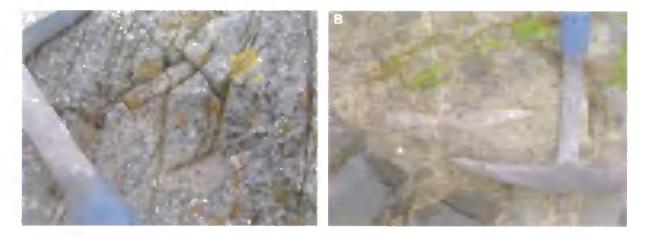


Figure 6.5 Typical preservation of Helmsdale belemnites. (A) Belemnite from the Kintradwell Boulder Beds Member on the Kintradwell coast (location HL1). (B) Belemnites from the Portgower Boulder Beds Member near Helmsdale Harbour (location HL5).

Stable isotope data were generated on a VG Optima mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), Keyworth, UK. Trace element data were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the NERC ICP facility, Department of Geology at Royal Holloway, University of London. For a full description of the methodology used see Chapter 4.

#### 6.4. Results

The belemnites sampled for this study were mostly translucent. The opportunity to conduct BSEM, CL and carbonate staining analysis on these specimens was limited due to lack of complete rostra collected. In total 11 out of 83 specimens were subject to optical analysis (Plates 4-6). Such analysis indicated that the periphery of the rostrum, the areas of the rostrum surrounding the apical canal, prominent fractures and strong growth bands were particularly susceptible to diagenetic alteration. These regions commonly appeared as pale grey-white in colour when subjected to BSEM analysis, luminescent under CL conditions and mauve-blue in colour after carbonate staining and were therefore removed prior to sampling.

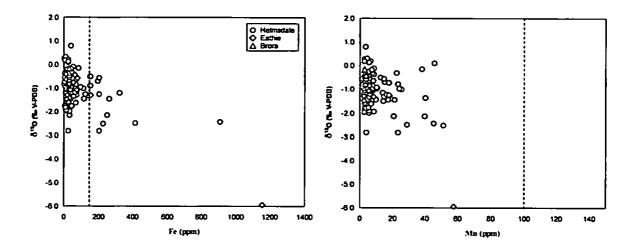


Figure 6.6 Cross-plots of  $\delta^{18}$ O against Fe (left) and Mn (right). The dashed line illustrates the cut off values for well preserved samples.

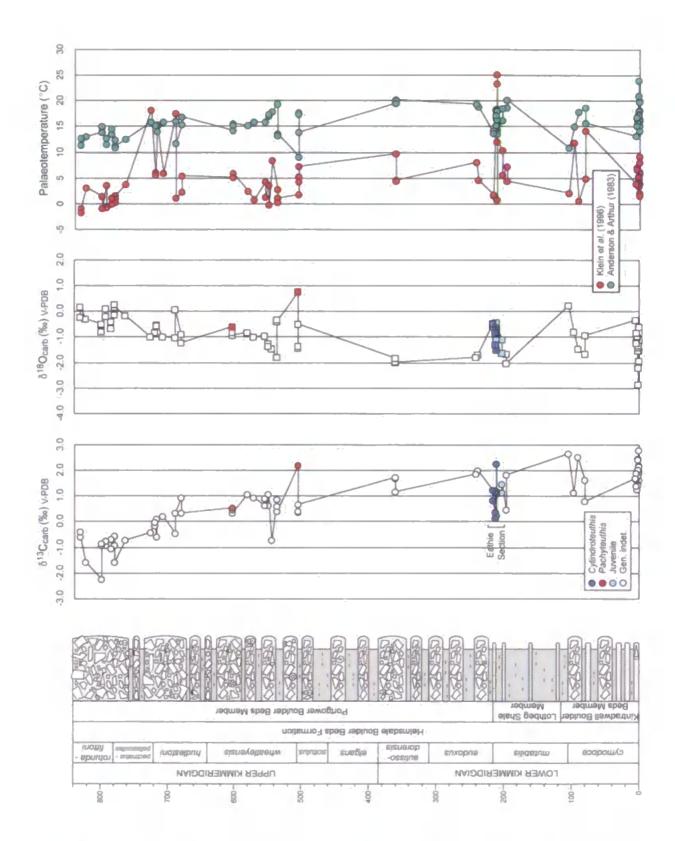
The Mn and Fe concentrations of the belemnites were also determined in order to provide an additional method by which to assess their state of preservation as noted previously. The determined values of Fe and Mn from the Helmsdale belemnite rostra were 5-910 ppm, mean 78 ppm and 2-51 ppm, mean 11 ppm respectively. The Fe and Mn values for the Eathie belemnites were 26-1154 ppm, mean 142 ppm and 3-57 ppm, mean 8 ppm respectively and the values for the Brora horizon were 30-32 ppm, mean 31 ppm for Fe and a mean of 3 ppm for Mn. Low Fe and Mn values were recorded for most of the belemnites, with a total of 17 samples rejected from this study on the basis of poor preservation. Trace element data (Fe and Mn) were plotted against  $\delta^{18}$ O to constrain any diagenetic alteration (Fig. 6.6). The higher amounts of Fe and Mn and occasional negative  $\delta^{18}$ O outliers are regarded as an artefact of diagenesis. The lack of correlation between the values, however, suggests minimal post-depositional alteration. Those samples with high Fe or Mn values that are considered to have possibly undergone some level of alteration were excluded from further analysis.

Additional elemental abundances derived from belemnite rostra from Helmsdale were as follows: Sr 676-1918 ppm, mean 1276 ppm, Mg 531-3280 ppm, mean 1189 ppm, Ca 22 % - 42 %, mean 30 %. Abundances for rostra from Eathie were: Sr mean 1172 ppm, Mg 1215-2971 ppm, mean 1792 ppm, Ca 30 % - 31 %, mean 30 %. For Brora the values were: Sr 905-950 ppm, mean 928 ppm, Mg 859-1194 ppm, mean 1066 ppm, Ca mean 30 %.

The oxygen and carbon isotope values of well preserved belemnites from Helmsdale range from -2.84 to 0.78 ‰ and from -2.25 to 2.82 ‰ respectively; from Eathie range from -1.60 to -0.41 ‰ and from 0.15 to 2.27 ‰ respectively; and from Brora range from -0.44 to -0.17 ‰ and 2.16 to 2.96 ‰ respectively. The Brora isotope values are similar to the isotope values derived from Callovian (*Koenigi* Zone) Isle of Skye belemnites, as noted previously. The *Koenigi* Zone is represented on the Isle of Skye by the Belemnite Sands Member (Morton & Hudson, 1995), a sandy glauconitic facies with abundant belemnites towards the top of the unit. The Brora belemnites were also sampled from a sandy, glauconitic unit (Early/Middle Callovian in age) with abundant belemnites. The mean values of  $\delta^{18}$ O and  $\delta^{13}$ C from the Brora belemnite rostra were -0.32 and 2.43 ‰ respectively, compared with values from the Isle of Skye of -0.33 ( $\delta^{18}$ O) and 2.65 ‰ ( $\delta^{13}$ C).

The oxygen and carbon isotope ratios from Helmsdale (*Cymodoce* to *Fittoni* zones) and Eathie (*Mutabilis* Zone) have some degree of stratigraphic overlap and so are

107



**Figure 6.7**  $\delta^{13}$ C and  $\delta^{18}$ O records from the Kimmeridgian succession at Helmsdale and Eathie, Sutherland, Scotland. Boreal British ammonite zones are illustrated here, however, it should be noted that the Upper Kimmeridgian (*sensu anglico*) is equivalent to the Tethyan Lower-Middle Tithonian. See Figure 4.2 for key to log symbols. Scale is in metres.

combined here to provide an almost complete succession of the Kimmeridgian (*Cymodoce* to *Fittoni* zones) for northeast Scotland (Fig. 6.7). Both the oxygen and carbon ratios show short and long-term variation. The overall oxygen isotope trend is one of values becoming gradually more positive, although, shorter-term variability is superimposed on this general trend, particularly for the Early Kimmeridgian *Cymodoce* and *Mutabilis* zones, where values become first more negative (-0.58 to -2.84 %<sub>0</sub>) before becoming more positive (-2.84 to -0.41 %<sub>0</sub>). From the *Eudoxus* Zone, the oxygen isotope values increase more consistently from -2.00 ‰ to 0.16 ‰ in the *Fittoni* Zone. The carbon isotope ratios generally become more negative throughout the Kimmeridgian, despite some degree of scatter. Values decrease from 2.22 ‰ in the lower *Cymodoce* Zone (where the most positive values can be observed) to -2.25 %<sub>0</sub> in the *Fittoni* Zone (where the most negative values can be observed). Increases in  $\delta^{13}$ C are mirrored by decreases in  $\delta^{18}$ O. This is confirmed by a cross-plot of  $\delta^{18}$ O vs.  $\delta^{13}$ C (Pearson's R<sup>2</sup> value, 0.498), which reveals a statistically significant negative correlation (at the 99% confidence level) (Fig. 6.8).

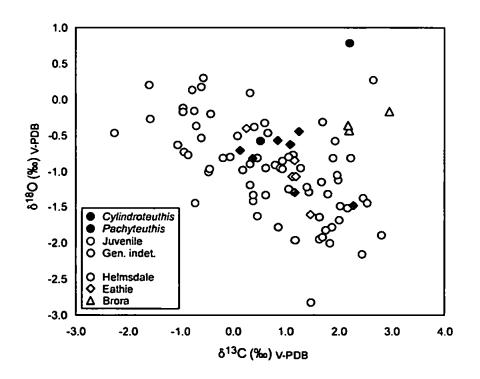


Figure 6.8 Cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C values from well preserved belemnites from Helmsdale, Eathie and Brora.

The belemnites sampled from these Callovian to Kimmeridgian successions were species of the boreal genera *Pachyteuthis* and *Cylindroteuthis* (although taxonomic identification was not always possible from these locations).

# 6.5. Discussion

#### 6.5.1. Stable Isotope, Geochemical & Taxonomic Records

As indicated above, taxonomic identification of belemnite rostra was very difficult with specimens from the Helmsdale region. The affect of taxonomic differences on stable isotope and geochemical records is, therefore, almost impossible to assess from this location. Whilst the data available do not indicate a taxonomic influence on the isotopic and elemental records, the limited nature of the data means that such an influence cannot be ruled out.

#### 6.5.2. The Oxygen Isotope Record & Palaeotemperature Implications

The oxygen-isotope data recorded from belemnites from the Helmsdale coast display some degree of scatter. Variation recorded from coeval belemnites ranged from 0.01 ‰ to 2.20 ‰, with an average of 0.59 ‰. This scatter could be the result of diagenetic alteration, salinity fluctuations, generic vital effects or generic palaeoecological variability as noted earlier. Major diagenetic alteration of the specimens has been ruled out by extensive screening, however, generic variations are impossible to rule out from this dataset due to the taxonomic identification problems encountered.

As discussed in Chapters 3 and 5 modern cephalopods are known to secrete their calcite very close to isotopic equilibrium with surrounding seawater (e.g., Taylor & Ward, 1983; Morrison & Brand, 1986; Rosales *et al.*, 2004a; Rexfort & Mutterlose, 2006) and at present no major seasonal or taxonomic differences in fractionation have been confirmed (Sælen *et al.*, 1996; Podlaha *et al.*, 1998; Rosales *et al.*, 2004a), although McArthur *et al.* 

(2004) suggest that a small  $\delta^{18}$ O offset (in the region of 0.4 ‰) may be observed between co-occurring specimens of different genera. As such, the  $\delta^{18}$ O data presented here is considered primarily to reflect changes in environmental conditions. McArthur *et al.* (2000) concluded that since belemnites are extinct it is unrealistic to calculate absolute palaeotemperatures from their  $\delta^{18}$ O composition. The palaeotemperatures calculated here should therefore only be regarded as a guide to the potential seawater temperatures in the region.

Palaeotemperatures calculated using the Anderson & Arthur (1983) equation are shown in Figure 6.7. The isotopic composition of the water was assumed to be that of nonglacial seawater at -1 ‰ SMOW (e.g., Marshall, 1992; Sælen *et al.*, 1996; Price & Sellwood, 1997; Podlaha *et al.*, 1998; Price & Mutterlose, 2004; Rosales *et al.*, 2004a, b). The calculated palaeotemperatures range from 9.1 to 24.0°C for the Kimmeridgian interval, with an average palaeotemperature of 15.8°C. This corresponds reasonably well with the Staffin Bay data, which record palaeotemperatures of 6.7°C to 20.6°C, with an average value of 12.4°C for the Callovian-Kimmeridgian interval. The warmest temperatures recorded from Helmsdale occur in the Lower Kimmeridgian *Cymodoce* Zone. Despite the degree of scatter present in the data a general trend of increasing  $\delta^{18}$ O (and therefore decreasing temperature) is observed, particularly from the *Wheatleyensis* to *Fittoni* zones.

#### 6.5.3. The Elemental Records & Palaeotemperature Implications

The use of combined *El/Ca* and  $\delta^{18}$ O palaeotemperature investigations was discussed in Chapter 5. McArthur *et al.* (2000), Bailey *et al.* (2003) and Rosales *et al.* (2004a, b) consider Mg/Ca and Sr/Ca to be the most useful ratios with which to investigate palaeoclimate, whilst Na/Ca and Li/Ca are of more limited use. Mg/Ca, Sr/Ca, Na/Ca and Li/Ca ratios were calculated here together with Mn/Ca ratios, which were calculated to assess preservation, with those displaying a value exceeding 100 µmol/mol excluded from

further analysis, since McArthur (1994) considers this to be the lower limit for samples that have experienced alteration under reducing conditions.

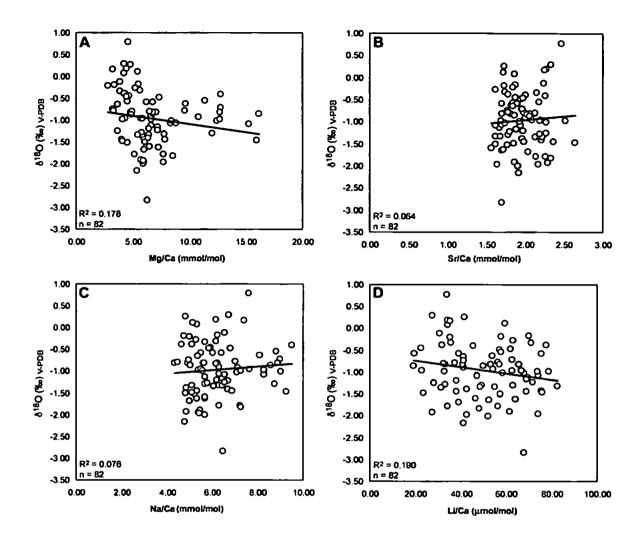


Figure 6.9 Cross-plots of  $\delta^{18}$ O against (A) Mg/Ca, (B) Sr/Ca, (C) Na/Ca and (D) Li/Ca.

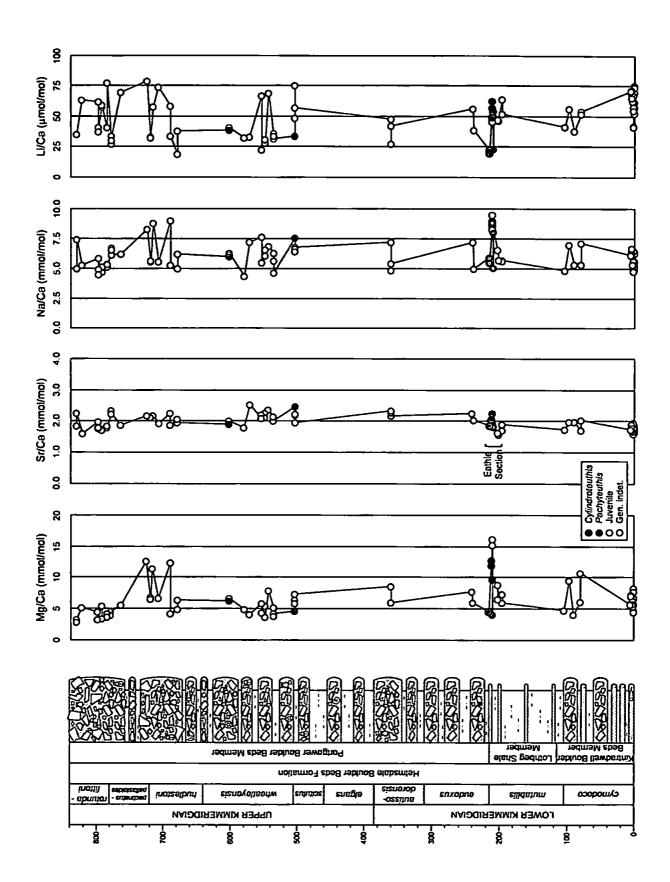
Cross-plots of *El/Ca* against  $\delta^{18}$ O for the Helmsdale belemnites show no statistically significant correlations (Fig. 6.9). The maximum R<sup>2</sup> value recorded here was 0.190 for Li/Ca and the lowest R<sup>2</sup> value recorded here is between  $\delta^{18}$ O and Sr/Ca, which according the McArthur *et al.* (2000) and Bailey *et al.* (2003) should be one of the strongest correlations. Mg/Ca and Sr/Ca are commonly considered to be the most appropriate *El/Ca* ratios with which to assess palaeotemperature and R<sup>2</sup> values for these ratios when plotted against  $\delta^{18}$ O are commonly in the region of 0.5 (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003). The R<sup>2</sup> values observed for these correlations here however are 0.178 for Mg/Ca and 0.064 for Sr/Ca. This lack of correlation could be the result of the

relatively static nature of the  $\delta^{18}$ O record during the Kimmeridgian. No distinctive longterm trend is discernable for much of this period and the record displays some degree of scatter. This may go some way towards explaining the lack of covariance observed in this succession (much like the Staffin Bay succession).

There are no distinctive long-term trends in the *El/Ca* records (Fig. 6.10). The Mg/Ca, Na/Ca and Li/Ca records are particularly noisy, which may act to obscure a long-term trend if one were present. Some of the observed scattered may be attributed to taxon or ontogenetic variations in the biological regulation of trace elements. For example, foraminifera display an Mg/Ca inter-species offset of <1.5 mmol/mol (Lear *et al.*, 2002; Billups & Schrag, 2003; Rosales *et al.*, 2004a). Such processes may be superimposed on the temperature control to contribute to the scatter of the data.

Previous studies have shown that Mg/Ca ratios are likely to be controlled mostly by temperature (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b), whilst Sr/Ca ratios are likely to be more significantly influenced by salinity, growth rate and metabolic activity (Klein *et al.*, 1997; Rosales *et al.*, 2004a). The palaeotemperatures calculated using the Klein *et al.* (1996) equation for molluscan Mg/Ca ratios are shown in Figure 6.7.

The palaeotemperature range calculated from the Mg/Ca ratios is -1.7 to 24.7°C, with an average palaeotemperature for the Kimmeridgian of 5.0°C. The offset observed between average  $\delta^{18}$ O and Mg/Ca derived temperatures is on average 10.8°C (compared with an offset of 8.6°C recorded from Staffin Bay). If this temperature difference was interpreted solely as the result of salinity input influencing the  $\delta^{18}$ O record it would require a change in salinity from 34 ‰ (normal marine conditions) to 24.1 ‰, which seems intuitively unlikely as modern *Sepia* have only occasionally been caught in water with a salinity of down to 29 ‰ (Schäfer, 1972; Wierzbowski, 2004). A similar technique was employed by Bailey *et al.* (2003) to investigate the influence of salinity on  $\delta^{18}$ O derived belemnite palaeotemperatures. Bailey *et al.* (2003) calculated a change in temperature



**Figure 6.10** El/Ca ratios from the Kimmeridgian succession at Helmsdale and Eathie, Sutherland, Scotland. Boreal British ammonite zones are illustrated here, however, it should be noted that the Upper Kimmeridgian (*sensu anglico*) is equivalent to the Tethyan Lower-Middle Tithonian. See Figure 4.2 for key to log symbols. Scale is in metres.

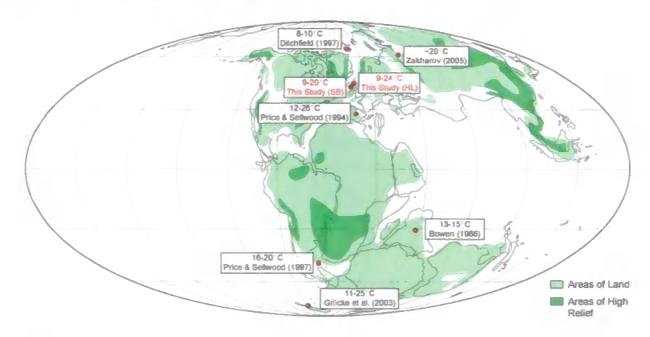
across the Toarcian Ocean Anoxic Event (OAE) from both  $\delta^{18}$ O and Mg/Ca, although their Mg/Ca temperature values were calculated using the equations of Dwyer *et al.* (1995), Elderfield & Ganssen (2000) and Lear *et al.* (2002) for foraminifera and ostracodes. They calculated a ~6°C warming, associated with a substantial freshening of seawater during the OAE event. The use of these equations seems inappropriate however, given that a mollusc-derived equation (that of Klein *et al.* (1996)) also exists.

The lowest palaeotemperatures recorded here occur during the Upper Kimmeridgian *Pectinatus* to *Fittoni* zones in both the Mg/Ca and  $\delta^{18}$ O records. However, the sub-freezing temperatures calculated from the Mg/Ca ratios for this time are impossible since marine cephalopods could not live in these conditions. Immenhauser *et al.* (2005) question the validity of applying the Klein *et al.* (1996) temperature equation to fossilised skeletal calcites. They suggest that it may only be appropriate for temperatures in the range of 5-23°C where the temperature-Mg relationship is linear and go on to suggest that the utility of Mg/Ca ratios may be limited by the ion regulating capability of the animals being considered. The data presented here lends support to the idea that the application of the Klein *et al.* (1996) palaeotemperature equation should be used with caution.

#### 6.5.4. The Carbon Isotope Record

The marine carbonate  $\delta^{13}$ C record shows a distinctive long-term trend towards more negative values throughout the Kimmeridgian (*sensu anglico*) interval (Fig. 6.7). Typical Early Kimmeridgian *Cymodoce* Zone values range between 1.3 and 2.8 ‰ compared with Late Kimmeridgian *Pectinatus-Fittoni* Zone values of -2.2 to -0.4 ‰. This trend is observed here despite some scatter in the belemnite data. The scatter however is consistent with that observed in other belemnite records (e.g., Bailey *et al.*, 2003; McArthur *et al.*, 2004; Rosales *et al.*, 2004a, 2006; Price & Mutterlose, 2004; Wierzbowski, 2004). A gradual shift to more negative  $\delta^{13}$ C values as observed here requires a continued input of <sup>12</sup>C to the oceanic carbon reservoir and consequently the incorporation of <sup>12</sup>C into the belemnite calcite. A decrease in  $\delta^{13}$ C ratios could be caused by upwelling of cold bottom waters enriched in <sup>12</sup>C (Küspert, 1982; Price & Gröcke, 2002), methane release from the dissociation of gas hydrates (e.g., Dickens *et al.*, 1995; Padden *et al.*, 2001), volcanism (e.g., Hesselbo *et al.*, 2002), or low carbon burial rates (Weissert & Erba, 2004).

The input of isotopically light carbon observed here is possibly associated with a relative sea-level fall (Voigt & Helbrecht, 1997), during which <sup>12</sup>C could be released by the weathering, erosion and oxidation of organic-rich sediments (Voigt & Helbrecht, 1997; Price & Gröcke, 2002). A eustatic sea-level fall has been proposed for the latest Jurassic-earliest Cretaceous (e.g., Haq *et al.*, 1987; Hallam, 1992) and <sup>87</sup>Sr/<sup>86</sup>Sr ratios rise throughout the Kimmeridgian (e.g., Jones *et al.*, 1994a; Veizer *et al.*, 1999; Jenkyns *et al.*, 2002) potentially indicating increased continental weathering, although this trend could also be attributed to decreased activity at ocean ridges (Price & Gröcke, 2002).

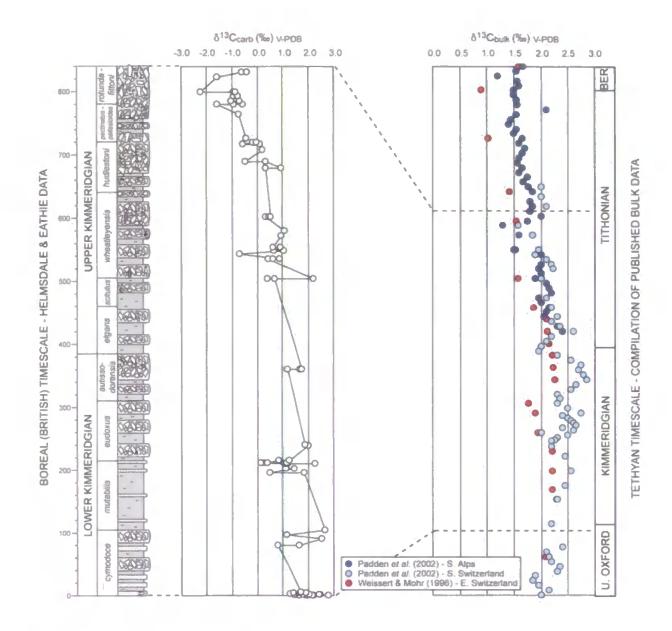


#### 6.5.5. Kimmeridgian Stable Isotope Records

**Figure 6.11** Kimmeridgian palaeogeography map showing published belemnite derived palaeotemperatures for this time period. (SB = Staffin Bay [Kimmeridgian data only]; HL = Helmsdale and Eathie).

The  $\delta^{18}$ O composition of belemnite calcite from the Helmsdale coast region was considered earlier in this chapter in terms of palaeotemperature, with the Anderson & Arthur (1983) equation regarded as the most appropriate with which to perform the temperature calculations. The Kimmeridgian temperatures calculated here (9.1-24.0°C, average 15.8°C) are generally consistent with palaeotemperatures calculated from belemnite-derived oxygen-isotope data published (Fig. 6.11). The highest palaeotemperature values predicted here are consistent with those previously published. which commonly predict temperatures in excess of 20°C. The lowest values recorded here agree with the data produced by Ditchfield (1997), which is the one of the highest latitude datasets published and is the only other study to predict palaeotemperatures this low for the Kimmeridgian.

Typical belemnite derived Kimmeridgian  $\delta^{13}$ C values range from -1 to 2 % (Price & Gröcke, 2002; Gröcke *et al.*, 2003). The range of  $\delta^{13}$ C ratios observed here however is slightly greater with values of between -1.76 and 2.96 ‰ recorded. The gradual shift (of  $\sim$ 5 ‰) to more negative carbon-isotope values observed here from the Helmsdale belemnites has also been recorded from other Kimmeridgian-Tithonian successions and has been shown to continue through the latest Tithonian and into the Early Berriasian (e.g., Weissert & Mohr, 1996; Weissert et al., 1998; Bartolini et al., 1999; Cecca et al., 2001; Padden et al., 2002; Price & Gröcke, 2002; Gröcke et al., 2003; Weissert & Erba, 2004) (Fig. 6.12). Such  $\delta^{13}$ C data have been compiled from predominantly bulk rock data from successions in Italy, Switzerland and France, although belemnite data have also been obtained from New Zealand and the Falkland Plateau (Price & Gröcke, 2002; Gröcke et al., 2003). The  $\delta^{13}$ C record presented here is the first high resolution record of the Kimmeridgian  $\delta^{13}$ C decrease documented from a relatively high latitude in the northern hemisphere. The fact that this pattern is observed in the Tethyan region and in the northern and southern high latitudes suggests that the total carbon reservoir was affected by global conditions.



**Figure 6.12** Kimmeridgian  $\delta^{13}$ C correlation between a composite Tethyan  $\delta^{13}$ C<sub>bulk</sub> curve and the  $\delta^{13}$ C curve from Helmsdale. Boreal British ammonite zones are illustrated here for the Helmsdale succession and scale is in metres. Timescale correlation is from Gradstein *et al.* (2004). See Figure 4.2 for key to log symbols.

The general decline to more negative  $\delta^{13}$ C values observed during the Kimmeridgian and Tithonian has been associated with a shift from silica-rich to carbonaterich pelagic deposition (Weissert & Channel, 1989; Padden *et al.*, 2002; Weissert & Erba, 2004). This expansion of carbonate sedimentation is believed to be the result of decreased sea floor spreading and an accompanying drop in global sea level (e.g., Haq *et al.*, 1987), which would have led to a deepening of the calcite compensation depth (CCD) (Weissert & Channel, 1989). A relative fall in sea level could result in the weathering, erosion and oxidation of newly exposed organic-rich sediments, during which <sup>12</sup>C would be released. Such a situation creates a paradox however, since increased weathering can also be associated with increased nutrient supply rates, increased oceanic productivity and therefore a positive carbon-isotope excursion (Price & Gröcke, 2002). It is postulated that the effect of the erosion of organic-rich sediments on the  $\delta^{13}$ C record at this time must be greater than the effect of increasing productivity. Substantial organic-rich deposits have been recorded from the Kimmeridgian-Tithonian, for example the Kimmeridge Clay Formation. Morgans-Bell *et al.* (2001) record very high TOC levels (up to 30 wt %) from the Kimmeridge Clay Formation in Dorset, with the highest values occurring in the *Eudoxus-Pectinatus* zones and coincident with a positive  $\delta^{13}C_{org}$  excursion. The erosion of these Kimmeridge Clay deposits if exposed, could account for a significant release of  $^{12}C$ and a negative carbon isotope excursion, although, the exposure of much older black shales is more likely. The observed decrease in  $\delta^{13}C_{carb}$  values from Helmsdale in the Early Kimmeridgian however, is difficult to account for, since a synchronous increase in  $\delta^{13}C_{org}$ values is observed from Dorset (Morgans-Bell *et al.*, 2001), although, this could be a local signal.

An increase in continental weathering is recorded during the Kimmeridgian-Berriasian interval, as indicated by rising  ${}^{87}$ Sr/ ${}^{86}$ Sr values (e.g., Jones *et al.*, 1994a; Veizer *et al.*, 1999; Jones & Jenkyns, 2001; Jenkyns *et al.*, 2002) and would serve to increase transfer rates of alkalinity (carbonate) from the continents and into the oceans, potentially lowering atmospheric CO<sub>2</sub> levels (Robinson *et al.*, 2002; Weissert & Erba, 2004). Weissert & Channell (1989) suggest that the decrease in atmospheric CO<sub>2</sub> levels would have ultimately resulted in a decelerated hydrological cycle and therefore decreased productivity in parts of the Atlantic and Tethys Oceans.

#### 6.5.6. Correlation of the Helmsdale & Staffin Bay Isotope Records

Helmsdale and Staffin Bay were situated at approximately the same palaeolatitude (~45°N) during the Late Jurassic (Smith *et al.*, 1994). It has been proposed that the

Hebrides Basin (in which Staffin Bay is situated) and the Moray Firth Basin (in which Helmsdale is situated) experienced coeval development as the result of activity along major onshore faults (Underhill, 1991; Wignall & Pickering, 1993; Hesselbo & Coe, 2000). As the development of these two basins was linked (i.e., the water masses were connected) it should be possible to correlate and combine the stable isotope records produced from the Helmsdale and Staffin Bay successions. The compilation of these two datasets then provides an almost complete carbonate isotope record from the Middle Callovian to Latest Kimmeridgian (*sensu anglico*) of Northern Scotland.

In order to assess the validity of this approach, isotope values from overlapping parts of the different successions were compared. These were the Lower Callovian *Koenigi* Zone and the Lower Kimmeridgian *Cymodoce* Zone deposits. The *Koenigi* Zone is represented on the Isle of Skye by the Belemnite Sands Member, a sandy glauconitic facies with abundant belemnites towards the top of the unit. In Brora, belemnites were collected from the Brora Shale Member, a sandy, glauconitic unit (Early/Middle Callovian in age) also with abundant belemnites. The mean values of  $\delta^{18}$ O and  $\delta^{13}$ C from the Brora belemnite rostra were -0.32 ‰ and 2.43 ‰ respectively, compared with values from Staffin Bay of -0.33 ‰ ( $\delta^{18}$ O) and 2.65 ‰ ( $\delta^{13}$ C). These values are very similar.

For the Early Kimmeridgian (*Cymodoce* Zone) the average values of  $\delta^{18}O$  and  $\delta^{13}C$  observed from Staffin Bay were -0.7 ‰ and 2.0 ‰ respectively. For the Helmsdale belemnites, the *Cymodoce* Zone values were -1.24 ‰ for  $\delta^{18}O$  and 1.88 ‰ for  $\delta^{13}C$ . The greater amount of offset observed between these values (compared with those from the *Koenigi* Zone) is to be expected because the Staffin Bay values represent the lowermost *Cymodoce* Zone, whilst the Helmsdale values represent the Upper *Cymodoce* Zone. The *Koenigi* Zone correlation, however, was undertaken on belemnites from one coeval horizon and therefore the offset between the isotope values is significantly lower. The extremely close match between the *Koenigi* Zone isotope values and reasonably good match between the *Cymodoce* Zone values confirms that the Helmsdale and Staffin Bay

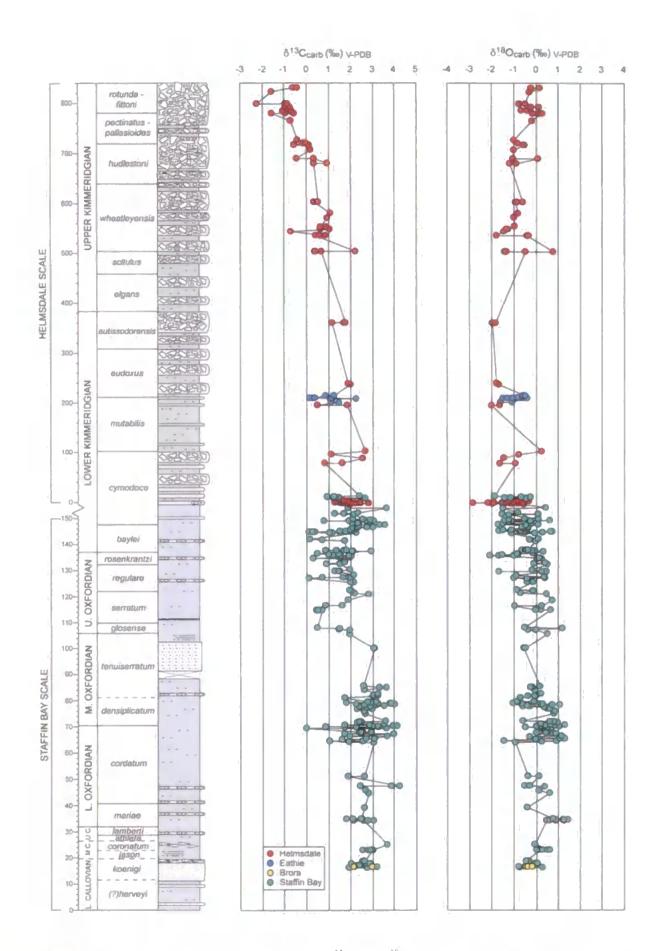


Figure 6.13 Composite Callovian-Kimmeridgian  $\delta^{13}$ C and  $\delta^{18}$ O records from northern Scotland (Staffin Bay, Helmsdale, Eathie and Brora). Note the change of scale between the Staffin Bay and Helmsdale sections. See Figure 4.2 for key to log symbols.

successions can be combined to produce a stable isotope record from the Middle Callovian to uppermost Kimmeridgian from this region.

The combined Helmsdale and Staffin Bay carbonate isotope data (Fig. 6.13) show a long-term  $\delta^{13}$ C trend of relatively static values (on average between 2-3 ‰) through the Early and Middle Oxfordian followed by a shift to more negative values during the Late Oxfordian and into the Kimmeridgian. Despite a brief positive fluctuation in the Early Kimmeridgian (*Baylei-Cymodoce* zones)  $\delta^{13}$ C values continue to decrease throughout the Kimmeridgian (to values as low as -2.25 ‰). The  $\delta^{18}$ O curve shows a considerable amount of scatter, however despite this noise a very slight, gradual shift to less positive values throughout the Oxfordian and into the Early Kimmeridgian is discernable (from values of 1.43 ‰ to -2.84 ‰). From the Early to mid-Kimmeridgian a gradual return to more positive values is inferred (0.78 ‰).

# 6.6. Conclusions

- The data presented here comprise the first relatively high-resolution stable isotope investigation of marine biogenic carbonate (belemnites) from the Helmsdale coast, Sutherland, Scotland.
- The average palaeotemperature derived from the Helmsdale δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) was 15.8°C and the palaeotemperature range was 9.1 to 24.0°C for the Kimmeridgian interval. This corresponds well with the Callovian-Kimmeridgian palaeotemperature data derived from belemnites from the Staffin Bay succession, Isle of Skye (6.7°C to 20.6°C, average 12.4°C). The Helmsdale palaeotemperature data is also consistent with previously published literature on the Kimmeridgian-Tithonian, particularly with regards to low palaeotemperatures recorded from the northern high latitude region (e.g., Ditchfield, 1997).
- Mg/Ca derived palaeotemperature estimates range from -1.7 to 24.7°C, with an average palaeotemperature for the Kimmeridgian of 5.0°C. Records of sub-freezing

temperatures are impossible however, because marine cephalopods could not live in these conditions. This casts doubt on the use of the Klein *et al.* (1996) Mg/Ca palaeotemperature equation when applied to fossilised skeletal calcite.

- The marine carbonate  $\delta^{13}$ C record shows a distinctive long-term trend towards more negative values throughout the Kimmeridgian. This input of isotopically light carbon is coincident with a relative sea-level fall during which <sup>12</sup>C would be released by the weathering, erosion and oxidation of organic-rich sediments.
- The shift to low  $\delta^{13}$ C values during the Kimmeridgian is also recorded from the Tethyan region and the northern and southern hemispheres. The Helmsdale data provide the first documented record of this pattern from a northern high latitude site. The widespread occurrence of this event suggests that the total global carbon reservoir was affected.
- The Helmsdale and Staffin Bay (Chapter 5) carbonate isotope data are correlated and combined here to produce an almost complete succession from the Middle Callovian to uppermost Kimmeridgian of northern Scotland. This is possible because the Hebrides and Moray Firth Basins experience coeval development during the Late Jurassic. This is confirmed by the almost identical δ<sup>13</sup>C and δ<sup>18</sup>O values recorded from Lower Callovian Koenigi Zone belemnites from both successions.

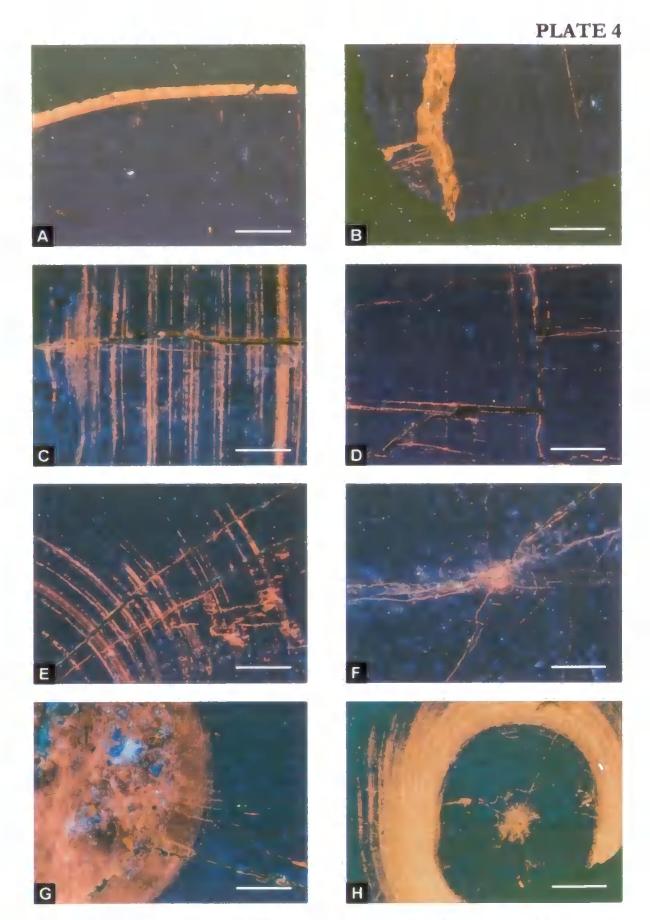


Plate 4. Cathodoluminescence images showing the state of preservation of belemnite rostra from Helmsdale, Scotland. All scale bars represent 1 mm. (A) Rostrum margin displaying alteration. (B) Fracture infilled by diagenetic cement. (C) Fracture and growth lines displaying alteration. (D) Fractures and growth lines displaying alteration. (E) Fractures and growth lines displaying alteration. (F) Fractures eminating from apical canal and showing alteration. (G) Apical canal with sediment infilling and some fine fractures. (H) Heavily altered growth bands surrounding the apical canal.

# PLATE 5



Plate 5. Backscattered SEM images showing the state of preservation of belemnite rostra from Helmsdale. Scotland. All scale bars represent lengths stated on images. (A) Well preserved calcite showing little alteration along fracture. (B) Well preserved calcite. (C) Slight alteration along growth bands. (D) Fracture running through apical canal. (E) Faint alteration around apical canal region. (F) Apical canal and surrounding growth lines displaying alteration. (G) Borings and fractures at rostrum margin. (H) Fractures showing little alteration.

# PLATE 6



Plate 6. Carbonate stained images showing the state of preservation of belemnite rostra from Helmsdale, Scotland. All scale bars represent 1 mm. (A) Very well preserved calcite with faint alteration at margin edge. (B) Rostrum margin with some pyritisation. (C) Rostrum margin with alteration along fractures and growth lines. (D) Wide fracture infilled with diagenetic cement. (E) Generally well preserved calcite. (F) Fracture and sections of adjacent growth bands displaying alteration. (G) Fractures eminating from apical canal. (H) Apical canal with sediment infilling surrounded by some areas of alteration.

# 7. BOYARKA RIVER, YENISEI-KHATANGA BASIN, SIBERIA

# 7.1. Location & Site Description

The Boyarka River lies within the Yenisei-Khatanga Basin of northern Central Siberia, south of the Taymyr Peninsula (Fig. 7.1). The section of the river considered here is located at ~70°N and is approximately 300 km south of the town of Khatanga. In total five major sites were examined along a 15 km stretch of river. These sites were also the main ones visited during the study of Shulgina *et al.* (1994). The exposures were generally low river-side cliffs cut perpendicular to strike and composed predominantly of soft sands or silty-sands (Fig. 7.2).

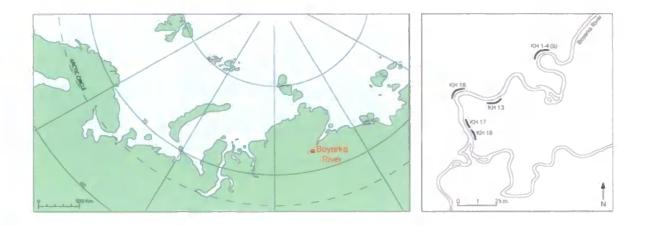


Figure 7.1 Location map of the Boyarka River, northern Central Siberia. The location of the Boyarka River is shown (left) together with the relative positions of each of the sites examined (right).

The composite Boyarka River section is approximately 300 m thick and ranges in age from the Ryazanian (*Kochi* Zone) to the Early Valanginian (*Bojarkensis* Zone).



Figure 7.2 River-side cliff exposure typical of the Boyarka River, northern Central Siberia (location KH1-4, Upper Valanginian, *Bidichotomus* Zone).

# 7.2. Geological Setting

The Yenisei-Khatanga Basin is a trough on the northeastern branch of the West Siberian rift system (Khain *et al.*, 1991) (Fig. 7.3). It is bounded to the west by the West Siberian Basin, to the north by the Taymir fold belt and to the south and southeast by the East Siberian Platform (Aplonov, 1995; Vyssotski *et al.*, 2006). It is worth noting, that all of these areas are known to have been affected by the emplacement of flood basalts from the East Siberian Traps at ~250 Ma (the Permo-Triassic boundary), at which time basalts would also have extended from northeastern Siberia into the Barents and Kara seas (Vyssotski *et al.*, 2006).

During the Middle Triassic, the Yenisei-Khatanga Rift experienced a period of inversion, where compression replaced rifting, to produce inversion structures in which oil and gas zones would later accumulate (Khain *et al.*, 1991). O'Reilly *et al.* (2005) describe

the Jurassic to Cretaceous evolution of the Yenisei-Khatanga Basin. They report a period of Jurassic rifting, followed by terrane collisions in East Siberia during the Valanginian to produce the Laptev Sea and Verkhoyansk fold belts. This collision diverted continental drainage systems towards the Yenisei-Khatanga Basin, where there was a resulting influx of sedimentation until the extensional fold belt collapse of the Barremian (O'Reilly *et al.*, 2005).

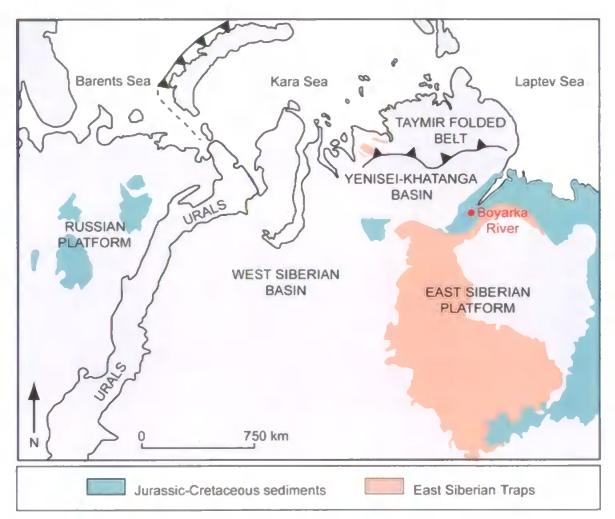


Figure 7.3 Simplified geological map of the Yenisei-Khatanga Basin and surrounding areas. Adapted after Vyssotski et al. (2006).

The basement of the Yenisei-Khatanga trough consists of Archean-Proterozoic igneous and metamorphic rocks similar to those of other Siberian Platform regions (Semenovich *et al.*, 1973). Jurassic to Paleogene deposits in the Yenisei-Khatanga Basin reach a thickness of 7 km (Vinogradov *et al.*, 1973), with the Jurassic to Cretaceous

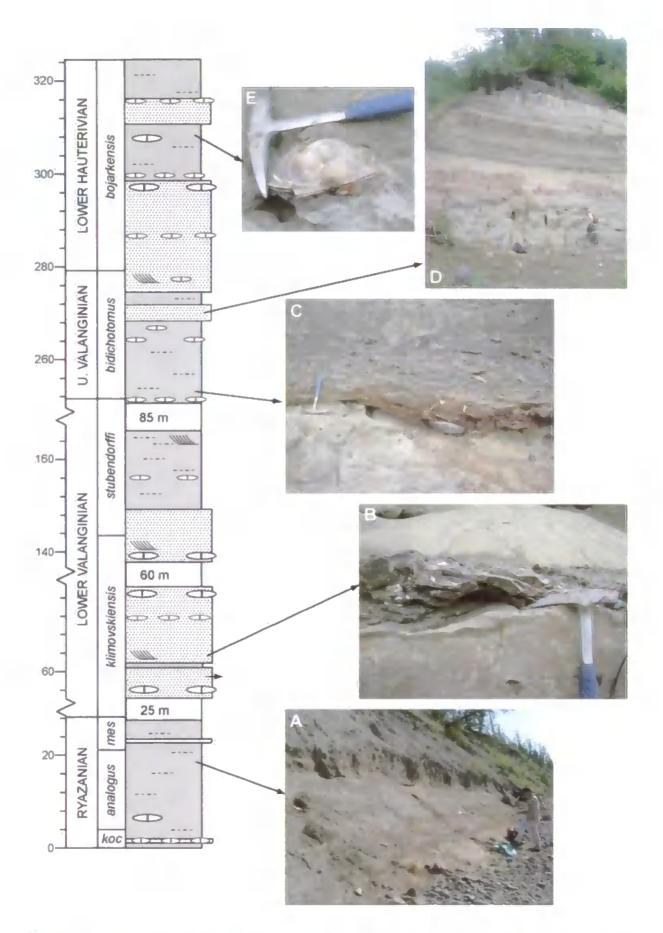


Figure 7.4 Sedimentary log and photographs of the Boyarka River succession. (A-E) described in text. Boreal (Russian) ammonite zones are illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

elements of the sedimentary epirift complex well known for their oil and gas potential (e.g., Semenovich *et al.*, 1973; Khain *et al.*, 1991; O'Reilly *et al.*, 2005). The Lower Cretaceous Boyarka River sediments are dominated by sandstones, clays and siltstones of shallow marine origin (Fig. 7.4). Exposure is generally good where outcrops exist, however, there are large breaks in the continuity of the Ryazanian to Hauterivian sequence where no viable outcrops could be identified. The Ryazanian (*Kochi, Analogus* and *Meseshnikowi* ammonite zones) sediments are approximately 30 m thick and are dominated by grey silty clays with occasional concretions or limestone bands (Fig. 7.4a). There are ~10m of very poorly exposed sediments occurring during the *Analogus* Zone, however, the sediments above and below this gap appear to be the same grey silty clays. Fossilised wood fragments and belemnites are common throughout the Ryazanian.

After a break in exposure of ~25 m (estimated using dip and strike) the Lower Valanginian (*Klimovskiensis* and *Stubendorffi* zones) sediments are exposed. They are composed of approximately 120 m of sands and silts, although the exposure of the ~60m in the middle of the succession is very poor. The basal Valanginian sediments are predominantly sandstones, although occasional thin claystone beds are also present. The sandstones are green in colour and display some cross-bedding. Isolated concretions and concretionary layers are distributed throughout the succession. Large bivalve (*Mcleania*) shells are particularly common in the Lower Valanginian, either isolated or in stacks and crinoid ossicles are also present in a lower *Klimovskiensis* Zone shell bed (Fig. 7.4b). Bioturbation is common (distinct *Rhizocorallium*-like burrows are present in the *Klimovskiensis* Zone shell bed together with the crinoid ossicles) and fragments of wood and coal are distributed throughout the Lower Valanginian succession.

The Upper Valanginian (*Bidichotomus* Zone) sediments were exposed after a break in outcrop of ~90 m and are approximately 20m thick. These sediments are predominantly clayey sands or sands that are generally pale grey in colour but mottled red in places from iron-staining (Fig. 7.4c). Thin, dark grey clay layers (<3m in thickness) are

131

commonly interbedded with the clayey sands and sandstones. At the bases of the claystone layers small tabular concretions and belemnites are relatively common.

The Lower Hauterivian (*Bojarkensis* Zone) section continues on from the Upper Valanginian succession without a break in outcrop. The Hauterivian succession is approximately 60m thick and composed of pale grey/green sandstones and clayey sands. The sandstone units are occasionally cross-bedded and often display some degree of ironstaining giving them a mottled orange/red appearance in places (Fig. 7.4d). Large isolated concretions, although rare, do occur towards the top of the succession. Condensed clay layers with small concretions at the base (and occasional belemnites) occur relatively regularly (at an interval of ~15m) in the Hauterivian section. Large bivalves (*Mcleania*) are distributed throughout the succession (Fig. 7.4e). Beds are often locally bioturbated and fossilised wood fragments are common (including large fossilised tree branches, 50 mm in diameter) particularly towards the base of the succession.

## 7.3. Sampling & Methodology

The five major Boyarka River outcrops form a succession from Early Ryazanian (*Kochi* Zone) to Early Hauterivian (*Bojarkensis* Zone) in age. Samples were taken from 210 different horizons throughout this succession. This included 64 belemnite horizons (Fig. 7.5) and 150 fossilised wood horizons (Fig. 7.5). Wherever possible multiple samples were taken from a horizon. The Boyarka River was visited for a three week period in August 2004.

Once again, belemnite rostra were assessed for preservation by stable isotope and trace element analysis, backscattered scanning electron microscopy (BSEM), cathodoluminescence (CL) and carbonate staining. Areas prone to diagenesis were removed prior to isotopic and trace element analysis.



**Figure 7.5** Belemnites and macroscopic wood from the Boyarka River succession. (A) Belemnite from the *Meseshnikowi* Zone (location KH17). (B) Belemnite from the *Kochi* Zone (location KH16). (C) Wood from the *Klimovskiensis* Zone (location KH13). (D) Wood from the *Bidichotomus* Zone (location KH1-4).

Stable isotope analysis was conducted on a Multiflow automated carbonate preparation module with Gilson 222XL autosampler, interfaced with an Isoprime isotope ratio mass spectrometer (GV Instruments, UK), at the University of Plymouth, UK. Trace element data were generated by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the NERC ICP facility, Department of Geology at Royal Holloway, University of London.

Representative macroscopic wood samples were photographed by scanning electron microscopy (SEM) on the University of Plymouth's JEOL 5600 SEM. In total 184 fossil wood samples were analysed for carbon-isotope ratios. Samples were treated with 5% HCl to remove any carbonate material and rinsed with deionised water before being oven dried and powdered with an agate pestle and mortar. Samples were analysed by Dr Darren Gröcke at McMaster University, Ontario, Canada, where samples were measured on a SIRA II Series 2 dual-inlet isotope-ratio mass-spectrometer for isotopic analysis. For a full description of methodology see Chapter 4.

### 7.4. Results

The belemnites sampled from this succession were of the Boreal genera *Cylindroteuthis, Acroteuthis, Pachyteuthis* and *Lagonibelus*. Most of the belemnites were composed of translucent calcite and retained the primary concentric banding that characterise belemnite rostra. Several specimens exhibited endolithic borings around the rostrum margins. BSEM, CL and carbonate staining analysis was conducted on 14 specimens (Plates 7-9) in order to identify the areas of the rostrum that were particularly prone to diagenetic alteration (e.g., the rostrum margins, the area surrounding the apical canal, well-developed fractures and strong growth bands). Such areas tended to be Fe-rich and were sometimes subjected to partial replacement by pyrite. These areas were removed prior to sampling or were avoided.

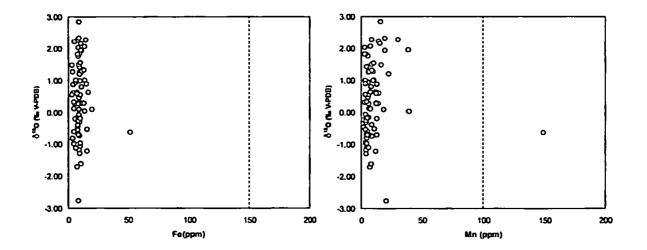


Figure 7.6 Cross-plots of  $\delta^{18}$ O against Fe (left) and Mn (right). The dashed lines indicate the cut off values for well preserved samples.

The concentrations of Fe and Mn were determined to provide an additional means of assessing preservation. The Fe and Mn values derived from the Boyarka River belemnites were 3-52 ppm, mean 9 ppm (for Fe) and 2-149 ppm, mean 11 ppm (for Mn). Fe and Mn data were plotted against  $\delta^{18}$ O to constrain any diagenetic alteration (Fig. 7.6). High values of Mn or Fe and occasional outliers with regards to  $\delta^{18}$ O values were regarded as an artefact of diagenetic alteration. Relatively low values of Fe (<150 ppm) and Mn (<100 ppm) were recorded from most of the Boyarka River belemnites, with only 1 sample excluded from further analysis.

Elemental abundances for additional trace elements are as follows: Sr 925-1701 ppm, mean 1187 ppm, Mg 297-1817 ppm, mean 876 ppm and Ca 28 % - 32 %, mean 30 %. The oxygen and carbon isotope values for well preserved Boyarka River belemnites range from -1.71 to 2.83 ‰ and from -1.07 to 4.24 ‰ respectively (Fig. 7.7). The oxygen isotope data from this location show a significant amount of scatter, for example the Lower Ryazanian (Kochi to Analogus zones) data show a c. 4.5 ‰ variation (from -1.71 to 2.83 ‰) compared to a c. 2.0 ‰ (from -1.07 to 0.96 ‰) variation in the concurrent carbon isotope values. The most positive oxygen isotope values are observed during the Lower Ryazanian (2.83 ‰). The carbon isotope data demonstrate an overall trend of increasing values from the Ryazanian and into the Lower Hauterivian, with a peak during the Upper Valanginian Bidichotomus Zone where values range from 1.68 to 4.24 ‰. After the positive carbon isotope excursion observed during the Upper Valanginian, carbon isotope values drop to a range of 1.00 to 1.72 ‰ in the Lower Hauterivian. The most negative carbon isotope values occur in the Lower Ryazanian (Kochi to Analogus zones) and are coincident with the most positive oxygen isotope values, although, a cross-plot of  $\delta^{18}$ O vs.  $\delta^{13}$ C reveals no statistically significant correlation (Fig. 7.8).

Macroscopic wood samples were identified as charcoal (43 samples), charcoal-coal (51 samples) or coal (61 samples) where possible and representative samples were photographed by SEM (Plates 10-11). The range of preservation did not have a significant impact on the overall long-term  $\delta^{13}C_{org}$  curve (as previously demonstrated by Hesselbo *et al.*, (2003) and Gröcke *et al.*, (2005)). Identification of the wood to a generic or specific level was not undertaken. The organic carbon isotope ratios derived from these fossilised

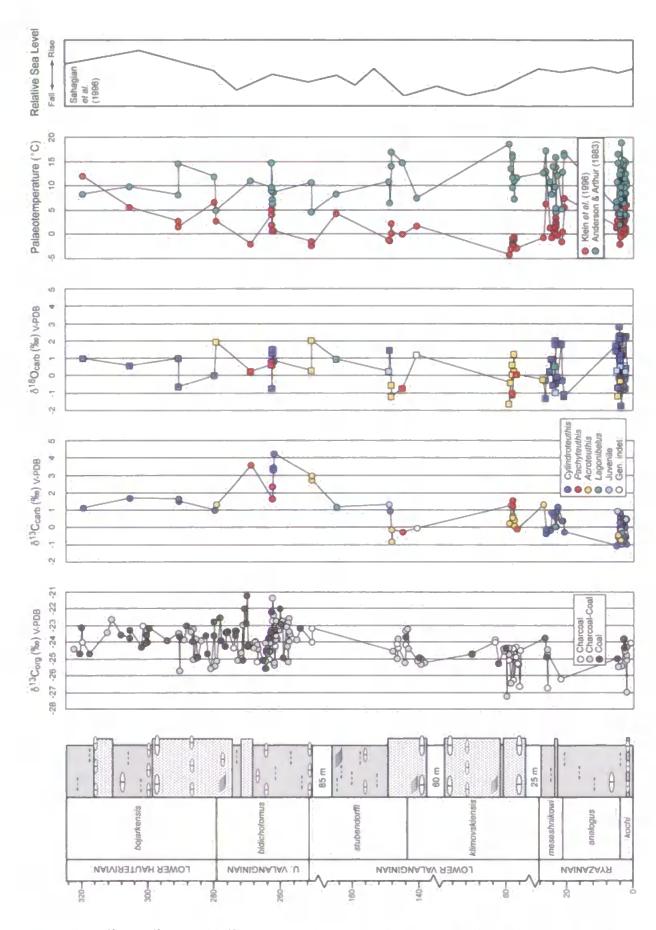


Figure 7.7  $\delta^{13}C_{org}$ ,  $\delta^{13}C_{carb}$ , and  $\delta^{18}O_{carb}$  records from the Ryazanian-Lower Hauterivian Boyarka River succession, northern Central Siberia. Calculated palaeotemperatures and sea level are also shown. Boreal (Russian) ammonite zones are illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

wood samples range from -27.20 to -21.21 ‰ (Fig. 7.7). The most negative  $\delta^{13}C_{org}$  values occur during the Upper Ryazanian to Lower Valanginian (*Kochi* to *Klimovskiensis* zones), with a range from -27.20 to -23.74 ‰, average -24.93 ‰. Upper Valanginian to Lower Hauterivian (*Bidichotomus* to *Bojarkensis* zones)  $\delta^{13}C_{org}$  values are in the range of -25.70 to -21.21 ‰, average -23.75 ‰. These are the most positive  $\delta^{13}C_{org}$  values in the succession. The  $\delta^{13}C_{org}$  curve shows a long-term increase in values from the Upper Ryazanian to Lower Hauterivian, although, the increase in values is only small (< ~2 ‰). A large positive carbon isotope excursion, like that observed in the  $\delta^{13}C_{carb}$  record (of ~4 ‰), is not identified in the  $\delta^{13}C_{org}$  record. The amount of scatter present in the Boyarka river wood data is similar to that observed in previous comparable studies (e.g., Gröcke *et al.*, 1999, 2005; Robinson *et al.*, 2004).

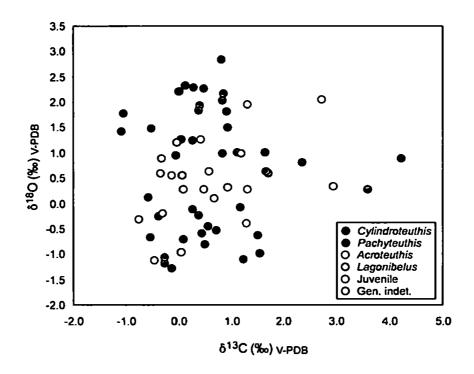


Figure 7.8 Cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C values derived from belemnites from the Boyarka River succession, northern Central Siberia.

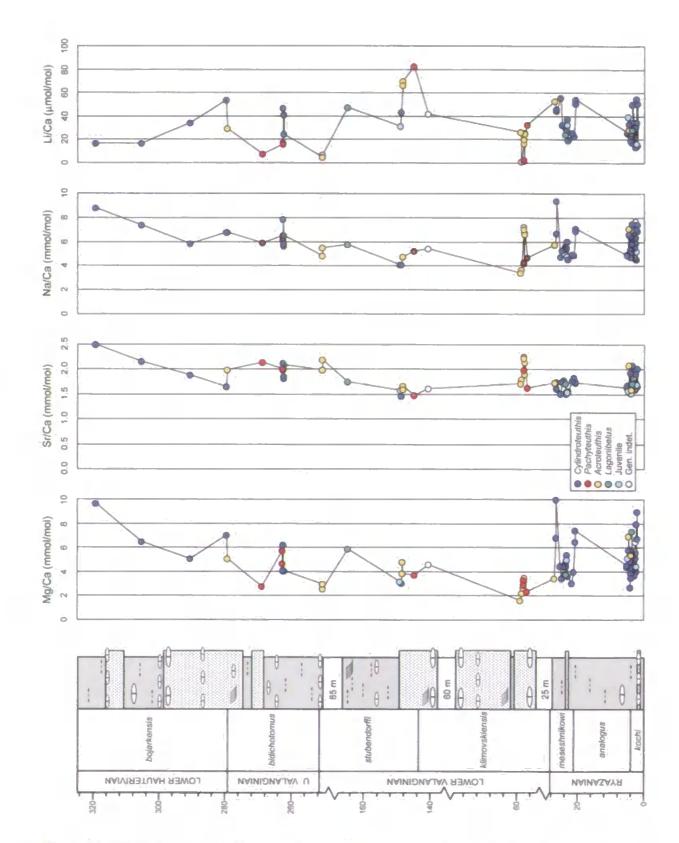
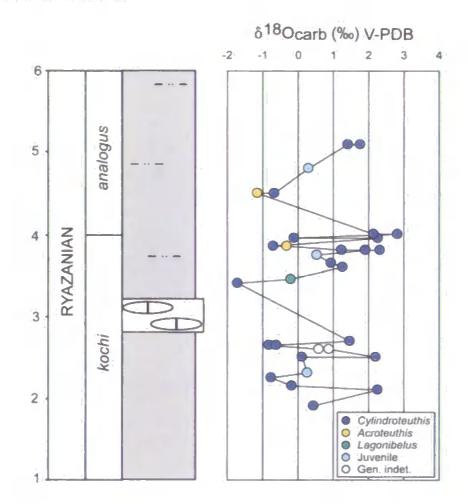


Figure 7.9 El/Ca ratios from the Ryazanian-Lower Hauterivian succession at the Boyarka River, northern Central Siberia. Boreal (Russian) ammonite zones are illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

### 7.5. Discussion

### 7.5.1. Stable Isotope, Geochemical & Taxonomic Records

McArthur *et al.* (2004) suggested that taxonomic differences may influence stable isotope (particularly oxygen) and trace element records. The data presented here, therefore, highlight the different belemnite genera (Figs 7.7 and 7.9) from which such measurements were taken in order to assess the potential influence of genus-specific differences in fractionation.



**Figure 7.10** Close-up of the Ryazanian *Kochi-Analogus* zones, Boyarka River, northern Central Siberia.  $\delta^{18}$ O record shown. Boreal (Russian) ammonite zones are illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

In neither the isotope nor elemental records does one genus consistently record either more negative or more positive values than any other genus, although co-occurring

belemnites of different genera are rare, making this difficult to assess with confidence. Perhaps the most striking taxonomic factor observed here is the high level of variability present in *Cylindroteuthis* specimens, particularly with regard to the  $\delta^{18}$ O record. Values derived from Cylindroteuthis specimens almost always exceed both the highest and lowest values recorded from other genera where both occurr in close proximity. The most notable example of this is in the Early Ryazanian Kochi-Analogus zones. The Cylindroteuthis  $\delta^{18}$ O values for this period range from -1.71 to 2.83 % compared with values of between -1.10 and 0.90 ‰ recorded from other genera (Fig. 7.10). This variability could be attributed to several factors, firstly to the abundance of Cylindroteuthis specimens compared to other genera, which are recording real and significant fluctuations of temperature or salinity or it could be the result of habitat and/or migration differences compared to other the genera. Interestingly, *Cylindroteuthis* is the only belemnite that is believed to have been able to withstand relatively deep water depths of down to 400m (compared to maximum water depths of 50-200m for other genera) (Westermann, 1973). The observed variability in the isotope and elemental records could, therefore, be the result of increased vertical migration within the water column compared to the other genera. This would account for the increased variability observed in the  $\delta^{18}O$  record as the result of temperature fluctuations relating to water depth.

### 7.5.2. The Oxygen Isotope Record & Palaeotemperature Implications

The  $\delta^{18}$ O record derived from belemnites of the Boyarka River displays a considerable amount of scatter. The Lower Ryazanian interval for example, shows a ~4.5 ‰ range of values (from -1.7 to 2.8 ‰). This degree of scatter is greater than would usually be expected for belemnite isotope data and is likely to be related to the shallow nature of the succession. It is also in part, probably the result of the condensed nature of the lower part of the Boyarka River succession. The succession becomes more expanded in the Valanginian and Lower Hauterivian and the scatter becomes less pronounced.

No long-term trend in the oxygen-isotope curve is discernable here, possibly as the result of the degree of scatter present in the data. The average oxygen-isotope value for the whole Lower Cretaceous succession is 0.45 ‰ and the data fluctuate about this value. Assuming that the oxygen-isotope record presented here primarily reflects changes in environmental conditions (temperature and salinity) rather than taxonomic or diagenetic processes a palaeotemperature estimate can be attempted. The problems associated with belemnite derived palaeotemperature estimates are discussed in previous chapters and so will not be repeated here, although, it must be acknowledged that any calculations presented can only be considered as a guide to the potential palaeotemperatures rather than definitive values for the region.

Figure 7.7 shows the seawater palaeotemperatures calculated using the Anderson & Arthur (1983)  $\delta^{18}$ O equation. An isotopic composition of -1 % SMOW was assumed for non-glacial seawater, which is consistent with previously published literature on the Cretaceous period (e.g., Pirrie & Marshall, 1990; Podlaha et al., 1998; Price & Mutterlose, 2004). The average palaeotemperature calculated using  $\delta^{18}$ O for the Boyarka River was 10.6°C and the palaeotemperature range was 2.1 to 19.0°C for the Ryazanian to Hauterivian interval. Both the lowest and highest palaeotemperatures occurred during the Lower Ryazanian Kochi to Analogus ammonite zones. These values are slightly higher than the modern temperature range for the region, which Polyak et al. (2003) estimate to be around -1 to 12°C based on foraminiferal isotope studies in the Kara and Pechora seas. Published belemnite derived palaeotemperatures for the Lower Cretaceous are consistent with those presented here. Van de Schootbrugge et al. (2000), for example, infer Early Valanginian temperatures of ~15°C from France and McArthur et al. (2004) record values of ~11°C at the base of the Hauterivian in England. Price & Mutterlose (2004) recorded a range of 7.0 to 21.4°C for the Volgian-Valanginian from the Yatria River in Siberia. The Yatria River was located at an Early Cretaceous palaeolatitude of 60-65°N (Price &

Mutterlose, 2004), which is  $5-10^{\circ}$  south of the Boyarka River. A difference in palaeotemperature of ~2.5-5.0°C between these palaeolatitudes seems reasonable.

The most positive  $\delta^{18}$ O value observed here (and therefore the most likely to represent the coolest palaeotemperature) is 2.8 ‰. According to the temperature-salinity model constructed by Railsback *et al.* (1989) and Woo *et al.* (1992) with modification by Price & Mutterlose (2004) this value corresponds to a palaeotemperature of 2.1°C, when a normal marine salinity (of 34 ‰) is assumed (Fig. 7.11). However, Roche *et al.* (2006) modelled  $\delta^{18}O_{seawater}$  values in past warm climates and several of their models indicated that  $\delta^{18}O_{sw}$  values could reach approximately -1.5 ‰ in the Arctic (this corresponds to a salinity value of ~32 ‰). If these new values of  $\delta^{18}O_{sw}$  and salinity are considered then the  $\delta^{18}O$  value of 2.8 ‰ for even a moderate palaeotemperature of 0.5°C. In order to resolve a  $\delta^{18}O$  value of 2.8 ‰ for even a moderate palaeotemperature of ~10°C a marine salinity of ~41 ‰ (or a  $\delta^{18}O_{sw}$  values as observed in the Ryazanian of the Boyarka River must, therefore, correspond to very low palaeotemperatures.

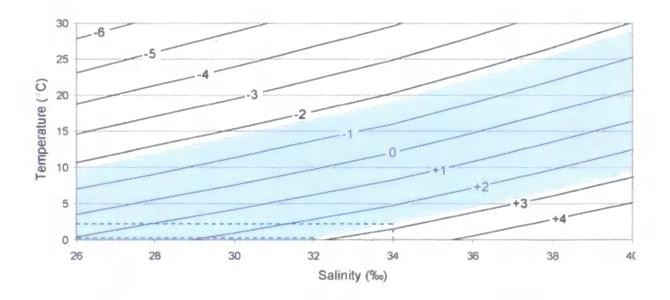


Figure 7.11 Temperature-salinity plot for the Boyarka River data. The continuous diagonal lines are isopleths of  $\delta^{18}$ O values and show the possible combination of temperature and salinity that corresponds to calcite of a given isotopic composition and for a given isotopic composition of seawater (-1 ‰). The shaded area shows the range of isotope values recorded from belemnite rostra from the Ryazanian-Hauterivian succession the Boyarka River. The dashed lines represent the values discussed in the text above.

#### 7.5.3. The Elemental Records & Palaeotemperature Implications

The rationale for, and implications of, considering *El/Ca* ratios together with  $\delta^{18}$ O data was discussed in Chapter 5. Mg/Ca and Sr/Ca ratios are generally considered to be the key proxies with which to assess palaeoclimate, whilst Na/Ca and Li/Ca are of limited use (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b). Mn/Ca values were calculated for each sample and only those samples with values below 100 µmol/mol were included here, as this is the lower limit for samples that are believed to have been altered under reducing conditions (McArthur, 1994).

The elemental ratios presented here (Mg/Ca, Sr/Ca, Na/Ca and Li/Ca) are quite noisy, however a long-term trend is apparent (Fig. 7.9). The most striking long-term trend observed here is that in the Mg/Ca record (and to a lesser degree also in the Na/Ca and Sr/Ca records). This is the relatively rapid shift to higher values during the Lower Hauterivian. This shift follows the  $\delta^{13}$ C positive isotope excursion observed in both the organic and carbonate data. The *El/Ca* data is particularly noisy during the Ryazanian interval, probably in part, as a result of the condensed nature of the lower part of the Boyarka River succession (the same pattern is observed in the  $\delta^{18}$ O data).

Cross-plots of *El/Ca* against  $\delta^{18}$ O record very poor correlations for the Boyarka River belemnites (Fig. 7.12). This may be because the  $\delta^{18}$ O record displays so much scatter. The only statistically significant correlation (at the 95% confidence level) recorded here is between Li/Ca and  $\delta^{18}$ O (R<sup>2</sup> value, 0.253), which according to the work of Bailey *et al.* (2003) should show the least significant correlation. Both Mg/Ca and Sr/Ca display an inverse relationship with  $\delta^{18}$ O as determined using a linear regression line. This is consistent with published belemnite data (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b) and for Mg/Ca the work of Steuber & Rauch (2005) on modern skeletal calcite.

The Mg/Ca ratio is commonly considered to be one of the most accurate palaeotemperature proxies available, primarily because, unlike  $\delta^{18}$ O it is not thought to be

significantly influenced by salinity fluctuations (e.g., Klein *et al.*, 1996; Lear *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b; Immenhauser *et al.*, 2005). The absence of correlation between Mg/Ca and  $\delta^{18}$ O is therefore surprising, although this could be the result of several factors, such as, interspecies offset, ontogenetic variations, metabolic activity, salinity or temperature. Assuming however, that temperature is the major control on Mg/Ca ratios and that belemnites have a similar temperature sensitivity as modern biogenic calcites, it seems likely that salinity has had an effect on the  $\delta^{18}$ O record, which is reflected by the poor correlation. The Boyarka River succession is a fully marine sequence (indicated by the abundant marine fauna, e.g., ammonites and belemnites), however the input of substantial quantities of wood suggests a very near-shore environment and fluvial, freshwater input from such a location would go some way to explaining a salinity effect on the  $\delta^{18}$ O record.

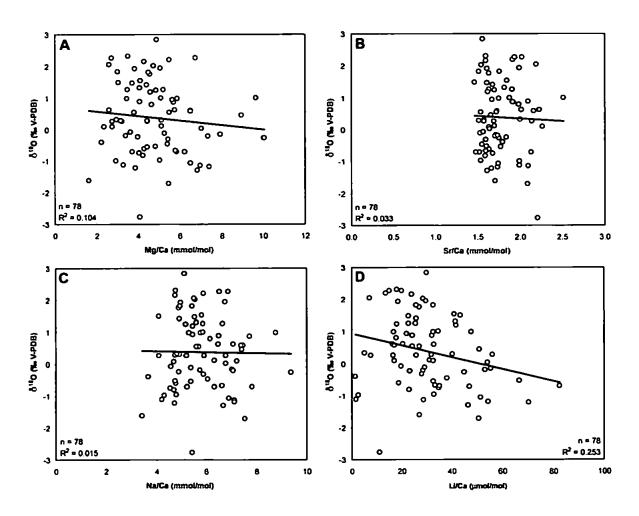


Figure 7.12 Cross-plots of  $\delta^{18}$ O against (A) Mg/Ca, (B) Sr/Ca, (C) Na/Ca and (D) Li/Ca for the Boyarka River belemnites.

Palaeotemperatures were calculated from the Mg/Ca ratios using the equation of Klein et al., (1996). The average Mg/Ca temperature is 2.2°C, with a range of -4.2 to 12.8°C compared to an average temperature of 10.6°C and range of 2.1 to 19.0°C as calculated from the  $\delta^{18}$ O data (Fig. 7.7). The average offset between the palaeotemperature calculations is 8.4°C. Bailey et al. (2003) calculated the potential influence of salinity during a warming event by using estimates of Mg/Ca and  $\delta^{18}$ O derived palaeotemperatures, although different Mg/Ca palaeotemperature equations were used. A similar technique was followed in Chapter 6 and will be used again here. If the 8.4°C temperature difference is interpreted solely in terms of salinity a freshening from a 'normal' marine salinity of 34 ‰ to a salinity of 25.8 ‰ is required, although, as mentioned in the previous chapter, modern Sepia have rarely been caught in waters with salinity values below 29 ‰ (Schäfer, 1972; Wierzbowski, 2004). An additional problem associated with the calculated palaeotemperature values and the assumption that Mg/Ca ratios represent temperature whilst  $\delta^{18}$ O values are assumed to represent temperature and salinity, is that a value of -4.2°C (the lowest value calculated using Mg/Ca ratios) is impossible, since marine cephalopods could not exist in these conditions. This casts serious doubt on the use of Mg/Ca as a palaeotemperature proxy for belemnites using the Klein et al. (1996) palaeotemperature calibration.

### 7.5.4. The Terrestrial Carbon Isotope Record

The wood-derived carbon-isotope ratios presented here are considered to primarily reflect changes in the terrestrial carbon-isotope reservoir. The limitations and reliability of fossil wood data were discussed in Chapter 4, where it was concluded that  $\delta^{13}C_{org}$  values could be used to confidently identify long-term shifts in the composition of atmospheric carbon. Recognisable plant fragments (e.g., charcoal and coalified material) were used to construct the organic carbon isotope record presented here rather than the bulk matter approach (as was used for Staffin Bay, Isle of Skye). The advantages of this sampling

strategy (over the bulk approach) are that only terrestrial matter is collected (not marine) and that the effects of variation in the organic matter source component or environment are minimised. The validity of this technique has been demonstrated by several Mesozoic studies (e.g., Hesselbo *et al.*, 2003; Robinson & Hesselbo, 2004; Gröcke *et al.*, 2005). The preservation of plant material ranged from charcoal to coal (see Plates 10 & 11), however this made no significant difference to the long-term  $\delta^{13}C_{org}$  trend. Several previously published studies confirm the lack of influence of preservation on isotopic values (e.g., Hesselbo *et al.*, 2003; Gröcke *et al.*, 2005).

The Ryazanian-Hauterivian  $\delta^{13}C_{org}$  curve from the Boyarka River succession records a positive carbon-isotope excursion with the maximum occurring in the Upper Valanginian *Bidichotomus* Zone (Fig. 7.7). The initiation of the positive isotope excursion occurs in the upper part of the Lower Valanginian *Stubendorffi* Zone, which is broadly time-equivalent to the Tethyan *Campylotoxia* Zone. Ryazanian to Lower Valanginian  $\delta^{13}C_{org}$  values fluctuate between -27.2 and -23.2 ‰, whilst Upper Valanginian values reach a maximum of -21.2 ‰ (Fig. 7.7). The carbon-isotope values fall gradually across the Valanginian-Hauterivian boundary and pre-excursion values are reached (~ -25 to -23 ‰) in the Lower Hauterivian *Bojarkensis* Zone. The scatter observed in this Boyarka River record is consistent with the degree of scatter observed in previously published Mesozoic wood records (e.g., Heimhofer *et al.*, 2003; Hesselbo *et al.*, 2003; Gröcke *et al.*, 2005).

The timing and duration of the  $\delta^{13}C_{org}$  positive excursion is consistent with previously published terrestrial data from the Crimea (Gröcke *et al.*, 2005). The values recorded by Gröcke *et al.* (2005) however, are ~ 3 ‰ heavier than those observed here. This may be the result of analysing different plant elements since modern C3 plants demonstrate significant variability in carbon isotope composition (< ±4 ‰) between discrete elements (Leavitt & Long, 1991; Loader *et al.*, 1995; Schleser, 1999; Robinson & Hesselbo, 2004). In addition, lighter isotope values are commonly recorded in regions where soil moisture content is high. Heavier high latitude isotope values therefore seem reasonable. The initiation of the excursion recorded by Gröcke *et al.* (2005) also occurs slightly later (in the Tethyan *Verrucosum* Zone) than that observed here (assuming accurate correlation). Prior to the work of Gröcke *et al.* (2005) the Upper Valanginian positive carbon isotope excursion had only been recorded in marine carbonates and marine organic matter (e.g., Lini *et al.*, 1992; Henning *et al.*, 1999; Wortmann & Weissert, 2000; Price & Mutterlose, 2004). The record presented here is the first Boreal Realm terrestrial record of this event.

### 7.5.5. The Marine Carbon Isotope Record

The  $\delta^{13}C_{carb}$  curve shows some degree of scatter, although this is consistent with previously published belemnite data. The lowest carbon-isotope values (-1.1 ‰) occur in the Lower Ryazanian *Kochi* Zone. Values increase slightly from the Ryazanian and into the Valanginian until the rapid positive excursion initiated in the upper part of the Lower Valanginian *Stubendorffi* Zone. The positive carbon-isotope excursion is of a magnitude of approximately 3 ‰ (reaching a maximum of 4.2 ‰). A return towards pre-excursion values occurs in the Lower Hauterivian *Bojarkensis* Zone.

The Upper Valanginian positive carbon-isotope excursion recorded here in marine carbonate from the Boyarka River can be compared to data published by Price & Mutterlose (2004) from the Yatria River, Western Siberia. Price & Mutterlose (2004) also recorded the positive excursion from belemnites. They recorded the positive excursion from two sites in the Yatria River, although less positive values were observed at the excursion maximum (< 3.7 %) and the excursion was of a slightly smaller magnitude (<  $\sim 2 \%$ ). The timing and duration of the excursion was compatible with that observed here, with initiation in the upper part of the Lower Valanginian and a return to pre-excursion values into the Hauterivian.

#### 7.5.6. The Carbon Isotope Records & Ocean-Atmosphere Correlation

As discussed in Chapter 5 the comparison of marine and terrestrial carbon isotope stratigraphy is essential to understanding perturbations in the global carbon cycle. Marine and terrestrial carbon-isotope records have been compared in a number of studies (e.g., Gröcke *et al.*, 1999, 2005; Ando *et al.*, 2002, 2003; Hesselbo *et al.*, 2003; Robinson & Hesselbo, 2004; Pearce *et al.*, 2005), however such work has almost always compared marine and terrestrial records from different successions. This presents problems in terms of accurate correlation that are often difficult to overcome. Geological successions containing terrestrial organic matter together with marine carbonate are very rare and consequently coeval marine and terrestrial records are not generally published. The Boyarka River succession however, presents this opportunity.

The observed offset between the  $\delta^{13}C_{org}$  and  $\delta^{13}C_{earb}$  data is approximately 25 ‰ on average. This is consistent with the average observed from the Staffin Bay, Isle of Skye data (~25.5 ‰). These values are larger than might be expected, for example, from Poland and Germany (~23 ‰) as recorded and discussed by Wierzbowski (2002, 2004) and Pearce *et al.* (2005). In Chapter 5 it was hypothesised that this difference in offset was likely to be the result of isotopically heavier belemnite values as a result of <sup>13</sup>C enrichment in the Boreal Realm, due primarily to high organic matter productivity in the partly isolated Boreal seas (Wierzbowski, 2004). The observed offset in the Boyarka River data lends further support to this hypothesis.

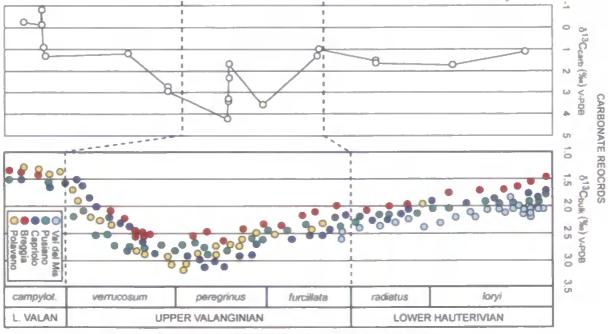
The initiation of the  $\delta^{13}C_{org}$  and  $\delta^{13}C_{earb}$  positive isotope excursions occurs simultaneously in the upper part of the Lower Valanginian *Stubendorffi* Zone. This suggests that the ocean-atmosphere system is strongly linked at this time. Previous studies of marine and terrestrial carbon isotope data have shown that the timing and duration of excursions are likely to be synchronous in terrestrial organic matter, marine organic matter and marine carbonate (e.g., Gröcke *et al.*, 1999, 2005). This can now be confirmed for terrestrial organic matter and marine carbonate by the Boyarka River data. The  $\delta^{13}C_{carb}$  excursion observed here is of a higher magnitude than that of the  $\delta^{13}C_{org}$  excursion. This is quite unusual, since the magnitude of shifts in the terrestrial record is normally considerably greater than those in the respective marine record (e.g., Gröcke *et al.*, 1999; Robinson & Hesselbo, 2004, Pearce *et al.*, 2005). A classic example of this relationship is the negative carbon isotope excursion recorded at the Palaeocene Eocene Thermal Maximum (PETM), where the excursion in the terrestrial record is approximately twice the magnitude of that observed in the marine record (e.g., Bowen *et al.*, 2004, 2006). Smith *et al.* (2006) hypothesise that this may be the result of an increase in  $\rho$ CO<sub>2</sub> concentrations at this time, causing increased warming and an increase in moisture, to which plants would respond with greater carbon isotope discrimination and ultimately an enhanced carbon isotope signature.

It is interesting that the inverse terrestrial-marine relationship is observed in the Boyarka River succession, which is coincident with a drop in  $\rho$ CO<sub>2</sub> (as determined below see section 7.5.7). Given this relationship, it is tempting to suggest that such a drop in  $\rho$ CO<sub>2</sub> would cause plants to reduce their carbon isotope discrimination and therefore lower the magnitude of the  $\delta^{13}C_{org}$  excursion. The problem with this model however, is that a fall in  $\rho$ CO<sub>2</sub> should also result in increasing oceanic alkalinity, which would potentially reduce carbonate fractionation in the marine realm. This effect has been observed in modern foraminifera (e.g., Spero *et al.*, 1997) and would presumably also lower the rate of fractionation in Valanginian belemnites during a drop in  $\rho$ CO<sub>2</sub>. It is possible however, that changes in  $\rho$ CO<sub>2</sub> have a stronger or more immediate influence on the terrestrial realm, which may account for the reduced carbon isotope signature in plants but not in belemnites at this time. The usual interpretation of changes in discrimination by plants however, is that they have experienced a change in available moisture. The decrease in discrimination observed here could therefore be the result of increased water stress under drier conditions (Francesca Smith pers. comm.).

#### 7.5.7. Ryazanian-Hauterivian Marine & Terrestrial Isotopic Records

Published marine carbonate stable isotope records for the Early Cretaceous have been constructed primarily from successions in the Tethyan region (e.g., Lini *et al.*, 1992; Weissert *et al.*, 1998; Price *et al.*, 2000; van de Schootbrugge *et al.*, 2000; Weissert & Erba, 2004), although Price & Mutterlose (2004) have also published data from a high latitude site. The overall pattern described from such research is one of decreasing  $\delta^{13}$ C values across the Jurassic-Cretaceous boundary, relatively stable  $\delta^{13}$ C values in the earliest Cretaceous, then a rapid mid- to Late Valanginian positive carbon-isotope excursion (occurring in the Tethyan *Campylotoxus* ammonite Zone) and a subsequent return to preexcursion values in the Upper Valanginian and Lower Hauterivian (Price & Mutterlose, 2004) (Fig. 7.13).

The Boyarka River positive carbon-isotope excursion observed in both the  $\delta^{13}C_{carb}$ and  $\delta^{13}C_{org}$  records begins in the upper *Stubendorffi* zone (which is correlatable with the Tethyan Campylotoxus Zone). The peak of the positive  $\delta^{13}C$  excursion occurs in the Bidichotomus Zone which corresponds well biostratigraphically with the timing of the Tethyan excursion in the Trinodosum and Callidiscus ammonite zones (e.g., van de Schootbrugge et al., 2000; Weissert & Erba, 2004), however, it should be noted that much of the uppermost Stubendorffi Zone is missing. Lini et al. (1992) hypothesised that the Valanginian carbon-isotope event represented the first episode of greenhouse conditions during the Cretaceous period. This event has frequently been related to episodes of platform drowning within the Tethys (e.g., Lini et al., 1992; Föllmi et al., 1994; Weissert et al., 1998; Wortmann & Weissert, 2000). Positive carbon isotope events are commonly attributed to increased organic carbon burial either as the result of enhanced surface water productivity or owing to enhanced preservation under reduced O<sub>2</sub> conditions (Weissert et al., 1998; Bersezio et al., 2002; Erba et al., 2004; Price & Mutterlose, 2004). Van de Schootbrugge et al. (2000) however, highlighted the problem with this model, which is that during the Hauterivian, at least two phases of platform drowning are not associated with



GRÖCKE ET AL. (2005) DATA - CRIMEAN AMMONITE ZONAL SCHEME

UPPER VALANGINIAN

bidichotomus

f

LOWER HAUTERIVIAN

bojarkensis

A

LOWER VALANGINIAN

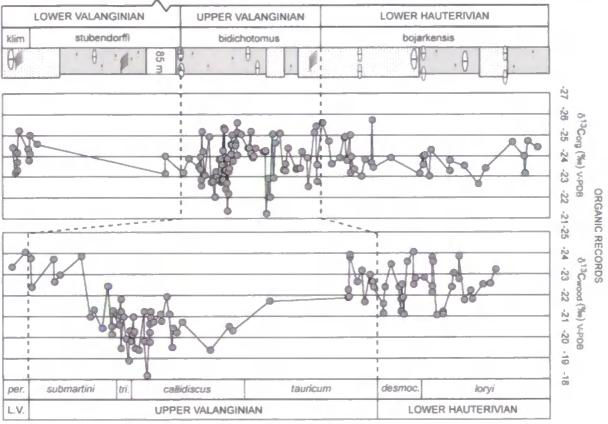
klim

H

stubendorffi

85

θ



BOYARKA RIVER DATA - BOREAL (RUSSIAN) TIMESCALE

Figure 7.13 Valanginian-Hauterivian 8<sup>13</sup>C correlation between the Boyarka River succession 5<sup>13</sup>C<sub>ong</sub> curve and a composite Tethyan and the Crimea (based upon data from Lini et al., 1992 and the S<sup>13</sup>C<sub>carb</sub> curve and a composite Tethyan bulk 5<sup>13</sup>C curve (based upon data from Lini et al., 1992 and Channell et al., 1993 and adapted after Gröcke et al., 2005). Boreal (Russian), Crimean and Tethyan ammonite zones are illustrated. See Figure 4.2 for key to log symbols.

positive carbon-isotope excursions. Wortmann & Weissert (2000) suggested that the sealevel rise and drowning of platform carbonates corresponded to the initiation of more positive carbon-isotope values.

According to the eustatic sea-level curve of Sahagian *et al.* (1996), based on Russian platform and Siberian stratigraphy, the Upper Valanginian *Bidichotomus* Zone witnesses a brief sea-level rise coincident with the initiation of the positive carbon-isotope excursion, then a sea-level fall synchronous with the excursion maximum and followed by another rise into the Hauterivian coinciding with the return to pre-excursion values (Fig 7.7). Although the Sahagian *et al.* (1996) sea-level curve is contrary to the sea-level curve of Haq *et al.* (1987), the Valanginian section of the Sahagian *et al.* curve was constructed from data taken from the Boyarka River section itself. Positive carbon-isotope excursions may be related to regressive conditions due to an increased input of nutrients resulting from the exposure and erosion of lowland areas (Brenchley *et al.*, 1994; Gröcke *et al.*, 1999; Price & Mutterlose, 2004). Partial separation of the Boreal and Tethyan Realms during periods of sea-level lowstand could have restricted ocean circulation and enhanced stratification to promote organic carbon burial in these high latitude locations (Price & Mutterlose, 2004).

The evidence for widespread Late Valanginian marine black shales is very limited. Perhaps the best evidence comes from organic carbon-rich black shales in the Southern Alps (Bersezio *et al.*, 2002) and from the Shatsky Rise in the West Pacific (Bralower *et al.*, 2002). Price & Mutterlose (2004) suggest that the absence of widespread Valanginian black shale deposits could be due to erosion (e.g., Weissert *et al.*, 1998) or due to burial away from typical marine settings (e.g., in terrestrial environments) or away from the Tethys (e.g., at high latitudes).

The terrestrial  $\delta^{13}$ C record presented here is the first Boreal Realm terrestrial record of the Upper Valanginian positive carbon-isotope event. Only one other terrestrial record of this event exists, that of Gröcke *et al.* (2005) from the Crimean Peninsula of the

southern Ukraine. Gröcke *et al.* (2005) also record the positive carbon-isotope excursion from macroscopic wood. Their excursion begins in the *Submartini* Zone (which is correlatable with the Tethyan *Verrucusum* Zone) and reaches a maximum in the Tethyan *Callidiscus* Zone. This excursion correlates well (within the limits of biostratigraphic resolution) with the carbon-isotope excursions identified in the Boyarka River and in Tethyan carbonates.

Delta-delta ( $\Delta \delta = \delta^{13}C_{carb} - \delta^{13}C_{org}$ ) relationships observed from the paired analysis of marine carbonate and marine or terrestrial organic matter have been used as a proxy for ρCO<sub>2</sub> concentrations (e.g., Weissert et al., 1998; Kump & Arthur, 1999; Hasegawa et al., 2003). Gröcke *et al.* (2005) calculated  $\Delta\delta$  values from their  $\delta^{13}C_{plant}$  data and a composite  $\delta^{13}C_{carb}$  record from the Tethyan region (compiled from the work of Lini et al. (1992) and Channell et al., (1993)). They observed a +2 ‰ shift between the Tethyan marine carbonate record and the terrestrial plant record for the Crimea, which they linked to a drop in atmospheric  $\rho CO_2$  in the order of ~40 % and consequently to a short-term Valanginian cooling event. This was calculated following the work of several authors, which suggested that a 10 % shift in  $\rho CO_2$  levels would result in a 0.5 % change in  $\delta^{13}C_{org}$  due to the alteration of photosynthetic isotopic fractionation (e.g., Körner et al., 1988; Gröcke, 1998; van de Water et al., 1994). An organic carbon burial event and associated positive  $\delta^{13}C$ excursion would lead to this drawdown of  $\rho CO_2$  (Gröcke et al., 2005) and, potentially, acidification. The  $\Delta\delta$  relationship observed from the Boyarka River dataset is consistent with that observed in the Crimea, although it is of a smaller magnitude (~1 ‰ rather than 2 ‰). The Boyarka River data therefore support the idea that the Valanginian period sees a drop in atmospheric  $\rho CO_2$  associated with the peak of the Valanginian carbon-isotope event. Atmospheric  $\rho CO_2$  values can also be affected by other factors however, such as volcanism, silicate weathering and deposition of calcium carbonate (Kump & Arthur, 1999; Berner & Kothavala, 2001; Gröcke et al., 2005).

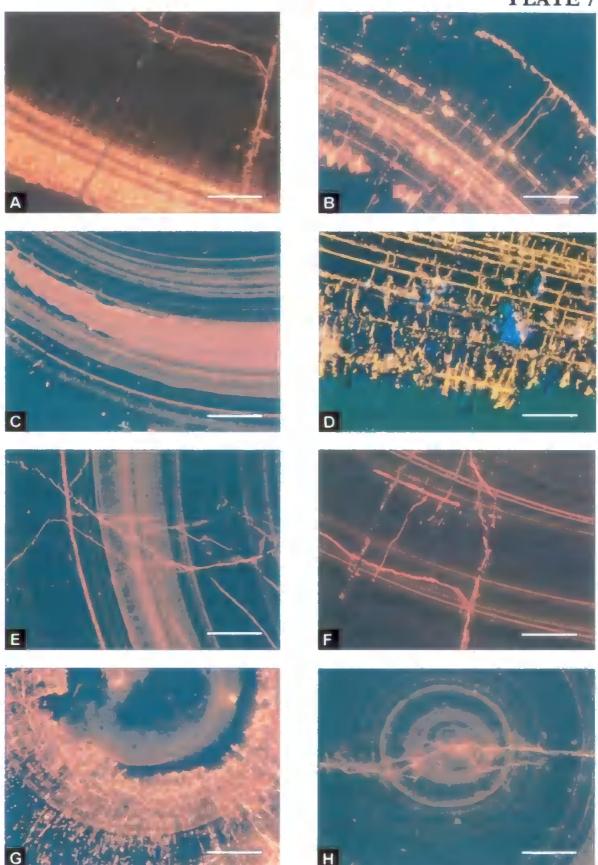
The idea of a Valanginian cooling event is consistent with other recently published evidence on this period (e.g., Mutterlose et al., 2003; Pucéat et al., 2003; Erba et al., 2004; Weissert & Erba, 2004; Kessels et al., 2006; McArthur et al., in press). Erba et al. (2004) provided nannofossil and oxygen-isotope evidence for a cooling event at the  $\delta^{13}C$ excursion maximum. Weissert & Erba (2004) suggest that the cooling event may have been the result of increased organic carbon burial (as reflected by the  $\delta^{13}C$  positive excursion) and the resultant pumping of CO<sub>2</sub> from the atmosphere and into the sediment. This model is supported by oxygen-isotope data from Tethyan fish tooth enamel, which indicate a major cooling event during the earliest Late Valanginian (Pucéat et al., 2003). It is further supported by a Late Valanginian boreal nannoplankton excursion in Romania (Melinte & Mutterlose, 2001) and the presence of glendonites in several Valanginian successions (e.g., Kemper, 1987; Tarduno et al., 2002). Unfortunately the oxygen-isotope data from the Boyarka River succession provides somewhat inconclusive evidence with For the  $\delta^{13}$ C positive excursion maximum a regards to palaeotemperatures. palaeotemperature range of 6.3 to 14.8 °C is recorded.

# 7.6. Conclusions

- The data presented here comprise the first combined high-resolution isotope investigation of  $\delta^{13}C_{org}$ ,  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  from the Boyarka River, Northern Central Siberia. It is also the first ever investigation of a coeval  $\delta^{13}C_{org}$  and  $\delta^{13}C_{carb}$  record (together with the data presented in Chapter 5).
- The average palaeotemperature derived from the Boyarka River δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) was 10.6°C and the palaeotemperature range was 2.1 to 19.0°C for the Ryazanian to Hauterivian interval. This suggests that the climate may have been very variable at this time or that salinity may have had a significant influence on δ<sup>18</sup>O ratios. The temperature range also indicates that the region was at

times considerably colder than previously thought, which could indicate the presence of limited polar ice.

- An Upper Valanginian positive carbon-isotope excursion is identified in both the  $\delta^{13}C_{org}$ and  $\delta^{13}C_{carb}$  records. The initiation of the excursion occurs simultaneously in the upper part of the Lower Valanginian *Stubendorffi* ammonite zone (broadly equivalent to the Tethyan *Campylotoxia* Zone). In both records the carbon-isotope values then decrease across the Valanginian-Hauterivian boundary and a return towards pre-excursion values occurs during the *Bojarkensis* Zone. This trend is consistent with that observed in Tethyan carbonate successions and therefore indicates a strong coupling of the oceanatmosphere system at this time and suggests that the total exchangeable carbon reservoir was affected.
- The initiation of the positive δ<sup>13</sup>C excursion is associated with a brief sea-level rise on the Russian platform, although the excursion maximum occurs during a period of overall regression. Exposure and erosion of lowland areas and restricted ocean circulation and enhanced stratification during a period of sea-level lowstand may account for increased rates of organic carbon burial.
- The Boyarka River  $\Delta\delta$  values may indicate a drop in atmospheric  $\rho CO_2$ . This is likely to be the result of enhanced organic carbon burial, which could lead to a drawdown of  $\rho CO_2$  and a period of cooling in the late Valanginian.



**Plate 7.** Cathodoluminescence images showing the state of preservation of belemnite rostra from the Boyarka River, Siberia. All scale bars represent 1 mm. (A) Rostrum margin displaying significant alteration. (B) Rostrum margin, growth bands and fractures displaying alteration. (C) Growth bands displaying significant alteration. (D) Strong alteration along the rostrum margin. (E) Fractures and growth bands displaying alteration. (G) Apical canal surrounded by area displying significant alteration. (H) Fractures eminating from and growth bands surrounding the apical canal.



Plate 8. Backscattered SEM images showing the state of preservation of belemnite rostra from the Boyarka River, Siberia. All scale bars represent lengths stated on images. (A) Well preserved calcite with some slight alteration along growth lines at the rostrum margin. (B) Generally well preserved calcite but with some alteration along growth bands towards the rostrum margin. (C) Pyrite growth along growth line fractures at rostrum margin. (D) Fracture at rostrum margin showing little alteration. (E) Fracture running through apical canal. (G) Apical Canal. (H) Rostrum margin with fractures and displaying alteration along growth bands.

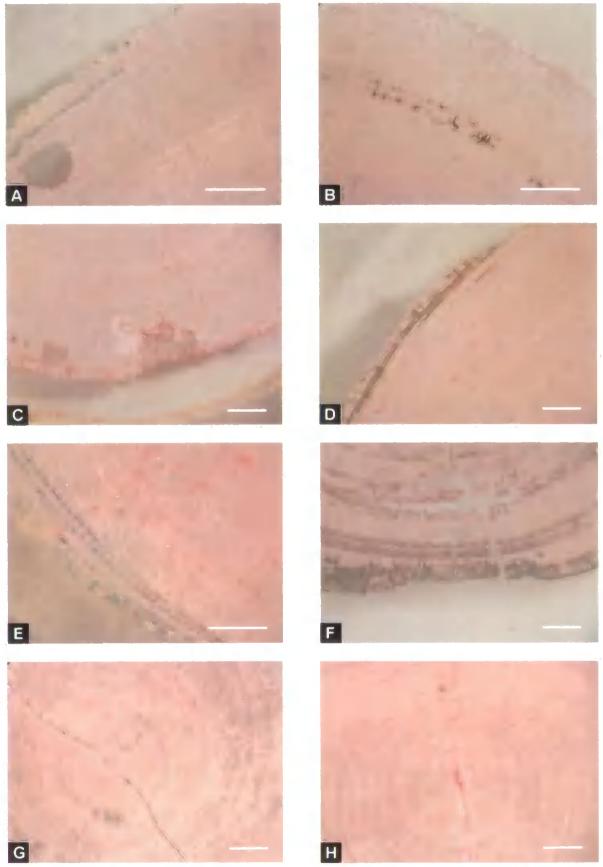


Plate 9. Carbonate stained images showing the state of preservation of belemnite rostra from the Boyarka River, Siberia. All scale bars represent 1 mm. (A) Very well preserved calcite at rostrum margin. (B) Generally well preserved calcite but with some pyrite growth along growth lines towards the rostrum margin. (C) Fractures and growth lines towards rostrum margin displaying alteration. (D) Generally well preserved calcite but with some pyrite growth at margin edge. (E) Rostrum margin showing alteration particularly along growth lines. (F) Rostrum margin showing alteration particularly along growth lines. (G) Fracture running through apical canal. (H) Fracture running through apical canal.

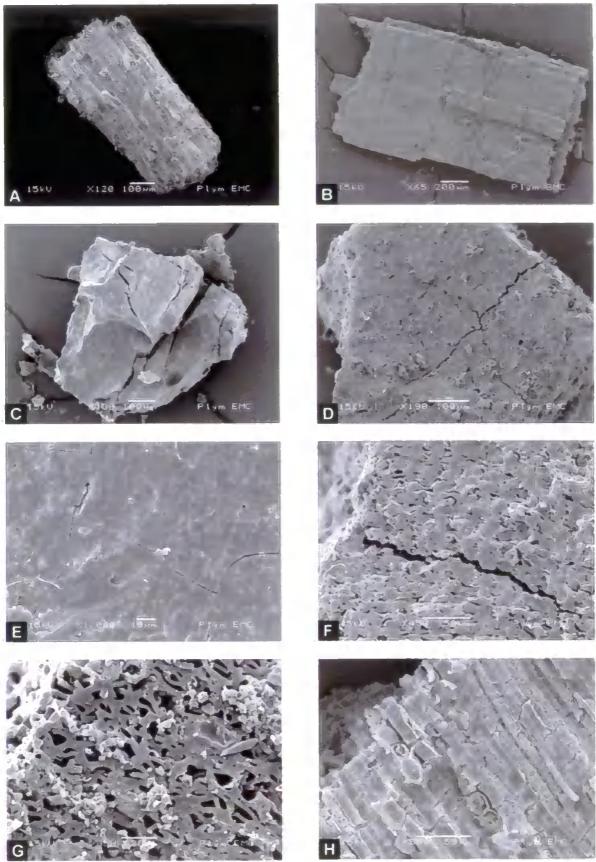


Plate 10. Scanning Electron Microscope images showing the state of preservation of fossil wood fragments from the Boyarka River, Siberia. All scale bars represent lengths stated on images. (A) Charcoal - woody structure preserved. (B) Charcoal - woody structure preserved. (C) Coal - blocky nature of fragment. (D) Charcoal-coal - mostly homogenised internal structure. (E) Coal - completely homogenised internal structure. (F) Charcoal-coal - homogenised and compacted internal structure. (G) Charcoal-coal - homogenised and compacted internal structure. (E) Charcoal-coal - homogenised and compacted internal structure.

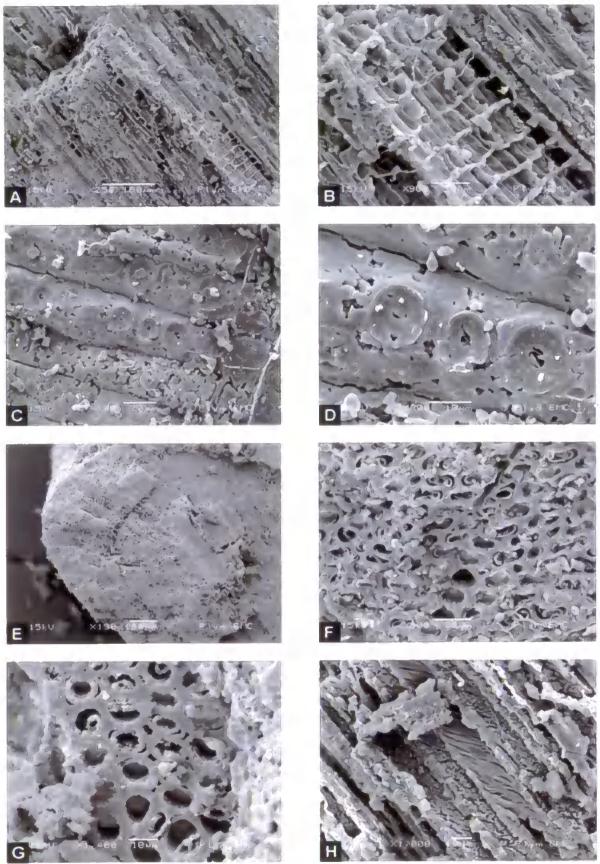


Plate 11. Scanning Electron Microscope images showing the state of preservation of fossil wood fragments from the Boyarka River, Siberia. All scale bars represent lengths stated on images. (A) Charcoal - internal cellular structure preserved. (B) Charcoal - internal cellular structure preserved (close-up of A). (C) Charcoal - internal cellular structure preserved (close-up of C). (E) Charcoal - internal cellular structure preserved. (D) Charcoal - internal cellular structure preserved (close-up of C). (E) Charcoal - internal cellular structure preserved. (F) Charcoal - internal cellular structure preserved (close-up of E). (G) Charcoal-coal - internal cellular structure displaying some signs of homogenisation. (H) Charcoal-coal - internal cellular structure displaying some signs of homogenisation.

## 8. IZHMA RIVER, TIMAN-PECHORA BASIN, RUSSIA

## 8.1. Location & Site Description

The Izhma River is a tributary of the Pechora River, both of which are situated within the Timan-Pechora Basin of north-eastern European Russia (Fig. 8.1). The Izhma River lies just west of the sub-Arctic Ural Mountains at a present-day latitude of ~64°N. The sections exposed on the banks of the Izhma River begin north of the towns of Ukhta and Sosnogorsk, which are approximately 200 km south of the confluence of the Izhma and Pechora Rivers.

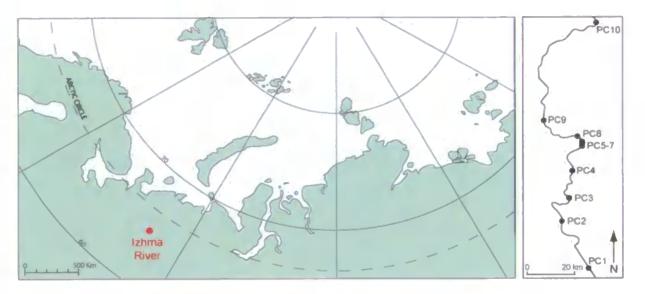


Figure 8.1 Location map of the Izhma River, Russia. The location of the Izhma River is shown (left) together with the relative positions of each of the sites examined (right).

Ten key locations were examined along the course of the Izhma River, ranging from Early Callovian (*Elatmae* ammonite Zone) to Early Hauterivian (*Bojarkensis* ammonite Zone) in age. The outcrops were in the form of low, river cuttings (containing belemnites) (Fig. 8.2) and pebbly river foreshores, with belemnites particularly common elements of the foreshore scree.



Figure 8.2 River-side cliff, exposure typical of the Izhma River, Russia.

# 8.2. Geological Setting

The Timan-Pechora Basin covers an area of ~440,000 km<sup>2</sup> (O'Leary *et al.*, 2004). It is a passive margin basin that extends from northern Russia and into the Barents Sea, where it merges with the South Barents Sea Basin (Requejo *et al.*, 1995; O'Leary *et al.*, 2004) (Fig. 8.3). On the western margin of the basin is the Timan Ridge, a major linear basement elevation (striking NW-SE) thought to represent the collision of one or more small continental blocks with the East European Platform during the Ediacaran (Zonenshain *et al.*, 1990; Ismail-Zadeh *et al.*, 1997; O'Leary *et al.*, 2004). The eastern and northeastern margins of the basin are formed by the Urals fold-and-thrust belt, which developed during the collision of the East European and Siberian blocks during the Late Carboniferous-Permian (O'Leary *et al.*, 2004). A series of deep depressions on the east margin of the basin are known as the Pre-Urals Depression and were formed above a zone of Palaeozoic peri-craton subsidence during the Uralian Orogeny (Ismail-Zadeh *et al.*, 2004).

1997). The Timan-Pechora Basin tapers southwards towards the convergence of the Timan Ridge and the Ural Mountains and broadens northwards where it extends offshore (O'Leary *et al.*, 2004). Zonenshain *et al.* (1990) divided the basin into two broad, stable, basement highs each with relatively thin sedimentary cover (the lzhma-Pechorskaya (within which the studied section of the lzhma River is situated) and Khoreyverskaya depressions) (Fig. 8.3). These highs are divided by fault-defined, linear mobile belts containing relatively thick sedimentary successions (O'Leary *et al.*, 2004).

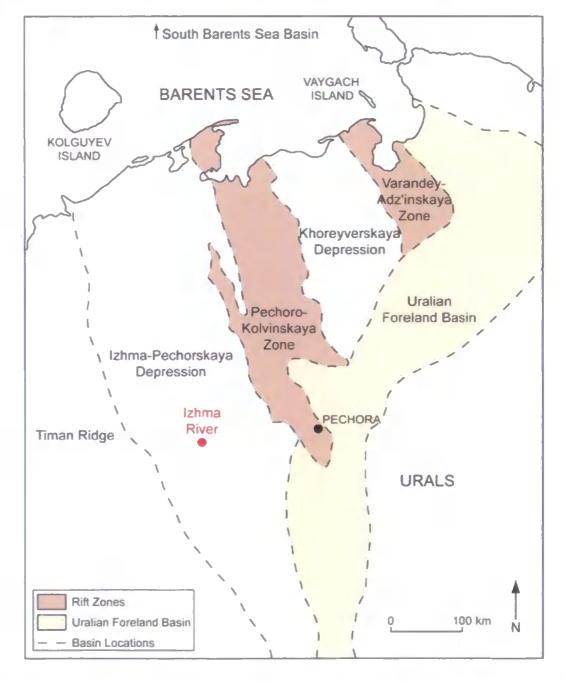


Figure 8.3 Simplified map of the Timan-Pechora Basin and surrounding areas. The principal structural zones are shown. Adapted after O'Leary *et al.* (2004).

During the Palaeozoic the Timan-Pechora Basin was a major extensional basin comprising a series of narrow grabens mainly orientated NNW-SSE (Banks *et al.*, 1997). Early Palaeozoic extension was particularly intense in the Middle-Late Devonian when the basin experienced rapid subsidence (Banks *et al.*, 1997; Ismail-Zadeh *et al.*, 1997). During the Early Permian another period of relatively rapid subsidence occurred in the Timan-Pechora Basin (Ismail-Zadeh *et al.*, 2004). This subsidence was the result of collision between the Baltic and Kazakstan plates at the time of the Uralian Orogeny, which was initiated in the Late Carboniferous/Permian (Banks *et al.*, 1997; Ismail-Zadeh *et al.*, 1997). Uralian activity was terminated in the Middle Triassic to Early Jurassic and a series of structural highs were formed, which now host over 250 known hydrocarbon accumulations in the region (Requejo *et al.*, 1995; Banks *et al.*, 1997).

The Timan-Pechora basement is exposed along the Timan Ridge and consists of metamorphosed sedimentary and volcanic rocks that have been intruded by granites (O'Leary *et al.*, 2004; Kuznetsov *et al.*, 2005). Overlying this thick metamorphosed basement are the Palaeozoic successions, which accumulated mainly in the western and central parts of the basin and are dominated by carbonate deposition, with episodes of siliciclastic sedimentation (Requejo *et al.*, 1995; O'Leary *et al.*, 2004). Finally, the continental to shallow marine siliciclastic Mesozoic sequence forms the dominant surface geology in the Timan-Pechora Basin (O'Leary *et al.*, 2004).

The Jurassic to Cretaceous Izhma River sequence is dominated by sandstones, siltstones and clays (Fig. 8.4), although, these are regularly affected by landslips and glacio-tectonic activity. The Lower Callovian (*Elatmae* Zone) outcrops ~2 km upstream of Porozhsk village and is represented by a poorly exposed, condensed sequence of clays containing abundant belemnites and phosphatic remains. A thin (15 cm) limestone horizon is also present. After a break in outcrop, Middle-Late Volgian sediments are exposed (*Panderi* to *Subditus* zones) ~1.8 km north of Kedvavom village. At the base, the sequence is dominated by calcareous grey claystones interbedded with black shales

containing belemnites. Belemnites become more abundant up sequence into the *Maximus* Zone, which is dominated by relatively well-bedded calcareous clays (layers of black shale are rare). Small carbonate concretions are scattered throughout and shells (mainly *Buchia*) are also common. The upper part of the *Maximus* Zone is composed of a relatively massive dark claystone. The Upper Volgian *Subditus* Zone is composed of phosphatic-rich silty claystone (similar to that of the *Panderi* Zone), with abundant shelly material and some belemnites.

The Basal Ryazanian *Pseudocraspedites/Surites* Zone (Fig. 8.4) outcrops ~6 km north of Kedvavom village, although, the exposure is generally poor. Silty sandstones at the base containing occasional small phosphatic nodules are overlain by dark grey/green sands containing rare *Surites* ammonites (~4 m thick). Above this sandy unit is a ~2 m thick band of heavily weathered, dark grey claystones with a pebble layer at the base. Belemnites occur throughout the succession, but are particularly common in a thin phosphatic horizon towards the top of the sand unit. Poorly preserved wood fragments also occur in this unit, but are quite rare.

The Upper Ryazanian *Tzikwinianus* Zone sediments (Fig. 8.4) are sandy at the base, but become increasingly clayey up sequence. The basal sands are grey, with abundant phosphatic concretions and belemnites. Abundant *Buchia* shells commonly occur in discrete horizons that are often associated with calcareous sands or phosphatic concretions. The sands become more iron rich towards the top of the sequence until the Ryazanian-Valanginian boundary, which is marked by an iron rich, red claystone bed of  $\sim$  30 cm thickness.

Above the iron rich bed is a unit of light grey claystones that are silty at the base and contain *Polyptychities* sp. ammonites. These lowermost Valanginian deposits also contain dark grey claystones, grey/green sandstones and phosphatic claystones. Belemnites are common, particularly within layers of light grey/green claystones.

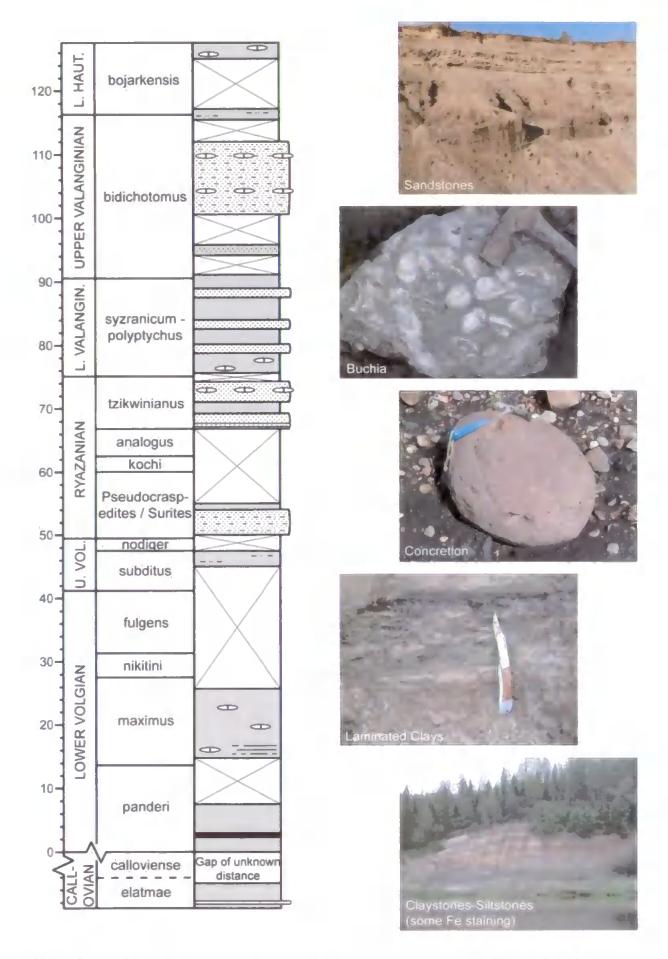


Figure 8.4 Sedimentary log and photographs of the Izhma River succession, Russia. Boreal (Russian) ammonite zones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

The Upper Valanginian (*Bidichotomus* Zone) (Fig. 8.4) is composed of poorly exposed fine, clayey to silty, dark grey/green sandstones. Large carbonate concretions containing abundant *Buchia* and some ammonites (*Dichotomites* sp.) occur in horizons <50 cm thick near the base of the unit. Smaller concretions however, occur towards the top of the unit. Belemnites are not common in Upper Valanginian strata and when present are extensively weathered. The Lower Hauterivian (*Bojarkensis* Zone) outcrop is reasonably well exposed, although, it has been subjected to a degree of glacio-tectonic activity. Dark grey clays with concretions that contain *Buchia* and belemnites are the dominant lithology.

## 8.3. Sampling & Methodology

The ten major sites visited along the Izhma River provided samples from the Early Callovian (*Elatmae* Zone) and from the Middle Volgian (*Panderi* Zone) to Early Hauterivian (*Bojarkensis* Zone). Belemnites were collected from 67 different horizons. Wherever possible multiple specimens were collected from the belemnite horizons. In addition, 86 sediment horizons and 13 fossilised wood horizons were sampled, although, these samples have not been analysed here. All samples were collected in the summer of 2003 by Dr Gregory Price, University of Plymouth.

The preservation of belemnite rostra was evaluated through trace element and stable isotopic analysis, backscattered scanning electron microscopy (BSEM), cathodoluminescence (CL) and carbonate staining. The areas most susceptible to diagenesis were removed prior to isotopic and geochemical analysis.

Stable isotope data were generated on an Isoprime isotope ratio mass spectrometer (GV Instruments, UK), at the University of Plymouth, UK and on a VG Optima mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), Keyworth, UK. Replicate analyses were run at both institutions to ensure reproducibility. Trace element data were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the

NERC ICP facility, Department of Geology at Royal Holloway, University of London. For a full description of the methodology used see Chapter 4.

### 8.4. Results

The Izhma River belemnites (Fig. 8.5) collected were of the Boreal Realm genera *Cylindroteuthis, Acroteuthis, Pachyteuthis* and *Lagonibelus*. Most of the belemnite rostra were composed of translucent calcite and displayed concentric banding. BSEM, CL and carbonate staining analysis (Plates 12-14) were conducted on 16 out of 60 specimens in order to assess the typical preservation. These techniques identified Fe-rich areas and some pyrite replacement particularly around the rostrum margins and apical canal as well as along fractures and strong growth bands. The areas shown to be especially prone to alteration were either avoided or removed prior to subsampling.

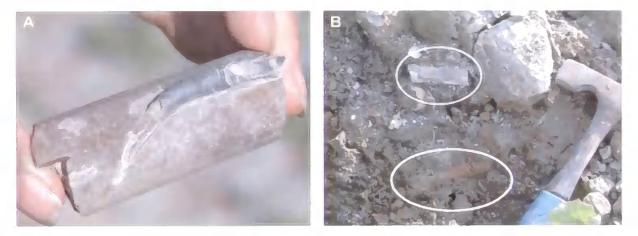
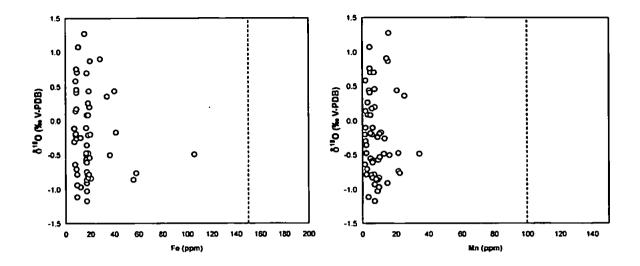


Figure 8.5 Photographs of belemnites from the Izhma River succession, Russia. Age and Formation unknown. (A) Belemnite with serpulid worm trace. (B) Belemnites in foreshore scree.

Trace element analysis of Fe and Mn concentrations was carried out on every belemnite sample in order to provide detailed information about the level of preservation. The concentrations of Fe and Mn range from 7-312 ppm, mean 25 ppm and 2-105 ppm, mean 10 ppm respectively. Plots of Fe and Mn against  $\delta^{18}$ O (Fig. 8.6) were used to constrain diagenetic alteration. A cross-plot of Fe and Mn is also provided to show the range of these trace element values (Fig. 8.7) as stable isotope analysis was not conducted on the most diagenetically altered specimens from this site. Belemnites with high concentrations of Fe (>150 ppm) and Mn (>100ppm) were considered post-depositionally altered and were excluded from further analysis.



**Figure 8.6** Cross-plots of  $\delta^{18}$ O against Fe (left) and Mn (right). The dashed lines indicate the cut off values for well preserved samples.

Additional element abundances are as follows: Sr 719-1504 ppm, mean 1192 ppm, Mg 281-1374 ppm, mean 621 ppm and Ca, 23% - 33 %, mean 31 %. Stable isotope analyses were conducted on 60 of the well-preserved belemnite samples. The carbon and oxygen isotope values of the Callovian to Early Hauterivian Izhma River belemnites were -0.98 to 2.67 ‰ and -1.32 to 1.27 ‰ respectively. The most negative carbon isotope values (-0.98 ‰) are observed in the Lower Volgian Panderi Zone and values remain relatively low to (between -0.98 and 0.83 ‰) until the Lower Valanginian Syzranicum-Polyptychus zones, where the initiation of a positive carbon isotope excursion is observed. The  $\delta^{13}C$ maxima (2.67 ‰) occur in the Upper Valanginian Bidichotomus Zone and are followed by a return towards pre-excursion values in the Early Hauterivian Bojarkensis Zone. A similar long-term trend is recorded in the  $\delta^{18}$ O data. Relatively low oxygen isotope values persist throughout the Volgian and Early Ryazanian (-1.32 to -0.11 ‰) until a shift towards more positive values occurs from the Upper Ryazanian and into the Lower Hauterivian. Maximum  $\delta^{18}$ O values (1.27 ‰) occur during the Upper Valanginian *Bidichotomus* Zone. A cross-plot of the  $\delta^{18}$ O and  $\delta^{13}$ C data (Fig. 8.8) shows a significant positive correlation (at the 99% confidence level).

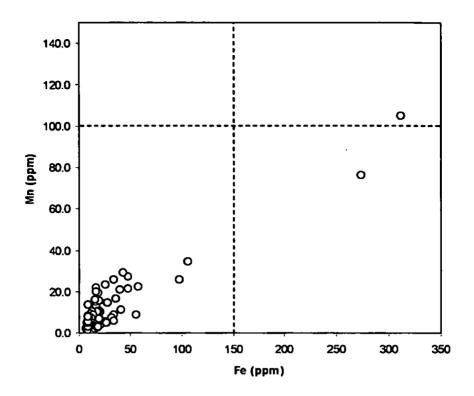


Figure 8.7 Cross-plot of Mn and Fe. The dashed lines indicate the cut off values for well preserved samples.

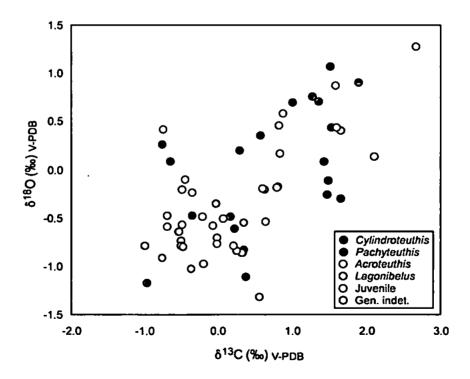


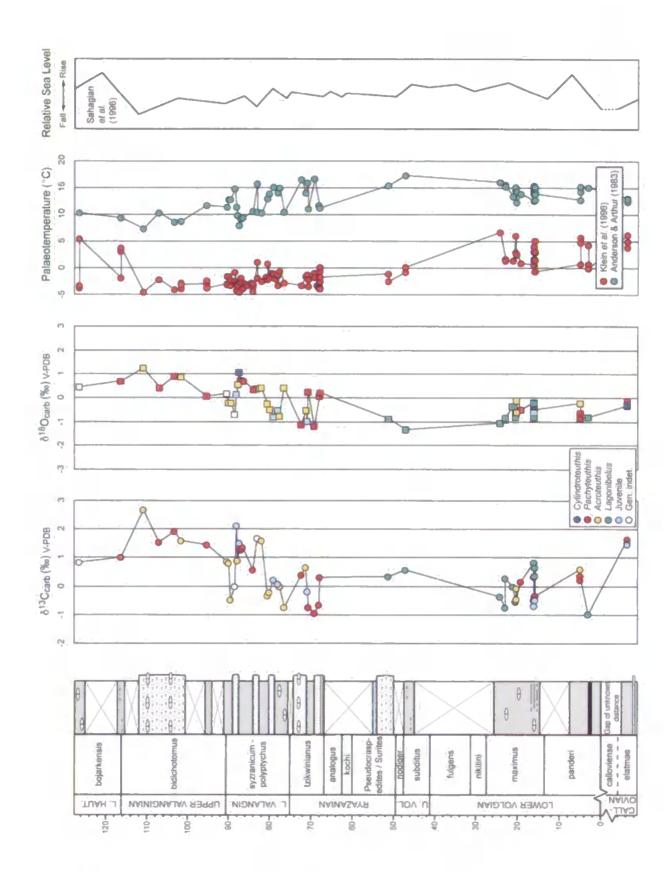
Figure 8.8 Cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C values derived from belemnites from the Izhma River succession, Russia.

### 8.5. Discussion

#### 8.5.1. Stable Isotope, Geochemical & Taxonomic Records

The stable isotope and trace element records from the Callovian-Hauterivian Izhma River succession have been presented here together with data pertaining to the generic classification of the belemnite specimens (Figs 8.9 & 8.10). The purpose of this was to assess the impact (if any) of genus-specific differences in isotope or trace element fractionation.

In neither the stable isotope nor El/Ca records does one genus appear to be consistently more positive or negative than the others. In addition, each genus displays a similar degree of scatter within the records presented (e.g., ~2.0 ‰ for isotopes). At Staffin Bay and the Boyarka River, the belemnite genus Cylindroteuthis displayed more scatter than any other genus in both the stable isotope and El/Ca records. It was hypothesised that this was in part due to the predominance of this genera compared with the others present. Interestingly, the number of specimens measured from each of the three dominant genera at the Izhma River section was very similar, for example 19 Pachyteuthis, 14 Acroteuthis and 13 Lagonibelus specimens were analysed. This provides some support for the idea that particularly dominant genera will display the most scatter. It should be noted however, that the genus Cylindroteuthis is especially rare in this succession (only 2 specimens analysed) so an enhanced degree of scatter in this genus cannot be ruled out. If taxonomic differences in fractionation do exist here, these data suggest that they are likely to have only a minor effect on the stable isotope and geochemical records. It is therefore highly unlikely that the trends observed here are caused solely by genus-specific effects. The trends are therefore interpreted as the result of environmental fluctuations.



**Figure 8.9**  $\delta^{13}$ C and  $\delta^{18}O_{carb}$  records from the Callovian-Lower Hauterivian Izhma River succession, Russia. Calculated palaeotemperatures and sea level are also shown. Boreal (Russian) ammonite zones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

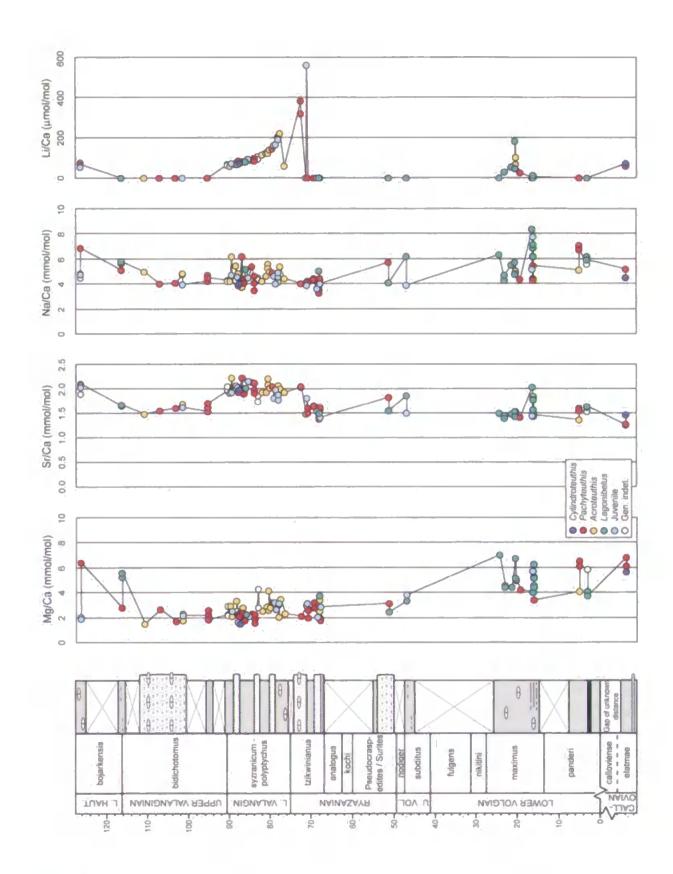


Figure 8.10 El/Ca records from the Callovian-Lower Hauterivian Izhma River succession, Russia. Boreal (Russian) ammonite zones illustrated. See Figure 4.2 for key to log symbols. Scale is in metres.

#### 8.5.2. The Oxygen Isotope Record & Palaeotemperature Implications

The oxygen isotope record (Fig. 8.9) shows a long-term trend of relatively stable values from the Volgian to Ryazanian (fluctuating between approximately -1.0 and 0.0 ‰) and then a shift to more positive values (1.27 ‰) from the Upper Ryazanian and into the Upper Valanginian. The oxygen isotope values presented here display approximately 1-2 ‰ scatter, which is consistent with published belemnite records (e.g., van de Schootbrugge *et al.*, 2000; Wierzbowski, 2002; Price & Mutterlose, 2004). Considerably less scatter is observed in the Izhma River succession than in the Boyarka River succession (see Chapter 7) which covers a similar time interval (Ryazanian-Hauterivian) and is approximately 10° further north in terms of palaeolatitude.

The scatter observed in the Izhma River data could be the result of taxonomic variability (as discussed previously), diagenetic alteration or salinity fluctuations. The presence of major diagenetic alteration has been ruled out by the extensive screening described earlier, although it is possible that subtle alteration may have escaped detection. The data are therefore considered to primarily reflect environmental fluctuations.

As discussed previously, belemnites are commonly believed to secrete their calcite very close to isotopic equilibrium with the surrounding seawater (e.g., Taylor & Ward, 1983; Morrison & Brand, 1986; Rosales *et al.*, 2004a; Rexfort & Mutterlose, 2006). It is therefore possible to estimate palaeotemperatures using the oxygen isotope composition of belemnite calcite, although calculations of absolute values are unlikely since belemnites are an extinct group of organisms. The palaeotemperatures calculated here should therefore be considered as a guide to the potential palaeotemperatures for the region.

The palaeotemperature estimates from the Izhma River succession (Fig. 8.9) were calculated using the equation of Anderson & Arthur (1983). The range of temperatures observed here is from 7.3 to 17.3°C, with an average value for the whole succession of 13.0°C. These values were calculated using a value of -1 ‰ SMOW, which is consistent with previously published literature on the Jurassic and Cretaceous periods (e.g., Pirrie &

Marshall, 1990; Marshall, 1992; Sælen *et al.*, 1996; Price & Sellwood, 1997; Podlaha *et al.*, 1998; Price & Mutterlose, 2004; Rosales *et al.*, 2004a, b). The palaeotemperatures decrease up succession with the highest values in the Upper Volgian *Subditus* Zone and the lowest values in the Upper Valanginian *Bidichotomus* Zone.

#### 8.5.3. The Elemental Records & Palaeotemperature Implications

The rationale and implications of considering *El/Ca* ratios together with  $\delta^{18}$ O data were discussed in Chapter 5. Long term trends are observed in the elemental ratios presented here (Fig. 8.10). The Mg/Ca ratios show a decrease in values from the Callovian and into the Upper Valanginian, with a brief fluctuation to higher values in the Lower Hauterivian. The Sr/Ca curve shows a slight increase in values until the Upper Valanginian, where a return to lower values occurs. The Na/Ca ratios reveal a slight shift towards lower values through the succession and the Li/Ca ratios show generally low values with occasional rapid fluctuations to very high values, most notably in the Upper Ryazanian *Tzikwinianus* Zone. The reason for these spikes is unclear.

Cross-plots of *El/Ca* against  $\delta^{18}$ O (Fig. 8.11) show no correlation between Sr/Ca and  $\delta^{18}$ O, Na/Ca and  $\delta^{18}$ O, and Li/Ca and  $\delta^{18}$ O. The correlation between Mg/Ca and  $\delta^{18}$ O however revealed a statistically significant negative correlation (at the 99% confidence level). This is the first instance where a significant correlation has been observed between Mg/Ca and  $\delta^{18}$ O in this study. The negative relationship is consistent with the published belemnite data (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b) and the work of Steuber & Rauch (2005) on modern skeletal calcite. The Mg/Ca ratio is commonly considered to be one of the most accurate palaeotemperature proxies available, primarily because unlike  $\delta^{18}$ O it is not thought to be significantly influenced by salinity fluctuations (e.g., Klein *et al.*, 1996; Lear *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b; Immenhauser *et al.*, 2005). The correlation between Mg/Ca and  $\delta^{18}$ O as observed here suggests that temperature is the major control of both proxies for the Callovian-Upper Valanginian interval at the Izhma River. This assumes that belemnites have a similar temperature sensitivity to modern biogenic calcites.

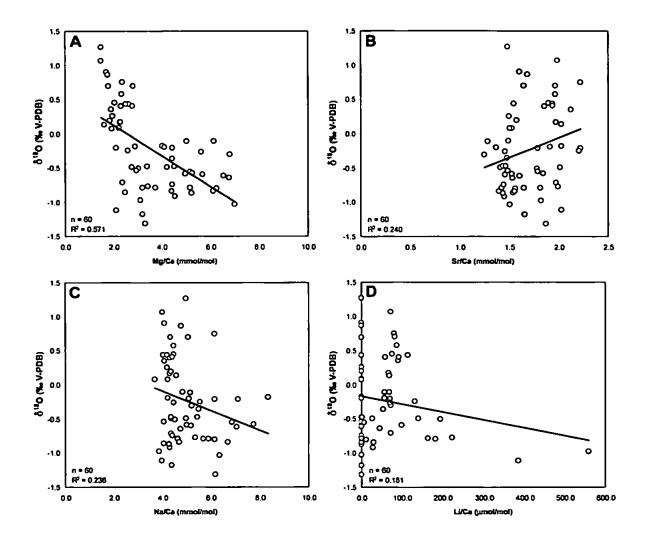


Figure 8.11 Cross-plots of  $\delta^{18}$ O against (A) Mg/Ca, (B) Sr/Ca, (C) Na/Ca and (D) Li/Ca for the Izhma River belemnites.

Palaeotemperatures were calculated from the Mg/Ca ratios using the equation of Klein *et al.* (1996) (Fig. 8.9). The calculated values ranged from -4.5 to 6.7°C, with an average temperature for the whole succession of -0.9°C. The average offset between the palaeotemperature calculations for the succession is 13.9°C. This value is extremely high, especially given the significance of the correlation and the obvious inverse relationship (observed using a linear regression line) between Mg/Ca and  $\delta^{18}$ O. The significance of the correlation suggests that both variables are influenced by one prevailing factor (presumable temperature). The observed offset between the calculated palaeotemperature averages, however, suggests that salinity must have had a highly significant and consistent impact on

 $\delta^{18}$ O, which seems unlikely. If the observed temperature difference was attributed solely to influence from salinity, a change in salinity of 13.8 ‰ is required, which seems impossible. Even if the  $\delta^{18}O_{seawater}$  value of Roche *et al.* (2006) for the high latitudes (-1.5) ‰ SMOW) is used to replace the standard estimate of -1 ‰ SMOW (which would give a  $\delta^{18}$ O palaeotemperature average of 11.0°C) a change in salinity of 12 ‰ would still be required. Episodes of freshening in the high latitudes can be caused by input from riverine runoff (which is particularly likely on the Russian platform) and seasonal ice melt. These factors are likely to have had an affect on the Izhma River  $\delta^{18}$ O data, however, such factors alone are unlikely to account for the required magnitude of salinity change. The Mg/Ca data must therefore be viewed with caution. As discussed previously, sub-freezing temperature values could not possibly be recorded by belemnites as they would not have been able to survive in such conditions. Immenhauser et al., (2005) suggest that it may only be appropriate to apply the Klein et al., (2996) equation to temperatures in the range of 5-23°C where the temperature-Mg relationship is linear. In addition, the data presented here suggest that the use of Mg/Ca palaeotemperature equations may be inappropriate for belemnites and that any subsequent calculation of salinity influence is probably not reliable, especially at relatively low temperatures.

#### 8.5.4. The Carbon Isotope Record

The marine carbonate  $\delta^{13}$ C record (Fig. 8.9) shows a shift to more negative values between the Callovian and Lower Volgian. Values remain fairly consistent (between -1.0 and 1.0 ‰) until the Lower Valanginian which witnesses the initiation of a positive carbon isotope excursion with the maximum (2.67 ‰) occurring in the Upper Valanginian *Bidichotomus* Zone. A return towards pre-excursion values is observed in the Lower Hauterivian. The positive carbon isotope excursion occurs at the same time as a shift towards more positive values in the  $\delta^{18}$ O record (which is consistent with a fall in palaeotemperature). Using data from Sahagian *et al.* (1996) the initiation of the positive carbon isotope excursion in the Izhma River succession occurs during a period of sea level fall. This is contrary the relationship observed in the Boyarka River succession, where the initiation of the positive excursion was coincident with a sea level rise. It should be noted, however, that the shift towards more positive values in the Izhma River succession occurs slightly earlier than that in the Boyarka River succession assuming that the correlation is correct. It is likely that these excursions did actually occur simultaneously and the differences observed in this study are the result of limitations in sampling resolution and biostratigraphy. The Upper Valanginian positive carbon isotope excursion occurs during a time of frequently fluctuating sea level on the Russian Platform and in Siberia. Given the limitations mentioned above, it is therefore impossible to determine whether the initiation of the  $\delta^{13}$ C excursion occurred during a period of relative sea level rise or fall, although if considered in terms of eustatic sea level change throughout the Jurassic and Cretaceous the excursion does occur during a period of relatively low sea level.

#### 8.5.5. Volgian-Hauterivian Stable Isotope Records

As discussed in Chapter 7, published marine carbonate stable isotope records for the Early Cretaceous have been constructed primarily from successions in the Tethyan region. In terms of the  $\delta^{13}$ C record, the overall pattern described from such research is one of decreasing  $\delta^{13}$ C values across the Jurassic-Cretaceous boundary, relatively stable  $\delta^{13}$ C values in the earliest Cretaceous, then a rapid mid- to Late Valanginian positive carbonisotope excursion (occurring in the Tethyan *Campylotoxus* ammonite zone) and a subsequent return to pre-excursion values in the Upper Valanginian and Lower Hauterivian (Price & Mutterlose, 2004). The nature of the  $\delta^{18}$ O record is obviously more variable, depending to a large degree on palaeolatitude.

Price & Mutterlose (2004) record palaeotemperature estimates of 7 to 21°C for the Volgian-Valanginian interval from the Yatria River, Siberia. This is compatible with the data presented here for the Izhma River succession, where a palaeotemperature range of

7.3 to 17.3 °C is predicted for the same interval. These two locations are situated on the same landmass and at approximately the same palaeolatitude so similar values are to be expected and the reproducibility of such palaeotemperatures provides considerable confidence in these values. The lower end of these temperature ranges provides substantial evidence for the existence of cold conditions in the northern high latitudes at this time. Polyak *et al.* (2003) estimated modern temperatures for the region of -1 to 12°C based on benthic foraminiferal isotope studies in the Kara and Pechora Seas. By comparison, it would be reasonable to consider that a palaeotemperature range of 7-21°C could be consistent with the existence of a seasonal ice cover at the Arctic pole during the Late Jurassic and Early Cretaceous. If the Boyarka River  $\delta^{18}$ O data are considered in addition to those of the Izhma and Yatria Rivers (which is again from the same landmass but approximately 10° further north in terms of palaeolatitude) the evidence for cold conditions is even more convincing. The calculated palaeotemperature range from the Boyarka River is from 2-19°C for the Ryazanian-Hauterivian interval based on oxygen isotopes.

The Izhma River data record a fall in palaeotemperature during the Valanginian period. This is consistent with a number of published studies that record evidence for a Valanginian cooling event (e.g., Mutterlose *et al.*, 2003; Pucéat *et al.*, 2003; Erba *et al.*, 2004; Weissert & Erba, 2004; Kessels *et al.*, 2006) (this evidence is discussed in Chapter 7). Ultimately, the studies presented here lend very strong support to the idea that the Late Jurassic and Early Cretaceous greenhouse climate was at times punctuated by sub-freezing conditions at the poles.

The Izhma River positive carbon isotope excursion observed here begins during the Lower Valanginian Syzranicum-Polyptychus zones (the Polyptychus Zone is correlatable with the Tethyan Campylotoxus Zone). The peak of the positive  $\delta^{13}$ C excursion occurs in the Bidichotomus Zone which corresponds well biostratigraphically with the timing of the Tethyan excursion in the Trinodosum and Callidiscus ammonite zones (e.g., van de Schootbrugge et al., 2000; Weissert & Erba, 2004). The excursion observed here also

correlates well with the positive carbon isotope excursion observed in the Boyarka River succession (Fig. 8.12). As discussed in the previous chapter, this excursion has been attributed to the first episode of greenhouse conditions during the Cretaceous period (Lini *et al.*, 1992) and episodes of platform drowning in the Tethys (e.g., Lini *et al.*, 1992; Föllmi *et al.*, 1994; Weissert *et al.*, 1998; Wortmann & Weissert, 2000). Van de Schootbrugge *et al.* (2000) however, recognised that during the Hauterivian at least two phases of platform drowning were not associated with positive carbon-isotope excursions and Wortmann & Weissert (2000) instead suggested that the sea-level rise and drowning of platform carbonates corresponded to the initiation of more positive carbon-isotope values.

The  $\delta^{13}$ C excursion recorded here in the Izhma and Boyarka rivers however, occurs during a period of relatively low eustatic sea level according to the sea level curve of Sahagian *et al.* (1996) constructed for the Russian Platform. A period of sea-level lowstand would have resulted in the partial separation of the Boreal and Tethyan Realms (as confirmed by belemnite provinciality) and could have restricted ocean circulation and enhanced stratification to promote organic carbon burial in these high latitude locations, although the evidence for widespread Late Valanginian global marine black shales is limited (Price & Mutterlose, 2004). In addition, an increased input of nutrients resulting from the exposure and erosion of lowland areas (Brenchley *et al.*, 1994; Gröcke *et al.*, 1999; Price & Mutterlose, 2004) could have contributed to the positive carbon isotope excursion at this time.

Interestingly, the most positive carbon isotope values coincide with the most positive  $\delta^{18}$ O values (and therefore the lowest palaeotemperatures). This could be explained by a fall in atmospheric CO<sub>2</sub> concentration and a subsequent drop in temperature as the result of a significant burial of sediments rich in organic carbon. Vincent & Berger (1985) termed this the 'Monterey Hypothesis'. Such a relationship was also observed by Price & Mutterlose (2004) for the Late Valanginian positive carbon isotope excursion

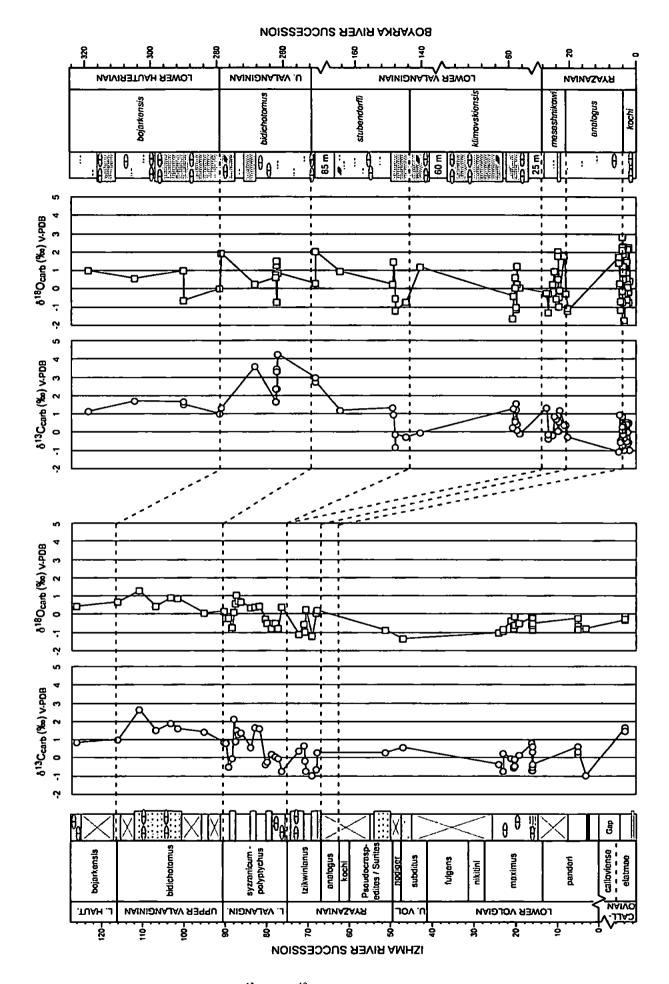


Figure 8.12 Ryazanian-Hauterivian  $\delta^{13}$ C and  $\delta^{18}$ O correlation between the Izhma River succession and the Boyarka River succession. See Figure 4.2 for key to log symbols.

from the Yatria River. This is not observed in the Boyarka River succession however, although this could in part, be due to the large degree of scatter present in the data.

# 8.6. Conclusions

- The data presented here comprise the first relatively high-resolution isotope investigation of marine biogenic carbonate (belemnites)  $\delta^{13}$ C and  $\delta^{18}$ O from the Izhma River, Russia.
- The average palaeotemperature derived from the Izhma River succession δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) was 13.0°C and the palaeotemperature range was 7.3°C to 17.3°C for the Callovian-Hauterivian interval. This suggests that contrary to popular opinion there was the potential for the existence of cold conditions during the Late Jurassic and Early Cretaceous greenhouse period.
- A fall in palaeotemperature is observed during the Valanginian. This is consistent with previously published evidence for a cooling event during the Valanginian period.
- The palaeotemperatures calculated from Mg/Ca ratios ranged from -4.5 to 6.7°C, with a average value of -0.9°C. The calculation of such low values casts doubt on the validity of using the Klein *et al.*, (1996) equation when applied to belemnites living in relatively low temperatures.
- The Late Valanginian positive carbon isotope excursion is recorded here in the Izhma River  $\delta^{13}$ C curve. The timing and duration of this excursion is consistent with that observed in previously published Tethyan records and with that observed from the Boyarka River succession. This suggests that the  $\delta^{13}$ C event influenced the total exchangeable carbon reservoir. The positive  $\delta^{13}$ C excursion occurs at a time of relatively low sea level in Russia and Siberia. The exposure and erosion of lowland areas and restricted ocean circulation (and therefore enhanced stratification) associated with a period of sea-level lowstand may account for increased rates of organic carbon burial.

• The most positive carbon isotope values coincide with the most positive oxygen isotope values (and therefore the lowest palaeotemperatures). This could be explained by a fall in atmospheric CO<sub>2</sub> concentration and a subsequent drop in temperature as the result of a significant burial of sediments rich in organic carbon.

#### **PLATE 12**

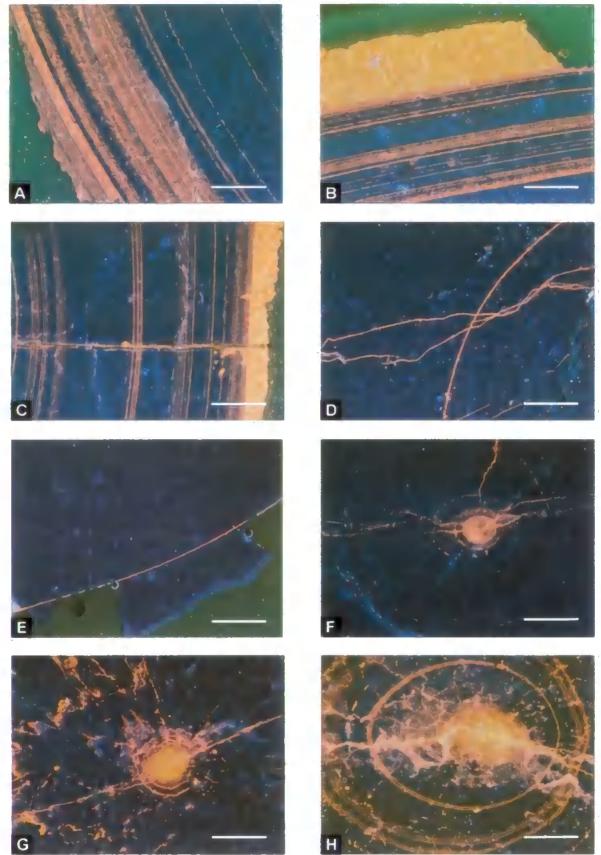


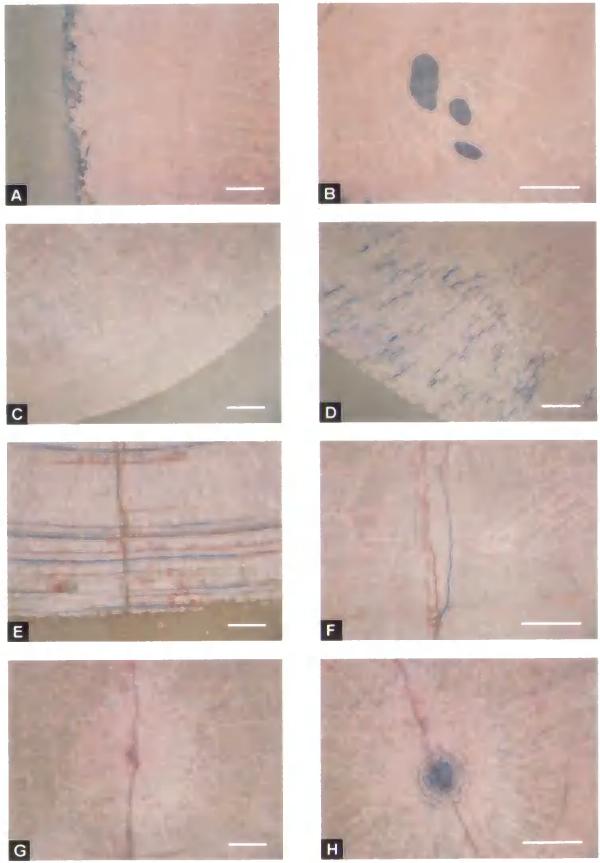
Plate 12. Cathodoluminescence images showing the state of preservation of belemnite rostra from the lzhma River, Russia. All scale bars represent 1 mm. (A) Growth bands towards rostrum margin displaying alteration. (B) Growth bands towards rostrum margin displaying alteration. (C) Fracture and growth lines displaying alteration. (C) Fracture and growth lines displaying alteration. (E) Generally very well preserved calcite. (F) Faint fractures eminating from apical canal and showing some alteration. (G) Apical canal with and some fractures displaying alteration. (H) Heavily altered growth bands and fractures surrounding the apical canal.

# PLATE 13



Plate 13. Backscattered SEM images showing the state of preservation of belemnite rostra from Staffin Bay, Isle of Skye. All scale bars represent lengths stated on images. (A) Very well preserved calcite. (B) Borings and growth line fractures at rostrum margin. (C) Fracture, borings and areas of alteration in rostrum. (D) Fracture running through apical canal. (E) Fracture eminating from apical canal. (F) Fracture running through diagenetically altered apical canal. (G) Generally well preserved calcite. (H) Fractures infilled with diagenetic cement.

# PLATE 14



**Plate 14.** Carbonate stained images showing the state of preservation of belemnite rostra from the lzhma River, Russia. All scale bars represent 1 num. (A) Rostrum margin displaying borings and alteration. (B) Borings infilled with diagenetic cement. (C) Very well preserved calcite. (D) Area near rostrum margin displaying alteration. (E) Fracture and growth lines displaying alteration. (F) Fractures displaying alteration in otherwise well preserved calcite. (G) Fracture running through apical canal. (H) Apical canal and surrounding growth lines displaying alteration.

# 9. FESTNINGEN & JANUSFJELLET, SVALBARD

### 9.1. Location & Site Description

Svalbard is an archipelago situated north of Norway on the edge of the Arctic Ocean. The islands have a latitudinal range of 74°N to 81°N and all are well within the present-day Arctic Circle. Festningen and Janusfjellet are both situated south of Isfjorden, on the principal island, Spitsbergen, at approximately 78°N (Fig. 9.1).

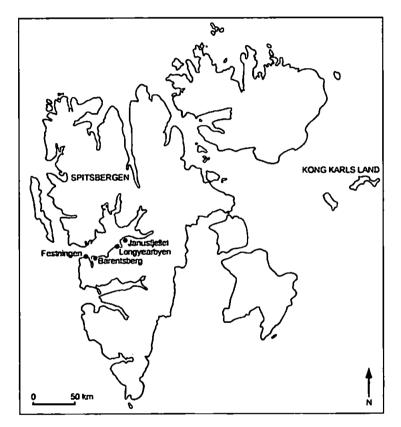


Figure 9.1 Location map of Svalbard. The field sites examined (Festningen and Janusfjellet) are shown.

Festningen is situated approximately 40 km southwest of the main town of Longyearbyen and near to the Russian mining town of Barentsburg. The outcrop at Festningen (Fig. 9.2) is in the form of a continuous low coastal cliff extending for approximately 7 km along the northern Nordenskiöld coast. Janusfjellet (Fig. 9.3) is situated inland, approximately 10 km north of Longyearbyen. The peak of Janusfjellet is approximately 800 m above sea level.



Figure 9.2 Low coastal cliff typical of the Festningen exposure. This photograph shows the Lower Valanginian Rurikfjellet Formation.



Figure 9.3 Typical exposure at Janusfjellet. This photograph shows the Volgian Argardhfjellet Formation.

# 9.2. Geological Setting

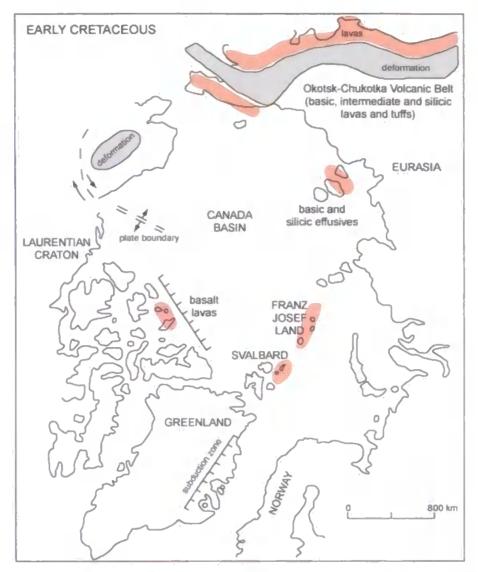


Figure 9.4 Simplified palaeogeographic map of the Arctic region. Structural and tectonic events are summarised. Adapted after Harland (1997)

During the Jurassic and Cretaceous, Svalbard was situated at a palaeolatitude of 60-70°N (Rowley & Lottes, 1988; Smith *et al.*, 1994; Ditchfield, 1997), just north of Greenland (Harland, 1969; McWhae, 1986) (Fig. 9.4). Throughout the Mesozoic, a stable platform regime prevailed on Svalbard, although, there is evidence for considerable igneous activity in the high Arctic region (north of Svalbard) during the Late Jurassic and Early Cretaceous (Worsley, 1986; Kelly, 1988; Bailey & Rasmussen, 1997; Maher, 2001). The magmatic activity on Svalbard was accompanied by significant vertical movements along major lineaments (Worlsey, 1986; Bailey & Rasmussen, 1997). Magmatic material includes sills, dikes and basalt flows that reveal increasingly intense activity eastwards (Harland, 1973, 1997; Worsley, 1986; Maher, 2001).

During the Early Jurassic, the Eastern Platform subsided (following a phase of uplift in the Triassic) whilst the main Spitsbergen Basin remained relatively stationary (Harland, 1997). This was caused by movement along the major Billefjorden lineament, the result of which was the existence of equivalent units of the Kapp Toscana Group immediately west and east of the lineament measuring 18 and 60-70 m respectively (Worsley, 1986).

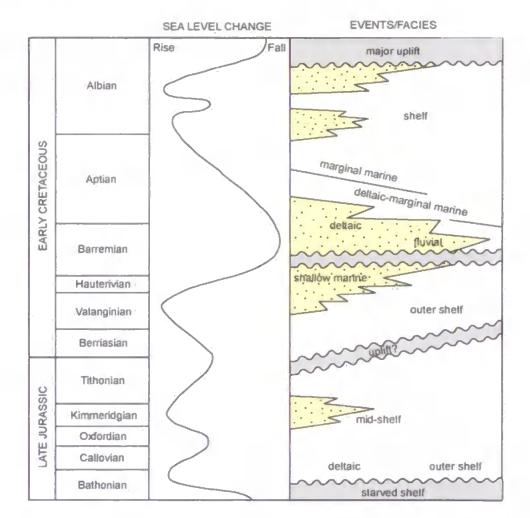


Figure 9.5 Summary of events and facies in the Late Jurassic and Early Cretaceous history of Svalbard. Adapted after Harland (1997).

A significant marine transgression commenced in the Late Bathonian and inundated both east and west Svalbard, whilst subsidence also became more pronounced in the west (Harland, 1997). This event led to the widespread deposition of the predominantly marine Adventdalen Group (Worsley, 1986; Harland, 1997; Dypvik *et al.*, 2002) (Fig. 9.5). During the Callovian, subsidence in the Pechora region created open marine conditions from the Barents Shelf, across the Russian Platform and into the Tethys for the first time during the Jurassic (Harland, 1997). The Late Bathonian transgression was followed by a mid-Callovian regression and a subsequent Late Callovian to Oxfordian renewed transgression (Dypvik *et al.*, 2002), which reached a maximum in the Early Volgian (Harland, 1997). A further marine regression initiated in the mid-Volgian continued into the Early Cretaceous (Harland, 1997; Dypvik *et al.*, 2002). By the Late Volgian, access from the Barents Shelf to the Tethys across the Russian Platform was closed south of the Volga region, however this route had re-opened by the Middle Berriasian (Harland, 1997).

A period of major uplift in the north affected the whole Mesozoic platform from the Late Jurassic and was probably linked to the opening of the Canada Basin (Worsley, 1986; Bailey & Rasmussen, 1997). Such uplift initiated basinal closure to the north and finally resulted in a break of deposition and subsequent extensive erosion throughout the Late Cretaceous (Worsley, 1986; Dypvik *et al.*, 2002). As a result of this uplift, Lower Cretaceous sequences tend to become thicker and more complete to the south (Worsley, 1986) and Upper Cretaceous deposits appear to be absent on Spitsbergen altogether as the result of major tectonic uplift (Dypvik *et al.*, 2002) (Fig. 9.5). Following a major regression in the Barremian (Harland, 1997; Dypvik *et al.*, 2002), a long-term transgression continued into the Albian, at which time globally high sea-levels prevailed (Harland, 1997).

Jurassic and Cretaceous sedimentation on Svalbard was dominated by marine shelf deposition. The Bathonian to Albian Adventdalen Group (Fig. 9.6) comprises a ~2 km thick sequence of black marine shales, deltaic sandstones and delta front clastics (Parker, 1967; Worsley, 1986; Harland, 1997). The Adventdalen Group lies (with varying degrees of minor unconformity) on top of the Triassic Kapp Toscana Group (Kelly, 1997).

The Adventdalen Group forms an asymmetric syncline plunging gently to the SSE, which is exposed most extensively in southern Spitsbergen, with the major exposure south

of Isfjorden (Kelley, 1997). The group has been divided into the Janusfjellet Subgroup (which is divided into the Agardhfjellet and Rurikfjellet formations), the Helvetiafjellet Formation and the Carolinefjellet Formation (Parker, 1967; Harland, 1973, 1997; Dypvik, 1992; Dypvik *et al.*, 2002).

EARLY CRETACEOUS	ADVENTDALEN GROUP			215 - 850m	Schönrockfjellet Mbr.	Shallow marine
					Zillerberget Mbr.	
			ROLINEFJELLET FORMATION		Langstakken Mbr.	
					Innkjegla Mbr.	
					Dalkjegla Mbr.	
		HEI	VETIAFJELLET FORMATION	50 - 100m	Glitrefjellet Mbr.	Marginal marine to fluvial
					Festningen Mbr.	
		JANUSFJELLET SUBGROUP	RURIKFJELLET FORMATION	300 - 800m	Ullaberget Mbr.	Distal marine to deep shelf
					Wimanfjellet Mbr.	
					Myklegardfjellet Bed	
MIDDLE - LATE JURASSIC			AGARDFJELLET FORMATION		Sløttsmoya Mbr.	
					Oppdalsåta Mbr.	
					Lardyfjellet Mbr.	
					Oppdaten Mbr.	

Figure 9.6 Stratigraphic chart for principal lithostratigraphic units of the Middle Jurassic to Early Cretaceous of Svalbard. Data from Harland (1997).

The Janusfjellet Subgroup (Fig. 9.6) (Bathonian to Barremian) was formed under marine shelf conditions and dominated by clay sedimentation, although silt and sand accumulation was also significant (Parker, 1967; Dypvik, 1985; Dypvik *et al.*, 1991a; Harland, 1997). The subgroup is ~300-800 m thick, has TOC values <10 % (although 1-4 % is more typical) and is dominated by Type III (with some Type II) kerogen (Hvoslef *et al.*, 1986; Harland, 1997). Belemnite and ammonite fossils are present throughout the Janusfjellet Subgroup (Parker, 1967; Harland, 1997).

The Agardhfjellet Formation (Fig. 9.6) (Bathonian to Volgian) has been divided into 4 different members (Dypvik *et al.*, 1991a, b). The formation is 243 m thick at the type locality and composed of dark grey-black shales exhibiting a fissile, papery appearance, with interbedded bioturbated siltstones, sandstones and thin carbonate bands (Parker, 1967; Dypvik, 1985; Hvoslef *et al.*, 1986; Dypvik *et al.*, 1991b; Harland, 1997; Kelly, 1997). The Agardhfjellet Formation was deposited during a transgressive phase on an open marine shelf, where stagnant conditions were relatively common (Dypvik, 1985). Dypvik *et al.* (1992) suggest that the Agardhfjellet Formation was deposited in mid- to outer shelf regions. The exposure at Festningen is heavily weathered and iron and sulphur staining are particularly common throughout the shales. At Janusfjellet, the exposure is mostly in the form of laterally continuous concretionary horizons that are also heavily weathered.

The Oppdalen Member is a fining-upwards transgressive sequence from a wellcemented conglomeratic unit at the base (formed by erosion and reworking of the underlying Wilhelmøya Formation), through glauconitic sands, to marine clays and silts at the top (Dypvik *et al.*, 1991a, b; Harland, 1997; Kelly, 1997). The Lardyfjellet Member is dominated by organic rich dark grey to black shales that are finely laminated and devoid of bioturbation (Dypvik *et al.*, 1991a, b; Harland, 1997; Kelly, 1997). The Oppdalsåta Member is composed of highly bioturbated silts and fine sands throughout which several coarsening upwards sequences can be identified (Dypvik *et al.*, 1991a, b; Harland, 1997; Kelly, 1997). Finally, the Slottsmøya Member consists of dark grey to black shales and paper shales similar to those of the Lardyfjellet Member (Dypvik *et al.*, 1991a, b; Harland, 1997; Kelly, 1997).

The Berriasian to Barremian Rurikfjellet Formation (Fig. 9.6) was deposited during regressive shelf sedimentation, with deposition occurring on the outer to inner shelf and in prodeltaic depositional conditions (Dypvik *et al.*, 1992), and is relatively enriched in volcanogenic components compared with the Agardhfjellet Formation (Dypvik, 1985). The formation is 176 m thick at the type location and consists of dark grey shales, siltstones and sandstones, frequently interbedded with reddish carbonate horizons (Parker, 1967; Dypvik, 1985; Dypvik *et al.*, 1991b; Kelly, 1997). It has been divided into 3 distinct

units: the Myklegardfjellet Bed (oldest), the Wimanfjellet Member and the Ullaberget Member (Dypvik et al., 1991a, b).

The Myklegardfjellet Bed was originally named by Birkenmajer (1980). It is a distinctive marker horizon that signals the transition between the Agardhfjellet and Rurikfjellet Formations across central and eastern Spitsbergen (Dypvik *et al.*, 1992). This bed varies in thickness from 0.5 to 10 m and consists of distinctive layers of white to yellow/green soft, plastic, weathered clays (Dypvik *et al.*, 1991b, 1992; Harland, 1997; Kelly, 1997). The bed was deposited by marine shelf processes at the culmination of a shallowing period in the depositional region (Dypvik *et al.*, 1992; Harland, 1997). The bed marks a change in depositional control, from global sea-level controlled shelf sedimentation to locally controlled, shallow shelf to prodeltaic/deltaic deposition (Dypvik *et al.*, 1992).

The Wimanfjellet Member comprises dark grey, silty, bioturbated shales containing irregular to cannon-ball shaped, reddish sideritic concretions (Dypvik *et al.*, 1991b; Harland, 1997). These are particularly common in the Festningen section. The Ullaberget Member consists of upwards-coarsening sequences of fine sands, silts and shales, with often well developed hummocky cross-stratification, planar cross-bedding and bioturbation (Dypvik *et al.*, 1991b; Harland, 1997; Kelly, 1997). Concretions similar to those of the Wimanfjellet Member are present in the lowermost beds of the Ullaberget Member (Dypvik *et al.*, 1991b). Harland (1997) attributes the deposition of the Ullaberget Member to progradation of the Festningen delta system.

The Barremian Helvetiafjellet Formation (Fig. 9.6) consists of a sequence of sandstones, shales and coals deposited in a continental environment (Parker, 1967; Steel *et al.*, 1977; Harland, 1997; Maher *et al.*, 2004). The unit varies from 50 to 100 m in thickness and contains coals of Type III and IV kerogen (Harland, 1997). The formation is divided into the Festningen and Glitrefjellet Members (Parker, 1967; Harland, 1997). The Festningen Member is a prominent, massive, hard light grey sandstone, weathering

yellow/orange (Parker, 1967). The Glitrefjellet Member is composed of coal measure-type facies, with abundant plant remains and poor quality coal (Parker, 1967; Harland, 1997). Steel *et al.* (1977) interpret this formation as a deltaic facies, with channel and crevasse splay sandstones, and interdistributary bay fines.

The Carolinefjellet Formation (Aptian to Albian) (Fig. 9.6) is divided into five members on the basis of sandstone-shale proportion. The formation is over 1200 m thick in places (Kelly, 1997) and signals a return to marine shelf deposition (Parker, 1967; Harland, 1997; Maher *et al.*, 2004). The succession is dominated by sandstones and shales, with some well developed ripple laminations, glendonites and rare fossils (Parker, 1967; Harland, 1997; Maher *et al.*, 2004). The top of the Carolinefjellet Formation is truncated by the Tertiary unconformity, the result of which is that post-Albian deposits have not been identified on Svalbard (Parker, 1967).

### 9.3. Sampling & Methodology

The Festningen samples ranged from Upper Oxfordian to Valanginian in age (although, it is worth noting that the Festningen section provides a complete succession from the Upper Carboniferous to Lower Cretaceous (Hoel & Orvin, 1937)). Belemnites were sampled from 25 well dispersed horizons from throughout the succession and glendonites were recorded from several horizons in the Valanginian. At Janusfjellet, belemnites were collected from 17 horizons and glendonites sampled from one major horizon only (again Valanginian in age). An attempt was made to collect multiple specimens from each horizon, however, the scarcity of belemnites at both Festningen and Janusfjellet meant that this was rarely possible. Sediment samples (~50) were collected from the Festningen section for nannofossil analysis by Dr Jörg Mutterlose, at the Ruhr-Universität, Bochum, Germany. All samples were collected in August 2005.

The preservation of belemnite rostra was assessed through trace element and stable isotope analysis in addition to BSEM, CL and carbonate staining. The areas of the rostrum most susceptible to diagenesis were removed prior to stable isotope and trace element analysis.

Stable isotope analysis was conducted on a VG Optima mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), Keyworth, UK. Trace element data were generated by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) using a Perkin Elmer Optima 3300RL ICP-AES system (with autosampler) at the NERC ICP facility, Department of Geology at Royal Holloway, University of London. For a full description of the methodology used see Chapter 4.

### 9.4. Results

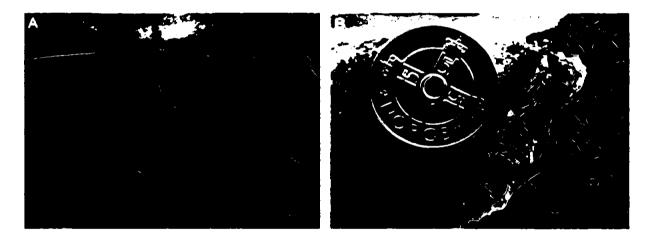


Figure 9.7 Typical preservation of Svalbard belemnites. (A) Highly ferroan and fractured belemnite from the Volgian Argardhfjellet Formation (Janusfjellet). (B) Recrystallised belemnite rostrum from the Callovian Argardhfjellet Formation (Janusfjellet).

The belemnite rostra collected from both Festningen and Janusfjellet were generally very poorly preserved and fragmented (Fig. 9.7) making generic identification difficult, if not impossible (although the belemnites were known to be of Boreal affinities from the work of Doyle & Kelly (1988) conducted on belemnites from Kong Karls Land). In total, 18 out of 38 specimens were subjected to BSEM, CL and carbonate staining (Plates 15-17) in order to assess which areas of the belemnite rostra were commonly affected by diagenesis. The majority of the specimens were severely altered, with some exhibiting an exclusively blue colouration after carbonate staining, indicating that the specimens were composed entirely of ferroan calcite (Plate 17). The CL technique, however, was much less effective at assessing the preservation of such specimens because the Fe levels were so high that they greatly exceeded the concentration of Mn (which is the catalyst for the CL reaction) and therefore, prevented luminescence. The BSEM analysis showed an abundance of sparry calcite and pyrite replacement, (which far exceeded any diagenetic alteration apparent in specimens from the other field locations considered here) particularly around the apical canal, the margins of the rostrum, on strong growth bands and along fractures (Plate 16). Also identified by these optical techniques was an infilling of quartz around the apical canal that was present in several specimens and the occurrence of deformation of the internal structure in some of the rostra. The areas prone to diagenetic alteration were either avoided or removed prior to subsampling.

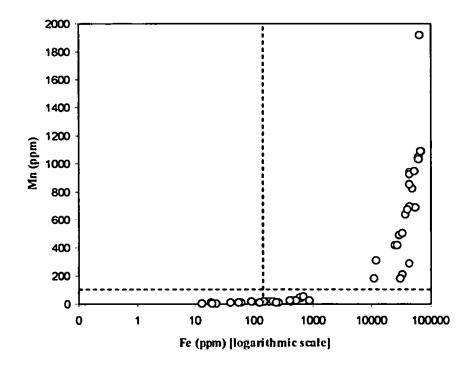


Figure 9.8 Cross-plot of Fe and Mn for belemnites from Svalbard. The dashed lines illustrate the cut off values from well preserved samples. Note the use of a logarithmic scale on the Fe axis.

Digenesis was further assessed using trace elements analysis, which was conducted on all 38 specimens in order to either confirm the presence of diagenetic alteration or to rule it out. The concentrations of Fe and Mn from the Festningen and Janusfjellet samples were as follows: Fe 12-68855 ppm, mean 19845 ppm; Mn 2-1911 ppm, mean 331ppm. A cross-plot of Mn and Fe was produced in order to constrain any diagenetic alteration (Fig. 9.8). Samples with concentrations of Fe and Mn exceeding 150 ppm and 100 ppm respectively were excluded from further analysis as they were considered likely to have undergone post-depositional alteration. In total 28 samples were rejected from further study on the basis of poor preservation.

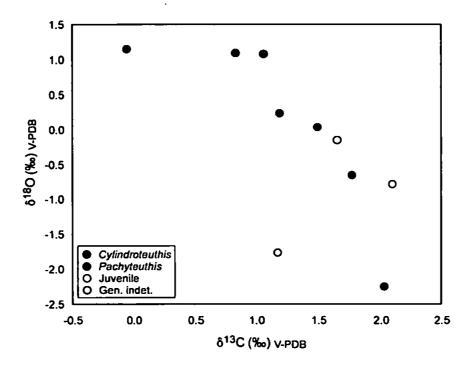


Figure 9.9 Cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C values derived from well preserved belemnites from Svalbard.

Additional trace element values were as follows: Sr 249-2857 ppm, mean 1117ppm; Mg 548-86290 ppm, mean 26404 ppm; Ca 7 % - 31 %, mean 22 %. Where diagenesis could be excluded oxygen and carbon isotope values ranged from -2.26 ‰ to 1.14 ‰ and -0.06 ‰ to 2.10 ‰ respectively. A cross-plot of  $\delta^{18}$ O and  $\delta^{13}$ C reveals a statistically significant negative correlation (at the 95 % confidence level) (Fig. 9.9). The well-preserved isotope data presented here comes from the Ryazanian-Upper Valanginian interval of the Svalbard succession, despite belemnite specimens also being collected from the Callovian-Volgian. In total, 9 separate belemnite horizons yielded potentially primary isotope values.

# 9.5. Discussion

# 9.5.1. Sedimentary Indicators of Palaeoclimate - Glendonites

Abundant stellate crystal aggregates were identified from the Upper Valanginian of the Rurikfjellet Formation at both the Festningen and Janusfjellet sections on Svalbard (Fig. 9.10). These mineral accumulations were yellow/orange/brown in colour, up to approximately 5 cm in size and composed of distinct crystals with pyramidal or flat terminations radiating out from a central nucleus. They were occasionally identified in Ferich concretions but were more commonly situated within dark mudstones or siltstones. These stellate aggregates are interpreted here as glendonites.

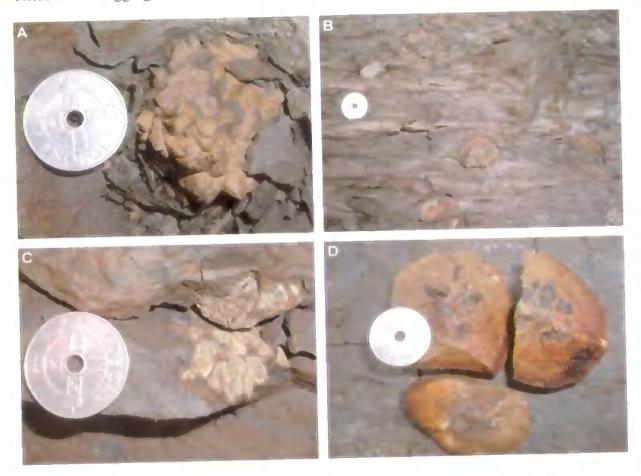


Figure 9.10 Glendonites from the Rurikfjellet Formation at Janusfjellet and Festningen. (A) Glendonite. (B) Abundance of glendonites. (C) Glendonite. (D) Glendonite in concretion.

Glendonites are calcite pseudomorphs after the metastable mineral ikaite (CaCO<sub>3</sub>  $\cdot$  6H<sub>2</sub>O) (DeLurio & Frakes, 1999). Sellwood & Price (1994) describe these pseudomorphs

as comprising of "obliquely striated and stepped crystals with a characteristic curved and tapered form". Glendonites are most commonly associated with fine-grained dark mudstones and shales indicating reducing conditions and often interpreted as offshore to offshore-transition facies (Kemper, 1975; Kemper & Schmitz, 1975; England, 1976; DeLurio & Frakes, 1999; Jones *et al.*, 2006).

Glendonites are generally considered to represent cold depositional conditions (Shearman & Smith, 1985; Sellwood & Price, 1994; DeLurio & Frakes, 1999; Swainson & Hammond, 2001; Jones *et al.*, 2006) due to the environmental conditions required for ikaite precipitation. Ikaite forms at low temperatures in carbonate and calcium rich waters (Lennie *et al.*, 2004) and has only been observed naturally at temperatures between -1.9 and 7°C (Larson, 1994; Johnston, 1995; DeLurio & Frakes, 1999; Jones *et al.*, 2006). The exposure of ikaite to higher temperatures results in the mineral becoming unstable after which it is transformed can be calcite (Jones *et al.*, 2006). Modern day occurrences of ikaite have been identified at Ikka, Greenland (Pauly, 1963), where a carbonatite intrusion flows into a marine fjord (Buchardt *et al.*, 1997), in Antarctic marine sediments (Suess *et al.*, 1982), the Nankai trough, Japan (Stein & Smith, 1985) and on the Alaskan coast (Kennedy *et al.*, 1987).

The unstable nature of ikaite prevents long-term preservation in the geological record. However, the transformation of ikaite to calcite provides an opportunity for preservation in the form of glendonites. Glendonites have been identified and described from many locations worldwide, including, in the Neoproterozoic Twitya Formation, Canada (James *et al.*, 2005), the Permian of eastern Australia (Jones *et al.*, 2006), the Dwyka Group in the Great Karoo Basin, South Africa (McLachlan *et al.*, 2001), the Aptian Bulldog Shale, Australia (DeLurio & Frakes, 1999), the Valanginian & Aptian of Spitsbergen (Kemper, 1983) and in the present day Sea of Okhotsk, Eastern Siberia (Greinert & Derkachev, 2004).

Limited stable isotope studies have been conducted on glendonites, with attempts made to estimate the seawater temperature at which they formed (e.g., DeLurio & Frakes, 1999; Greinert & Derkachev, 2004). The major problems associated with such investigations however, are firstly that the oxygen-isotope composition of the source water is unknown and secondly, that equilibrium crystallisation cannot be guaranteed. Presumably the recorded oxygen-isotope composition represents the transition from ikaite to calcite. This transition is observed to occur when temperatures exceed a given range (probably near 8°C (Stein & Smith, 1985; DeLurio & Frakes, 1999)), however, the rate of temperature rise influences the level of preservation (only a gradual rise in temperature will preserve the ikaite morphology) and the exact temperature at which transition occurs is dependent on water chemistry (DeLurio & Frakes, 1999). Oxygen-isotope ratios derived from the Bulldog Shale glendonites yield palaeotemperature estimates of 12-18°C, which seems peculiarly high and could be the result of several factors, for example, the majority of the calcite may represent later infilling or the estimate of  $\delta^{18}O_{seawater}$  may have been incorrect (DeLurio & Frakes, 1999).

Despite the problems associated with glendonite isotope studies it is probably reasonable to assume that the presence of glendonites in a geological succession represents cold conditions. The formation of the precursor mineral ikaite almost certainly took place in temperatures below 7°C and in marine successions at temperatures below 4°C, since marine ikaite has never been reported at temperatures exceeding this value (Bischoff *et al.*, 1993; Buchardt *et al.*, 1997). The presence of abundant glendonites in both the Festningen and Janusfjellet successions, therefore, confirms the presence of cold depositional conditions during the Late Valanginian in the region of Svalbard.

#### 9.5.2. Sedimentary Indicators of Palaeoclimate - Outsized Clasts

Outsized clasts are fairly common in the Valanginian part of the Janusfjellet Subgroup at Festningen (Fig. 9.11). The clasts are small, dark, sub-rounded and often subspherical, polished pebbles (< ~2cm) and are preserved either as individual stones or small clusters of stones within fine-grained facies, such as mudstone or fine-grained sandstone. The presence of relatively large clasts within a fine host sediment present a potential "hydrodynamic paradox" between the low energy depositional requirements of the host rock and higher energy conditions required to transport relatively large clasts (Bennett *et al.*, 1996). Clasts of this nature are often described as dropstones, a name derived from the likely method of deposition. Dropstones are introduced vertically or obliquely into the host sediment usually from some form of raft (Bennet & Doyle, 1996; Bennet *et al.*, 1996). The most common mechanism invoked to account for the presence of dropstones in a succession is deposition from icebergs or sea-ice (e.g., Frakes, 1979; Hambrey & Harland, 1981; Gilbert, 1990).



Figure 9.11 Outsized clast. Upper Valanginian Rurikfjellet Formation, Festningen.

Dropstones have been identified from Cretaceous sediments in Australia (Frakes & Francis, 1988; Francis & Frakes, 1993), from Late Jurassic and Early Cretaceous deposits

in Siberia (collated in Hambrey & Harland, 1981) and from Cretaceous and Paleogene sediments in Svalbard (Pickton, 1981). These deposits (and many others like them) have been attributed to ice-rafting and are therefore considered representative of cold climatic conditions, although, Bennett & Doyle (1996) question the reliability of dropstone evidence in demonstrating the presence of ice.

Dropstones may be transported and deposited in many ways. They could be either volcanic or meteoric projectiles (Bennett *et al.*, 1996) or they could be rafted by something other than ice. Bennett & Doyle (1996) describe several biological and physical processes that could deposit dropstones, for example, they could be rafted from vegetation such as seaweed, kelp and driftwood (e.g., Woodborne *et al.*, 1989; Bennett *et al.*, 1994; Doublet & Garcia, 2004), they could be gastroliths (e.g., Stokes, 1987; Clarkson, 1988) or indigestible stomach contents (e.g., Emery, 1965) or they could be floating stones. Gastroliths and indigestible stomach contents would be expected to form a small cluster of stones (Bennett *et al.*, 1996) and therefore cannot account for at least some of the deposits identified at Festningen. In addition, the stones at Festningen are never associated with skeletal remains. Floating stones are usually flat and are very limited in occurrence (Bennett *et al.*, 1996) and are therefore also unlikely to account for the outsized clasts identified. Perhaps the most likely alternative is rafting from vegetation, since this mechanism could deposit both individual stones and small clusters (Bennett *et al.*, 1994).

Polishing on at least one side of a pebble would be expected if it had been entrained in ice. In addition, the presence of striations on outsized clasts could be used to confirm deposition from ice-rafting. The pebbles observed here were often highly polished but no striations were observed, although this does not rule out deposition by ice. Other features often displayed by dropstones include evidence of sediment depression or deformation around the clasts, which would have been formed during impact and the draping of overlying sediments (Thomas & Connell, 1985; Jones *et al.*, 2006). Again, neither of these

features was observed at Festningen, although this is most likely due to the small size of the pebbles and consequently a low velocity of impact.

Although, ice-rafting cannot be confirmed as the mechanism of deposition for the outsized clasts observed at Festningen, the presence of such deposits lends some support to the idea that deposition could have occurred during cold conditions. Some of the pebbles identified were located within a few metres, stratigraphically, of glendonite deposits. The occurrence of both of these sedimentological features in the same succession is significant and goes some way to proving that cold conditions did occur in Svalbard during the Early Cretaceous.

#### 9.5.3. Stable Isotope, Geochemical & Taxonomic Records

As discussed previously, taxonomic identification of belemnite rostra was very difficult with specimens from the Svalbard region due to generally poor preservation. The affect of taxonomic differences on stable isotope and geochemical records is therefore almost impossible to assess from this location. This problem is exacerbated by the limited nature of the isotope record as recorded here. Whilst the data available does not indicate a taxonomic influence on the isotope and elemental records, the limited nature of the data means that such an influence cannot be ruled out.

## 9.5.4. The Oxygen Isotope Record & Palaeotemperature Implications

Palaeotemperatures (Figs 9.12 & 9.13) were again calculated using the equation of Anderson & Arthur (1983) and assuming an isotopic composition for the water of nonglacial seawater at -1 ‰ SMOW and a typical marine salinity of ~ 34 ‰. The palaeotemperature range for the Ryazanian-Upper Hauterivian succession at Janusfjellet was 7.7 to 8°C, compared to a palaeotemperature range of 11.1 to 21.4°C for the Upper Valanginian interval of the Festningen succession. Combined, these two records provide a palaeotemperature range of 7.7 to 21.4°C for the Ryazanian-Upper Valanginian of

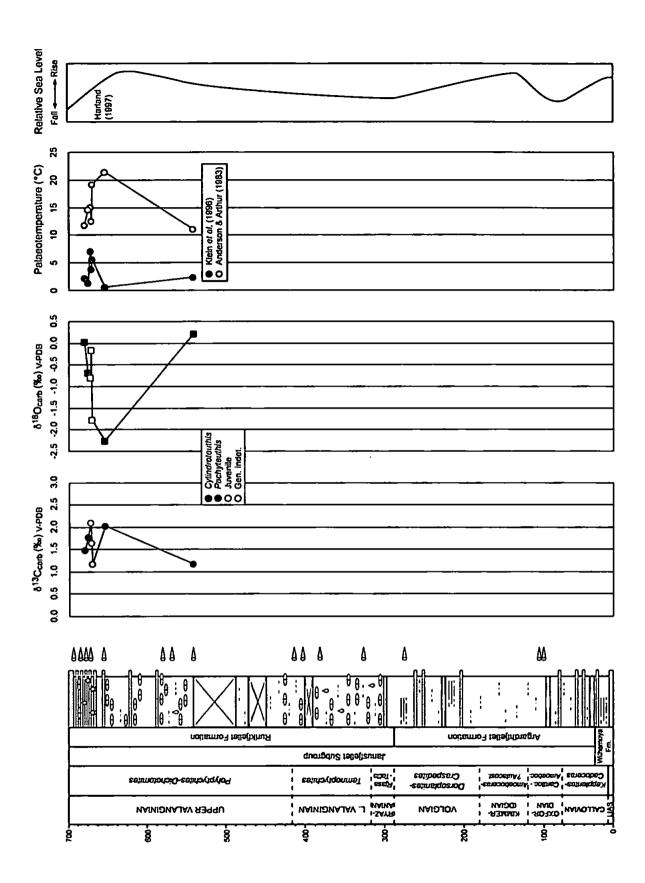


Figure 9.12  $\delta^{13}$ C and  $\delta^{18}$ O records from the Upper Valanginian succession at Festningen, Svalbard. Calculated palaeotemperatures and a sea level curve are also shown. Svalbard/Barents Sea ammonite zonation is illustrated (see references within Harland (1997)). Indicated to the right of the sedimentological log (with a belemnite symbol) are the horizons from which belemnites were collected. See Figure 4.2 for key to log symbols. Scale is in metres.

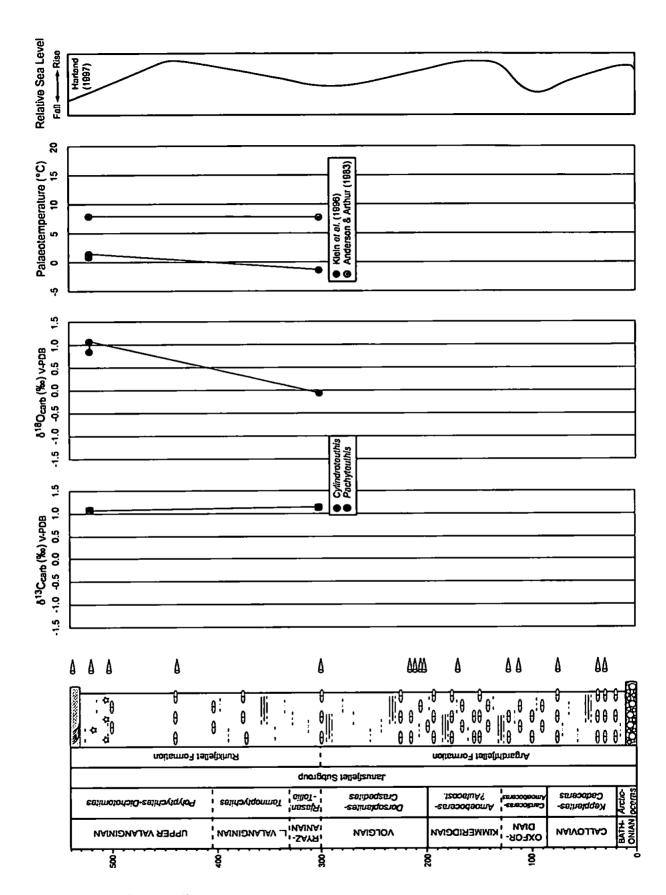


Figure 9.13  $\delta^{13}$ C and  $\delta^{18}$ O records from the Ryazanian-Upper Valanginian succession at Janusfjellet, Svalbard. Calculated palaeotemperatures and a sea level curve are also shown. Svalbard/Barents Sea ammonite zonation is illustrated (see references within Harland (1997)). Indicated to the right of the sedimentological log (with a belemnite symbol) are the horizons from which belemnites were collected. Figure 4.2 for key to log symbols.

Svalbard and an average temperature of 13.0°C. The lowest values occur in the Ryazanian and the highest values in the Upper Valanginian *Dichotomites* ammonite zone. Surprisingly, the highest palaeotemperature estimates occur just prior to (~10 m below) the glendonite occurrences in the Festningen section, although the temperatures do drop significantly (from 21.4 to 11.1°C) where glendonites are most abundant. At Janusfjellet, belemnites and glendonites also co-occur during the Upper Valanginian. Here  $\delta^{18}$ O derived palaeotemperatures give values of ~8.0°C. Interestingly, this is the estimated basal transition temperature for the change from ikaite to calcite in glendonites (e.g., Stein & Smith, 1985; DeLurio & Frakes, 1999).

#### 9.5.5. The Elemental Records & Palaeotemperature Implications

Mg/Ca, Sr/Ca, Na/Ca and Li/Ca ratios were calculated here (as in the previous chapters) together with Mn/Ca in order to assess preservation. Those samples with Mn/Ca values exceeding 100 µmol/mol were excluded from further analysis. Cross-plots of *El/Ca* against  $\delta^{18}$ O for the Ryazanian-Upper Valanginian Svalbard belemnites (Fig. 9.14) show statistically significant correlations (at the 99% confidence level) for Na/Ca with  $\delta^{18}$ O and Li/Ca with  $\delta^{18}$ O but not for Mg/Ca or Sr/Ca. The R<sup>2</sup> values for the correlations are as follows, 0.447 (Mg/Ca), 0.062 (Sr/Ca) 0.899 (Na/Ca) and 0.799 (Li/Ca). The strength of the correlations between Na/Ca and  $\delta^{18}$ O and between Li/Ca and  $\delta^{18}$ O is surprising as such correlations have not been observed in published belemnite studies (e.g., McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004a, b) nor have they been observed in the previous chapters (although Li/Ca and  $\delta^{18}$ O did show a statistically significant correlations is unclear.

Long-term trends cannot be observed from the Janusfjellet succession (Fig. 9.15) because the succession contains only three data points (one in the Ryazanian and two in the Valanginian), however, there appears to be little change in the *El/Ca* values recorded at

Janusfjellet. The long-term trends recorded from the Festningen succession (Fig. 9.16) are also difficult to interpret due to the sparsity of data. As is expected from the correlations observed in the *El/Ca* and  $\delta^{18}$ O cross-plots (Fig. 9.14) Na/Ca and Li/Ca show a distinct shift to more negative values, which is followed by a return towards more positive values at the top of the succession (as is observed in the  $\delta^{18}$ O record).

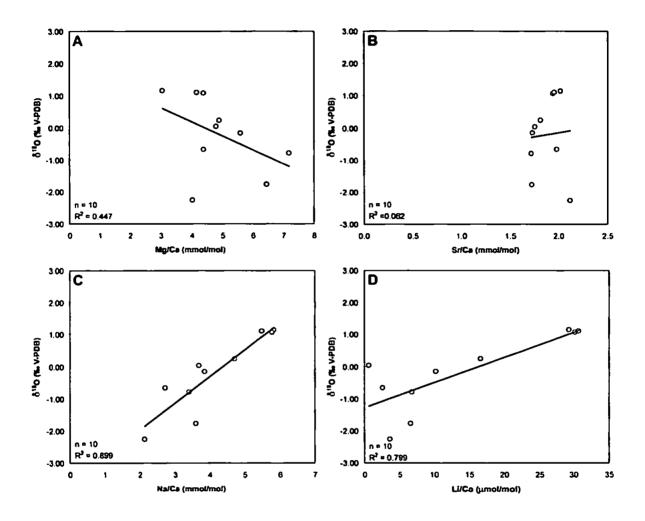


Figure 9.14 Cross-plots of  $\delta^{18}$ O and (A) Mg/Ca, (B) Sr/Ca, (C) Na/Ca and (D) Li/Ca.

Mg/Ca ratios were used to calculate palaeotemperatures (Figs 9.12 & 9.13) for the Ryazanian-Upper Valanginian interval using the equation of Klein *et al.* (1996) (as in the previous chapters). The average palaeotemperature (for the Janusfjellet and Festningen sections combined) is 2.4°C and the range is -1.3 to 5.6°C. The average offset between the  $\delta^{18}$ O derived values and Mg/Ca derived values for the combined Svalbard successions is 10.6°C. This temperature difference is linked to a distinct freshening of ~10 ‰, which equates to a change from a 'normal' marine salinity of 34 ‰ to a value of 24 ‰.

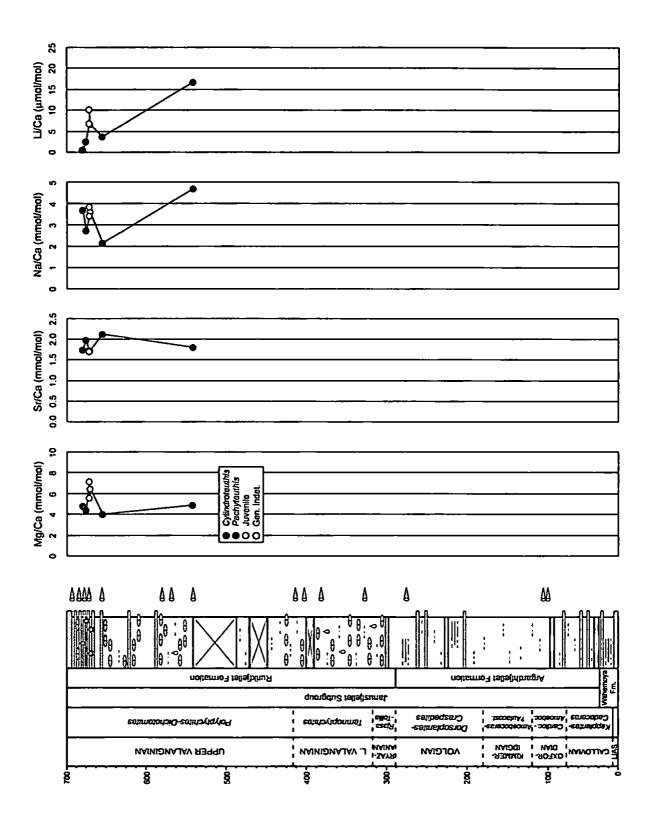


Figure 9.15 El/Ca ratios from the Upper Valanginian succession at Festningen, Svalbard. Svalbard/Barents Sea ammonite zonation is illustrated (see references within Harland (1997)). Indicated to the right of the sedimentological log (with a belemnite symbol) are the horizons from which belemnites were collected. See Figure 4.2 for key to log symbols. Scale is in metres.

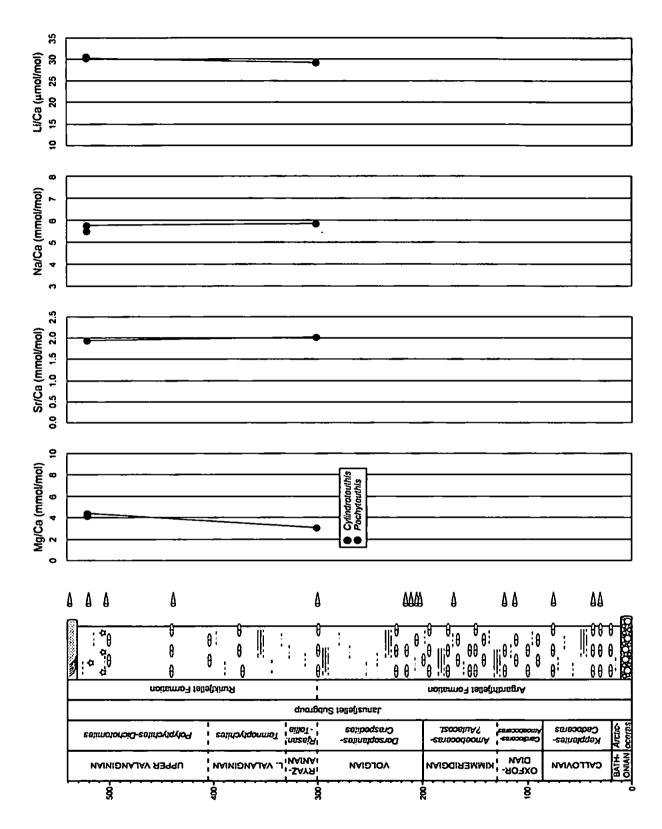


Figure 9.16 El/Ca ratios from the Ryazanian-Upper Valanginian succession at Janusfjellet, Svalbard. Svalbard/Barents Sea ammonite zonation is illustrated (see references within Harland (1997)). Indicated to the right of the sedimentological log (with a belemnite symbol) are the horizons from which belemnites were collected. See Figure 4.2 for key to log symbols.

This amount of freshening seems unlikely since belemnites are always associated with other marine organisms and are therefore unlikely to have survived in seawater with a salinity that low. If the oxygen isotope composition of seawater is assumed to be -1.5 ‰ (the value predicted by Roche *et al.* (2006) for the high latitudes) the average  $\delta^{18}$ O derived palaeotemperature is 11.0°C (instead of 13.0°C). A change in temperature of 8.6°C can be interpreted as the result of an 8.4 ‰ change in salinity. This value still seems high, which suggests that Mg/Ca derived palaeotemperature estimates must be viewed with caution, particularly as the Mg/Ca calculations used here produce sub-freezing values for parts of the succession and such temperatures could not possibly be recorded by belemnite calcite.

## 9.5.6. The Carbon Isotope Record

Carbon isotope values from the Festningen and Janusfjellet successions range from -0.06 ‰ in the Ryazanian to 2.1 ‰ in the Upper Valanginian. Once again, the sparsity of data makes it difficult to interpret a long-term trend here. In spite of these difficulties however, a shift to more positive values in the Upper Valanginian is observed. This is consistent with the timing of the global carbon isotope positive excursion that occurs during this interval (and has been identified from carbonate and organic records presented in this study - see Chapters 7 & 8). The shift towards more positive carbon isotope values observed here is coincident with a relative sea level rise, although the maximum values occur during the onset of a sea level fall. This relationship observed between carbon isotope values and sea level is very similar to that observed from the Boyarka River succession, where the initiation of the positive carbon isotope excursion coincides with a sea level rise but the excursion maximum coincides with a sea level fall. As discussed previously, positive carbon-isotope excursions may be related to regressive conditions due to an increased input of nutrients resulting from exposure and erosion of lowland areas (Brenchley et al., 1994; Gröcke et al., 1999; Price & Mutterlose, 2004). In addition, the partial separation of the Boreal and Tethyan Realms during periods of sea-level lowstand

could have restricted ocean circulation and enhanced stratification to promote organic carbon burial in these high latitude locations (Price & Mutterlose, 2004).

### 9.5.7. Ryazanian-Valanginian Stable Isotope Records

The Ryazanian-Upper Valanginian temperatures calculated here (7.7 to 21.4°C, average 13.0°C) are consistent with palaeotemperatures calculated from published belemnite-derived oxygen-isotope data. Ditchfield (1997) calculated palaeotemperatures of 5.3 to 10.9°C for the Tithonian-Valanginian interval from Kong Karls Land, Svalbard. Other palaeotemperature estimates include those of Price *et al.* (2000) at 10-15°C for Yorkshire, England, McArthur *et al.* (2004) at 9-14°C also for Yorkshire, England, van de Schootbrugge *et al.* (2000) at 12-16°C for southeastern France and Price & Mutterlose (2004) at 7-21°C for the Yatria River, Siberia (Fig. 9.17). The palaeotemperature data presented here is consistent with the lowest values previously recorded for Ryazanian-Valanginian interval but also presents some surprisingly high temperature values.

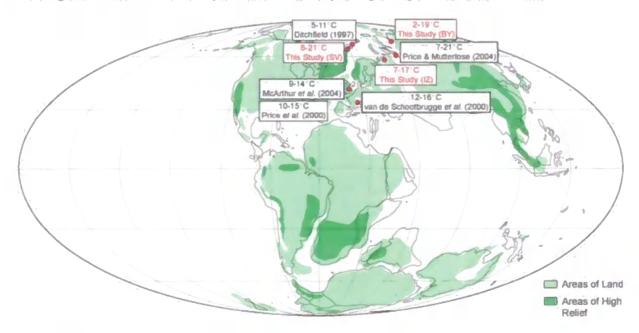


Figure 9.17, Valanginian palaeogeography map showing published belemnite derived palaeotemperatures for this time period. (SV = Svalbard; BY = Boyarka River; IZ = Izhma River).

The palaeotemperature estimates from the Ryazanian-Valanginian northern high latitudes (calculated from this study and by Price & Mutterlose (2004)) are more variable than the estimates derived from the mid-latitudes (e.g., Price *et al.*, 2000; van de Schootbrugge *et al.*, 2000; McArthur *et al.*, 2004). This could be the consequence of several factors, firstly, increased seasonal temperature differences in the high latitudes compared with those in the mid- to low latitudes, secondly, the proximity of these sites (and in particular those in Russia and Siberia, which show the greatest variability) to a substantial landmass and hence the likely influence of riverine runoff and thirdly, the potential influence of seasonal ice-melt to these high latitude sites. An additional factor that could account for the observed high latitude variability is that Boreal Realm belemnite taxa could have a greater tolerance to changing environmental conditions than their Tethyan counterparts.

As discussed in previous chapters an Upper Valanginian positive carbon isotope excursion has been identified from the Tethyan region (e.g., Lini *et al.*, 1992; Channell *et al.*, 1993) and from the high latitudes (e.g., Price & Mutterlose, 2004; Boyarka River and Izhma River (this study)) and from both carbonate (e.g., Lini *et al.*, 1992; Channell *et al.*, 1993) and organic carbon records (e.g., Gröcke *et al.*, 2005; Boyarka River (this study)). The  $\delta^{13}$ C shift to more positive values observed in the Svalbard successions is consistent with the timing of this seemingly global excursion.

# 9.6. Conclusions

- The data presented here comprise the first belemnite stable isotope study to be conducted from the Ryazanian-Upper Valanginian interval at Festningen and Janusfjellet, Svalbard.
- The preservation of belemnites at this site was very poor, although stable isotope analyses were possible from ~25% of the collected specimens.
- Glendonites and outsized clasts (interpreted here as glacial dropstones) were identified from the Svalbard successions. The presence of such deposits occurring in close

stratigraphic proximity lends definite support to the idea that cold conditions occurred in the northern high latitudes during the Early Cretaceous.

- The palaeotemperature range calculated from the belemnite δ<sup>18</sup>O data is 7.7 to 21.4°C, with an average temperature of 13.0°C. This is consistent with previously published data for this time interval. Despite the variability observed, the existence of cold conditions is further supported by these data.
- The Mg/Ca derived palaeotemperature estimates range from -1.3 to 5.6°C, with an average temperature of 2.4°C. As noted in previous chapters, it would be impossible for belemnites to record sub-freezing temperatures, which casts doubt on the use of Mg/Ca palaeotemperature equations when applied to belemnite calcite.
- The δ<sup>13</sup>C data display a shift to more positive values from the Ryazanian and into the Upper Valanginian (of ~2 ‰). This shift is consistent with the timing of the Upper Valanginian positive carbon isotope excursion, which has been recorded from the Tethyan region, from the high latitudes, from carbonate and from organic carbon records.

## PLATE 15

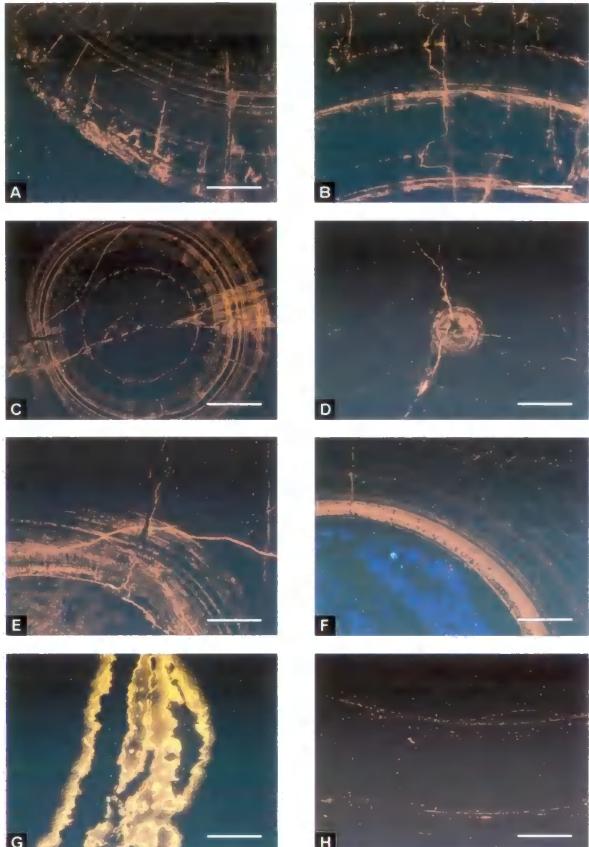


Plate 15. Cathodoluminescence images showing the state of preservation of belemnite rostra from Festningen and Janusfjellet, Svalbard. All scale bars represent 1 mm. (A) Rostrum margin, growth bands and fractures displaying alteration. (B) Grwoth bands and fractures displaying alteration. (C) Apical canal surrounded by growth bands displaying alteration. (D) Fractures eminating from apical canal. (E) Fractures and growth bands near apical canal displaying alteration. (F) Apical canal with sediment infilling. (G) Distinct cracks partially infilled with diagenetic cement. (H) Generally well preserved calcite.

# PLATE 16

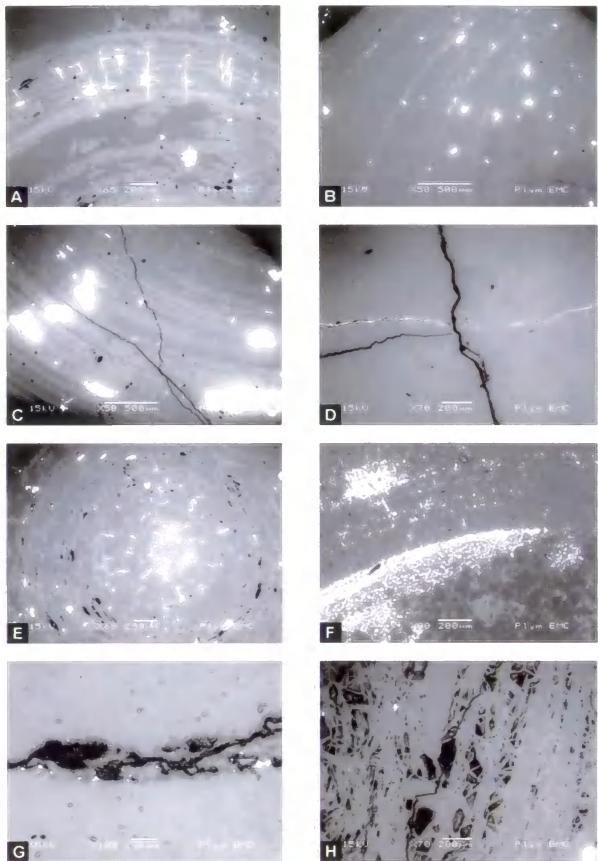


Plate 16. Backscattered SEM images showing the state of preservation of belemnite rostra from Festningen and Janusfjellet, Svalbard. All scale bars represent lengths stated on images. (A) Growth lines displaying strong alteration and some pyrite growth. (B) Growth lines displaying alteration. (C) Growth lines displaying strong alteration and the presence of pyrite. (D) Fractures running through apical canal, one infilled with pyrite. (E) Apical canal and surrounding growth lines displaying alteration and the presence of pyrite. (F) Edge of apical canal with presence of pyrite. (G) Fractures surrounded by alteration and with some pyrite infilling. (H) Deformed internal structure and areas of altered calcite around deformation.

# PLATE 17

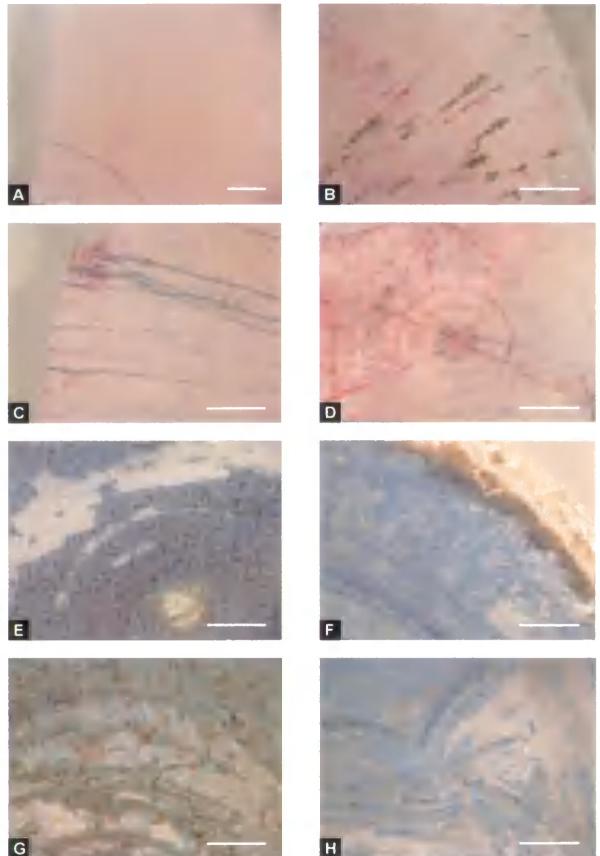


Plate 17. Carbonate stained images showing the state of preservation of belemnite rostra from Festningen and Janusfjellet, Svalbard. All scale bars represent 1 mm. (A) Very well preserved calcite. (B) Pyrite growth along fractures at rostrum margin. (C) Fractures eminating from rostrum margin displaying alteration. (D) Apical canal, fractures and growth lines displaying alteration. (E) Ferruginous calcite with some quartz replacement. (F) Ferruginous calcite. (G) Ferruginous calcite with some quartz replacement and pyrite growth. (H) Ferruginous calcite with some quartz replacement and deformation of internal structure.

## **10. DISCUSSION**

This chapter will discuss two major themes in relation to the data presented in this study. Firstly, it will evaluate the use of belemnites as palaeoenvironmental indictors. This is of particular importance for appreciating both the limitations and the potential of the data investigated here. Secondly, the contribution of this study to the understanding of Late Jurassic and Early Cretaceous global palaeoenvironment will be examined.

## 10.1. Evaluating Belemnites as Palaeoenvironmental Indicators

## 10.1.1. Preservation

The belemnite specimens analysed in this research are considered to be generally well preserved and, therefore, represent the original isotopic and geochemical composition of the belemnite calcite. A range of methods were used in this study in order to assess the preservation of belemnite rostra. These methods were: CL, BSEM, carbonate staining and trace element analysis. In addition to these techniques, a preliminary visual inspection of each belemnite rostrum was conducted and opaque or cloudy specimens were rejected.

Each of the aforementioned techniques is extremely useful for assessing preservation, although, there are a number of limitations associated with their use. CL microscopy, for example, is not effective where the concentration of Fe greatly exceeds that of Mn, which is the catalyst for the luminescence reaction. Ferroan calcite highly enriched in Fe, therefore, does not show luminescence despite being severely diagenetically altered. This problem was encountered with several of the belemnite specimens analysed from Svalbard in the present study.

The major limitation associated with Backscattered Scanning Electron Microscopy is the ambiguity present in the generated image. Areas of alteration are highlighted by a change in tone on the greyscale image (i.e., lighter and darker greys) and subtle alteration is therefore often difficult to distinguish. The BSEM technique however, provides a higher level of magnification than is available from any of the other screening methods, which allows more minor areas of alteration to be identified, although, such resolution is often unnecessary since those areas of minor alteration will often be confined to the segment of the rostrum being analysed and will not be present in the subsample from which subsequent isotope and geochemical analysis will be conducted.

Carbonate staining of belemnite rostra produces a very clear visual representation of preservation and is probably the most illustrative of the optical screening techniques applied here. The carbonate staining technique responds to the occurrence of Fe, unlike the CL technique, which utilises the presence of Mn. Well preserved calcite displays a pale pink colouration after staining, whilst Fe-rich areas appear as dark pink-mauvepurple-blue colours, depending on the abundance of Fe (blue represents highly ferroan calcite). This technique, therefore, shows not only the presence of diagenetic products but also the degree of alteration present. CL microscopy is also capable of this because a greater amount of Mn will create stronger luminescence. The problem with interpreting the CL reaction in this sense however, is that the strength of luminescence can be altered manually by modifying the gun current and gun voltage and a change in luminescence strength is not as visually striking as a change in colour (as demonstrated in the carbonate stained specimens).

Trace element analysis is perhaps the most useful of the tests for diagenesis as it provides a quantitative rather than qualitative assessment of alteration. High concentrations of Fe and Mn more or less guarantee that diagenetic calcite is present, although it should be noted that alteration can take place in the absence of Fe and Mn, for example under oxidising conditions (Marshall, 1992; Jones *et al.*, 1994).

In conclusion, it is important to assess belemnites for diagenetic alteration using a combined approach that incorporates both geochemical and optical techniques. Firstly, belemnite rostra must be examined using the naked eye. Only those specimens that display

219

a predominantly honey coloured and translucent appearance should be considered for further analysis. In addition, care should be taken where obvious signs of bioerosion are present on the rostrum margin. Optical screening techniques should then be performed on a representative range of samples, or where possible (with small datasets for example) such analyses should be carried out all specimens. Finally, trace element analysis (for Fe and Mn) should be conducted on every specimen. If this process is followed, all specimens affected by modest to severe post-depositional alteration, as well as many of those affected by very slight alteration should be recognised and removed. The remaining specimens can then be analysed for stable isotopes and trace element concentrations with the confidence that any trends recorded will not be the result of preservational factors.

### 10.1.2. Natural Variability in Belemnite Records

For each of the belemnite isotope or elemental records presented here a significant degree of scatter is present. This variability is not considered to be the result of diagenetic alteration as an extensive screening process was employed in order to eliminate altered specimens (as outlined above). The variability is therefore likely to be the result of real environmental change (e.g., temperature, salinity, ice volume), genus- or species-specific, ontogenetic or gender related differences in fractionation.

McArthur *et al.* (2004) observed a small (<0.4 ‰) offset in the  $\delta^{18}$ O ratios recorded from co-occurring belemnites of the genera *Hibolites* (typically a Tethyan Realm genus) and *Acroteuthis* (typically a Boreal Realm genus) from the Early Cretaceous at Speeton, Yorkshire. This led them to allude to the possibility of genus related differences in the fractionation of biogenic calcite. Such differences could be caused by a difference in habitat (e.g., one genus inhabited the shallow shelf, whilst the other inhabited deeper waters), differences in migratory habits (possibly related to mating and feeding differences) or a slight offset from equilibrium fractionation in one or both of the genera. The major problem with assessing whether or not different genera record slightly different stable isotope or geochemical signatures is that co-occurring belemnites consisting of a variety of genera are not common in the geological record. In the successions investigated here, only 10 belemnite horizons out of approximately 375 contained more than one genus (where taxonomic identification could be undertaken with confidence) and even then only one or two specimens from each genus were suitable for collection and analysis. Furthermore, if only one or two specimens from each genus is analysed, it is difficult to determine whether an observed difference in composition is attributable to generic factors or whether it is instead the result of changing environmental conditions between the deposition of each individual. Belemnites probably only lived for a few years (based on analogy with modern cephalopods) (Rexfort & Mutterlose, 2006), whilst deposition of a sedimentary horizon containing belemnites could require a considerably greater period of time to form. Doyle & Macdonald (1993) suggest that belemnite assemblages on a single bedding plane could require several thousand years to form. This, therefore, provides the opportunity to preserve a number of belemnites in a sedimentary horizon that would have lived at slightly different times and consequently would also have recorded slightly different geochemical compositions.

The analysis of co-occurring belemnites in this study (Table. 10.1) is inconclusive with regards to the influence of generic differences upon fractionation. In total, 23 belemnite horizons containing either co-occurring belemnites of the same genus (only 13 horizons out of ~375) or co-occurring belemnites of different genera (10 horizons) were identified. The offset observed in both the oxygen and carbon isotope values is highly variable, with offsets ranging between 0.04 and 2.39 ‰ for oxygen and between 0.02 and 1.96 ‰ for carbon (Fig. 10.1). The maximum offset in oxygen isotope values is observed between belemnites of the same genus (*Cylindroteuthis*), whilst the maximum offset in carbon isotope values is observed between different genera (*Cylindroteuthis* and *Pachyteuthis*). There appears to be no consistency in the amount of offset observed between co-occurring belemnites of the same genus and co-occurring belemnites of different genera. In addition, there is no consistency between the nature of the offset observed where different genera are considered, for instance, where *Cylindroteuthis* and *Pachyteuthis* co-occur, neither genus records consistently heavier nor lighter isotope

Horlzon No.	Age	Am. Zone	Genus	δ <sup>18</sup> Ο	δ <sup>18</sup> O Offset	δ <sup>13</sup> C	δ <sup>13</sup> C Offset	Mg/Ca	Na/Ca	Ll/Ca	Sr/Ca
KH1-4; 32.30	ValHaut.	D.bidH.boy.	Cylindro.	-0.64	1.64	1.52	0.13	4.45	5.21	22.93	1.82
	ValHaut.	D.bidH.boy.	Cylindro.	1.00		1.65		5.08	5.86	34.47	1.88
KH1-4b; -20.00	L. Val.	D.bidichot.	Arcto.	2.05	1.73	2.73	0.23	2.60	5.50	7.24	2.19
	L. Val.	D.bidichot.	Arcto.	0,32		2.96		2.95	4.85	5.16	2.00
KH16; 2.80	E. Ryaz.	H.kocS.an.	•	1.92	0.68	0.41	0.13	3.84	4.99	18.56	1.62
	E. Ryaz.	H.kocS.an.	•	1.24		0.28		4.86	5.18	17.93	1.70
KH16; 2.95	E. Ryaz.	H.kocS.an.	Cylindro.	2.27	2.39	0.31	0.03	2.71	6.54	19.90	1.94
	E. Ryaz.	H.kocS.an.	Cylindro.	-0.12		0.28		5.27	5.39	29.18	1.54
PC1	E. Callov.	C.elatmae	Pachy.	-0.31	0.04	1.66	0.18	6.79	5.20	72.62	1.25
	E. Callov.	C.elatmae	Cylindro.	-0.26		1.48		5.62	4.49	71.82	1.46
PC2.1	Volg	D.max	Lagonib.	-0.64	0.15	-0.53	0.03	6.76	4.76	45.17	1.54
	Volg	D.max	Lagonib.	-0,79		-0.50		5.17	5.69	183.27	1.42
PC2.9	Volg	D.max	Lagonib.	-0.92	0.08	-0.75	1.02	4.55	4.32	28.60	1.45
	Volg	D.max	Lagonib.	-0.84		0.27		4.42	4.70	30.19	1.40
PC2.11	Volg	D.max	Lagonib.	-0.56	0.08	0.36	0.70	5.16	6.86	6.84	1.79
	Volg	D.max	Pachy.	-0.48		-0.34		3.41	5.44	2.47	1.47
SK1; 4.50	E. Oxf.	Mar-Cor	Cylindro.	1.24	0.34	2.14	0.89	7.53	6.14	38.03	1.45
	E. Oxf.	Mar-Cor	Cylindro.	0.90		3.03		8.41	6.44	50.12	1.28
SK1; 5.90	E. Oxf.	Mar-Cor	Cylindro.	1.43	0.17	2.13	0.02	6.54	5.17	29.56	1.30
	E. Oxf.	Mar-Cor	Cylindro.	1.26		2.11		8.00	6.97	31.11	1.59
SK2; 1.05	M. Oxf.	Den-Ten	Cytindro.	0.75	0.34	2.64	0.51	5.44	5.67	41.66	1.39
	M. Oxf.	Den-Ten	Cylindro.	1.09		3.15		4.68	5.78	42.58	1.38
SK2; 1.30	M. Oxf.	Den-Ten	Cylindro.	-0.61	0.88	4.02	1.77	4.75	4.91	32.15	1.36
	M. Oxf.	Den-Ten	Cylindro.	0.27		2.25		7.39	5.99	62.95	1.22
SK3; 6.40	E-M. Oxf.	Cor-Den	Cytindro,	0.66	0.64	2.87	1.13	5.09	4.81	57.01	1.24
	E-M. Oxf.	Cor-Den	Pachy.	1.30		1.74		4.54	5.01	47.06	1.35
SK4; 0.20	E-L. Call.	Koe-Lam	Cylindro.	0.27	1.01	2.74	0.82	5.35	5.84	43.50	1.55
	E-L. Call.	Koe-Lam	Pachy.	-0.74	<u>.</u>	1.92		7.83	6,17	55.07	1.49
SK4; 1.80	E-L. Call.	Koe-Lam	Cylindro.	-0.31	0.27	2.71	0.16	5.73	4.58	41.24	1.31
	E-L. Call.	Koe-Lam	Cylindro.	-0.03		2.87		4.63		30.66	1.52
SK4; 6.80	E-L. Call.	Koe-Lam	Cylindro,	0.27	0.24	2.57	0.23	6.73		33.84	1.30
	E-L. Call.	Koe-Lam	Belemn.	0,03		2.79		6.45		59.40	1.21
SK5; 4.15	E. Kimm.	Bay-Cym	Cylindro.	-0.58	0.23	2.17	0,11			32,92	1.45
	E. Kimm.	Bay-Cym	Pachy.	-0.35		2.28		3.74		36.37	1.54
SK5; 5.70	E. Kimm.	Bay-Cym	Cylindro.	-1.70	1.79	3,57				31.54	1.72
	E. Kimm.	Bay-Cym	Pachy.	0.09		3.31		3.26		39.77	1.50
SK5; 7.40	E. Kimm.	Bay-Cym	Pachy.	0.62	2.01	0.80	1.96				1,49
	E. Kimm.	Bay-Cym	Cylindro.	-1.39		2.76		4.42		40.60	1.45
SK5; 8.10	E. Kimm.	Bay-Cym	Pachy.	-0.49	0.66	2.11	0.87			70.25	1.66
	E, Kimm.	Bay-Cym	Cytindro.	-1.15		2.98		3.78		<u>35.56</u>	
SK6; 1.50	E. Kimm.	Cym	Cylindro.	-0.97	0.15	2.49				40.14	1.42
	E. Kimm.	Cym	Cylindro.	-1.12		2.24		8.00		51.56	1.52
SK6; 7.50	E. Kimm.	Сут	Cylindro.	-0.25	1.21	1.24	0.59			55.73	
	E. Kimm.	Cym	Cylindro.	-1.46	i	1.83		4.50		42.17	1.69
SK7; 5.70	OxfKim.	Reg-Bay	Pachy.	0,41		1,30				45.47	
	OxfKim.	Reg-Bay	Cylindro.	0.24		1.49		5.78	5.41	47.84	1,53
-											

Table 10.1 Table showing genus-level differences in stable isotope and geochemical measurements from coeval belemnites. Coeval belemnites of different genera are highlighted. Key to notation: KH (Boyarka River); PC (Izhma River); SK (Staffin Bay).

Sample No.	Age	Am. Zone	Genus	ô <sup>18</sup> 0	δ <sup>18</sup> 0 Offset	δ¹³C	δ <sup>13</sup> C Offset	Mg/Ca	Na/Ca	LI/Ca	SrlCa
				_					_ <u></u>	_	
EA1; 0.05	L. Kimm.	Mutabilis	Cylindro.	-0.63	0,69	1.10	0.53	9.66	8.09	54.06	1.83
EA1; 0.05 B	L. Kimm.	Mutabilis	jv.	-1.32		1.63		7.46	6.55	32.52	1.98
KH17b; 1.55	L.Ryaz.	B.meses.	Cylindro.	-0.47	0.50	0.58	0.52	5,40	6.06	37,97	1.56
КН17ь; 1.55 В	L.Ryaz.	B.meses.	jv.	-0.97		0.06		5.02	4.81	32.90	1.54
PC2.11	Volg. (?)	D.max (?)	Lagonib.	-0.56	0.02	0.36	0.84	5.16	6.86	6.84	1.79
	Volg. (?)	D.max (?)	jv.	-0.58		-0,48		5.25	7.76	-1.92	1.84
PC2.13	Volg. (?)	D.max (?)	Lagonib.	-0.18	0.42	0.83	1.51	4.03	8.35	0.00	2.03
	Volg. (?)	D.max (?)	jv.	-0.60		-0.68		5.68	<u>5.17</u>	0.00	1,46
SK3; 3.00	E-M. Oxf.	Cor-Den	įv.	0.72	0.17	3.97	2.24	3.50	5.10	46.97	1.32
010, 0.00	E-M. Oxf.	Cor-Den	jv.	0.89		1.73		14.22	11.00	100.12	1.80
SK3; 5.20	E-M. Oxf.	Cor-Den	jv.	0.69	0.36	0.01	3.64		5.49	54.49	1.39
	E-M. Oxf.	Cor-Den	jv.	0.33		3.65		4.59	5.29	46.85	1.37
SK4; 1.80	E-L. Call.	Koe-Lam	Cylindro.	-0.03	0.09	2.87	0.85	4.63	5,64	30.66	1.52
- • ·	E-L. Call.	Koe-Lam	jv.	0.05		2.02		4,79	4.28	30.73	1.38
SK5; 6.25	E. Kimm.	Bay-Cym	Cylindro.	-1.48	1.29	2.32	0.26	4.74	4.70	46.30	1.51
	E. Kimm.	Bay-Cym	jv.	-0.19		2.05		4,35	4.48	49.77	1.41
SK5; 7.20	E. Kimm.	Bay-Cym	jv.	-1.11	0.12	2.94	0.11	3.61	4.41	41.65	1.47
	E. Kimm.	Bay-Cym	Cylindro.	-1.23		3.06		5.57	4.49	37.28	1.47
SK6; 0.00	E. Kimm.	Cym	jv.	0.09	1.62	1.29	0.40	7.92	6.26	72.04	1.52
	E. Kimm.	Cym	Cylindro.	-1.53		1.69		6.19	4.65	45.09	1,46
SK6; 5.90	E. Kimm.	Cym	jv.	-1.74	0.85	0.84	0,15	7.42	5.89	55.60	1,43
	E. Kimm.	Cym	Cylindro.	-0.89		0.69		6.85	5.89	47.13	1.67
SK6; 7.20	E. Kimm.	Cym	Cylindro.	-0.67	0.09	1.31	0.71	4,70	5.17	46.05	1.54
· · ·	E. Kimm.	Cym	_jv	-0.76		2.01		4.84	5.00	38.50	1.51
SK6; 7.80	E. Kimm.	Cym	jv.	-1.85	0.97	2.39	1.20	4.84	4.90	40.10	1.62
	E. Kimm.	Cym	jv.	-0.88		1.19		10.28	7.02	65.23	1.56
SK7; 1.20	OxfKim.	Reg-Bay	jv.	0.38	1.36	1.87	0,22	4.37	4.84	36.03	1.50
	OxfKim.	Reg-Bay	jv.	-0.98		1.65		4.97	5.28	54.39	
SK7; 14.80	OxfKim.	Reg-Bay	jv.	0.05	0.20	1.56	1.25			46.12	
	OxfKim.	Reg-Bay	_jv	0.25		0.31		6.05		28.28	
SK7; 15.40	OxfKim.	Reg-Bay	jv.	0.13	0.19	1.90	0.45			33.02	
	OxfKim.	Reg-Bay	Cylindro.	0.32		1.44		6.05		36.50	
SK7; 17.80	OxfKim.	Reg-Bay	jv.	-0.79	1.34	1.02				34.07	
	OxfKim.	Reg-Bay	jv.	0.55		1.34		4,17		23.41	1.39
SK7; 20.90	OxfKim.	Reg-Bay	jv.	-0.43						25.37	
	OxfKim.	Reg-Bay	_jv	-0.35		1.81		4.36		20.48	
SK8; 27.20	E. Oxf.	Cor	Cylindro.	0.60						32.14	
	E. Oxf.	Cor	_ <u>iv</u>	0.03		3.33		4.48			
SK8; 27.40	E. Oxf.	Cor	jv.	0.50							
	E. Oxf.	Cor	jv.	0.62		2.98		3.91			
SK8; 35.80	E. Oxf.	Cor	jv.	-0.17							
	E. Oxf.	Cor	jv.	-0.26		3,30		4.19			
SK10; 0.40	L. Oxf.	Ser-Reg	jv.	0.68							
	L. Oxf.	Ser-Reg	jv.	0.22		0.44		5.03			
SK10; 14.30	L. Oxf.	Ser-Reg	jv.	0.09	0.04						
	L. Oxf.	Ser-Reg	jv.	0.13		1,20	1	10.82	? 7.12	39.64	1.39

**Table 10.2** Table showing ontogenetic differences in stable isotope and geochemical measurements from coeval belemnites. Coeval belemnites of different ontogenetic stages are highlighted (i.e., adult and juvenile). Key to notation: KH (Boyarka River); PC (Izhma River); SK (Staffin Bay).

values. Ultimately, the data presented here cannot be used to either confirm or refute the existence of genus-specific differences in fractionation, because despite obvious offsets

between different genera occurring in the same horizon, similar levels of offset are also observed between co-occurring belemnites of the same genus.

Also analysed during this study was the effect of ontogeny on fractionation. This is because it is possible that juvenile specimens may record different geochemical values to adults. For example, belemnites may have lived in a different part of the water column whilst young (as seen in modern cephalopods) or there may have been a slight difference in fractionation at this age, possibly in response to rapid growth during the juvenile stage. Rexfort & Mutterlose (2006) recognise the rarity of juvenile rostra in the geological record, which they suggest may indicate extremely rapid early growth. The general absence of such material in the fossil record however may be explained solely by its relative fragility.

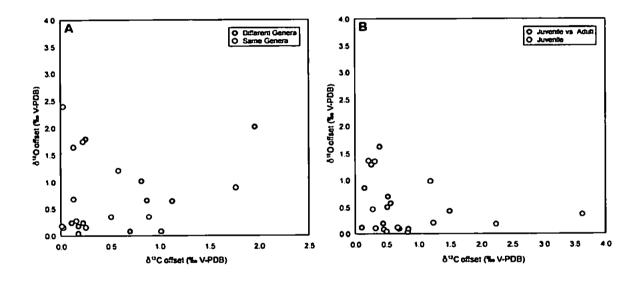


Figure 10.1 Cross plots of  $\delta^{18}$ O and  $\delta^{13}$ C offsets observed from coeval belemnites. (A) Genus-specific differences. (B) Ontogenetic differences.

Juvenile specimens were collected and analysed in this study (principally from Staffin Bay), with their stable isotope and geochemical composition recorded and subsequently compared with those of adult specimens (Table 10.2). The ontogenetic record displays great variability in the offset between isotope values, much like the generic record discussed above. High levels of offset were observed where juveniles were coeval with adult specimens as well as where different juvenile individuals were analysed from the same horizon (Fig. 10.1). Again, these data are inconclusive and cannot be used to either confirm or refute the potential influence of ontogeny on the stable isotope and elemental records.

It seems likely that as the belemnite rostra studied here display significant variability even where taxonomic and ontogenetic effects can be ruled out, something else must be influencing that variability (either in conjunction with, or in isolation from, these factors). Recent analysis of extant specimens of *Sepia officinalis* (the common cuttlefish, which is commonly believed to be one of the closest living relatives of the belemnite) records significant variation in isotopic composition across the cuttlebone that has been attributed to changes in seasonal temperatures and migration (Rexfort & Mutterlose, 2006). It seems reasonable to assume that belemnites could also exhibit similar changes in isotopic composition across the rostrum. A preliminary investigation of this was conducted by Podlaha *et al.* (1998) where the internal variability of individual rostra was shown to be as much as 2 ‰ for both  $\delta^{18}$ O and  $\delta^{13}$ C, suggesting that the variability observed in the belemnite record could be associated with this internal variability. It may, therefore, not be wise to drill small holes into the belemnite rostrum in order to collect a sample for isotopic analysis when a homogenised signal is preferred and instead to homogenise a larger segment of calcite (this approach was adopted here).

The scatter observed in the belemnite data presented here is generally consistent with that of published belemnite records from other successions (e.g., van de Schootbrugge *et al.*, 2000; Bailey *et al.*, 2003; McArthur *et al.*, 2004; Price & Mutterlose, 2004; Wierzbowski, 2004). Only the Boyarka River data displayed a greater amount of scatter than would have been expected. This is likely to be the result of the shallow nature of the Boyarka River succession, which presents a relatively dynamic depositional environment. By comparison, the Izhma River succession records significantly less variability over the same time period, probably as a consequence of the less variable nature of the deeper water succession.

225

Bulk rock records tend to produce much smoother curves than belemnites, which is the result of time averaging and the homogenisation of constituent particles. These processes dampen natural variability to produce less noisy curves than those generated from belemnites. For example, a 1 mm bulk sediment sample could represent anything in the range of 100-1000 years or more and could contain a number of different microscopic organisms, which may have inhabited a range of levels in the water column, whilst a 1 mm sample of belemnite calcite represents the environment of one individual and probably only for a period of months.

The scatter observed in belemnite data is, therefore, likely to be the result of real and natural variability. It is important to stress that in terms of palaeoenvironmental interpretation this natural variability is not a significant problem so long as long-term trends rather than small-scale fluctuations are interpreted.

#### 10.1.3. Oxygen Isotopes

Oxygen isotope values in biogenic calcite reflect temperature as well as global (ice volume) and local (precipitation, runoff and evaporation) variations in  $\delta^{18}O_{seawater}$ . Only organisms which precipitate their calcite in equilibrium with their surroundings and remain unaltered after deposition will retain a pristine isotopic signal that reflects these factors. Belemnite rostra are believed to satisfy these criteria. It is commonly accepted that belemnites exhibited equilibrium fractionation for the oxygen isotope, although for the carbon isotope a slight offset from equilibrium precipitation may have been the norm. This is based on observations from modern cephalopods, which are known to secrete their shells very close to equilibrium with seawater (Taylor & Ward, 1983; Morrison & Brand, 1986; Rexfort & Mutterlose, 2006). In addition, belemnite rostra are composed of low-magnesium calcite, which is relatively resistant to post-depositional alteration. Belemnites therefore, frequently preserve a pristine isotopic signal that can be used to provide information about palaeoenvironments and palaeoenvironmental change.

Belemnites are relatively abundant in the fossil record, and can therefore be used to compare palaeotemperature estimates on considerable spatial and temporal scales. As mentioned previously, calculations of absolute palaeotemperature are highly problematic for an extinct group of organisms. This abundance of belemnites therefore provides the opportunity to compare relative values of temperature from successions worldwide, providing that the same temperature equation is utilised. Fortunately, the palaeotemperature equation of Anderson & Arthur (1983) for molluscan calcite is almost always used in belemnite studies together with an isotopic composition of -1 ‰ SMOW for an ice-free world (e.g., Price & Sellwood, 1994, 1997; Ditchfield, 1997; Price et al., 2000; Price & Gröcke, 2002; Gröcke et al., 2003; McArthur et al., 2004; Price & Mutterlose, 2004). This equation and a  $\delta^{18}O_{seawater}$  value of -1 % SMOW were used throughout this study (despite evidence to suggest that a  $\delta^{18}O_{scawater}$  value of -1.5 ‰ SMOW may be more appropriate for very high latitude locations - as discussed later). The belemnite derived palaeotemperatures can therefore be compared with each other (if not in terms of absolute values, then at least in terms of relative change) as well as with data generated from published studies.

The importance of being able to compare belemnites on a global scale is highlighted by the work of several authors that shows that different organisms can give different palaeotemperature results from the same locations, e.g., belemnites and ammonites (Tan *et al.*, 1970; Anderson *et al.*, 1994; Wierzbowski & Joachimski, 2006), belemnites and brachiopods (Voigt *et al.*, 2003) and belemnites and planktonic foraminifera (Huber *et al.*, 1995; Price *et al.*, 1996; Huber & Hodell, 1996). Tan *et al.* (1970), Anderson *et al.* (1994) and Wierzbowski & Joachimski (2006) record a lower range of palaeotemperatures for belemnites than for ammonites of the same succession, which the authors interpret as belemnites inhabiting colder, deeper waters than the ammonites that inhabited the warmer surface waters. It should also be noted that Voigt *et al.* (2003) recorded colder palaeotemperatures (by ~6°C) from belemnites than from co-

227

occurring brachiopods, although they interpreted this as the result of belemnite migration from higher latitudes during a cool event. Ultimately, belemnites appear to record cooler palaeotemperatures than known shallow water taxa (Lowenstam & Epstein, 1954; Pirrie & Marshall, 1990; Ditchfield *et al.*, 1994). At high latitudes, like those investigated in this study, belemnites are considered to represent minimum estimates of sea-surface temperatures at high latitudes as vertical ocean temperature gradients in relatively shallow, high latitude regions will be minimal (Barrera *et al.*, 1987; Price *et al.*, 1996). The results presented here are consistent with this theory, for example the calculated palaeotemperature range from the Boyarka River succession (of 2 to 19°C) is compatible with the modern temperature estimate for bottom waters in the region (of -1 to 12°C) as calculated by Polyak *et al.* (2003) from benthic foraminifera.

As mentioned previously a  $\delta^{18}O_{scawater}$  value of -1 % SMOW is commonly used for palaeotemperature calculations for the Jurassic and Cretaceous periods. As discussed in the previous chapters however, a spatially invariant estimate of  $\delta^{18}O_{seawater}$  may not be appropriate. The uncertainty encountered with regards to the isotopic composition of Jurassic/Cretaceous seawater is one of the major problems associated with the calculation of absolute palaeotemperatures for this time. Roche et al. (2006) suggested that palaeolatitudinal differences in  $\delta^{18}O_{seawater}$  composition would have significant implications for palaeotemperature calculations, namely that, for the late Mesozoic, existing lowlatitude calculations have underestimated palaeotemperatures, whilst high latitude Such a situation has further calculations have overestimated palaeotemperatures. implications in terms of reconstructing latitudinal temperature gradients and ocean Despite these new data, the traditional view of  $\delta^{18}O_{seawater}$ circulation patterns. composition (using a value of -1 ‰ SMOW for the Jurassic and Cretaceous) has been adopted here. This provides the potential for a more direct comparison of the data generated from this study with that from previously published studies, although, the affect of using the Roche *et al.* (2006)  $\delta^{18}O_{seawater}$  compositions is discussed later (see section 10.2.2).

## 10.1.4. Elemental/Ca Ratios

In many modern calcifying groups, the Mg/Ca, Sr/Ca, Na/Ca and Li/Ca ratios reflect calcification temperature, although each to a varying degree. As mentioned previously,  $\delta^{18}$ O reflects temperature, salinity and ice-volume. Comparison of the two proxies should, therefore, provide an indication of the influence that such factors have had on the  $\delta^{18}$ O ratio. Where strong correlations between  $\delta^{18}$ O and *El/Ca* exist, temperature should be the dominant controlling factor. Conversely, where correlations are not observed, changes in salinity or ice-volume, interspecies or ontogenetic offset, metabolic activity or diagenesis may have had an influence.

Statistically significant correlations between  $\delta^{18}$ O and *El/Ca* from this study were observed in the following cases: between  $\delta^{18}$ O and Mg/Ca (Izhma River),  $\delta^{18}$ O and Sr/Ca (Staffin Bay),  $\delta^{18}$ O and Na/Ca (Svalbard) and  $\delta^{18}$ O and Li/Ca (Boyarka River; Svalbard). An absence of correlation between  $\delta^{18}$ O and *El/Ca* is therefore the norm for this study. This can be interpreted in one of two ways, either as the result of environmental factors (salinity and ice-volume) influencing the  $\delta^{18}$ O record and therefore degrading the correlation, or as the result of physiological factors (metabolic activity and growth rate) influencing the *El/Ca* ratios. A significant impact from interspecies or ontogenetic offset or from diagenesis is unlikely as discussed previously (see sections 10.1.1 and 10.1.2), although these factors may account for some degree of scatter within the data.

If the absence of correlation is interpreted as being solely the result of environmental factors, significant salinity and ice-volume fluctuations are required throughout the northern high latitudes during the Late Jurassic and Early Cretaceous. Alternatively, if the absence of correlation is attributed primarily to physiological factors then the use of El/Ca ratios as belemnite palaeotemperature proxies becomes highly questionable. Unfortunately, it is impossible to confirm which of these two mechanisms is controlling the general lack of correlation. It may be that environmental factors dominate certain relationships, whilst physiological factors dominate others. Previously published studies on El/Ca ratios have tended to suggest that for Li/Ca, Na/Ca and, in some circumstances, Sr/Ca physiological factors have controlled fractionation (e.g., Delanev et al., 1985; Klein et al., 1996; McArthur et al., 2000; Bailey et al., 2003), whilst for Mg/Ca fractionation is controlled by temperature (e.g., McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004a, b). A physiological effect on Li/Ca, Na/Ca and Sr/Ca would certainly be consistent with the data presented here, since in most cases no correlation is observed with  $\delta^{18}$ O. This is equally true for the Mg/Ca ratios, however, and if, as is supposed by most authors, Mg/Ca is controlled by temperature rather than physiological effects, the lack of correlation observed here would be the result of environmental influences (temperature and variation in  $\delta^{18}O_{scawater}$ ) on the  $\delta^{18}O$  record. In this case, the absence of correlation between the other El/Ca ratios would also be consistent with environmental influences on the  $\delta^{18}$ O records rather than physiological influences on the El/Ca records. Ultimately, the El/Ca data generated from this study are inconclusive with regards to the nature of the factors influencing the *El/Ca* and  $\delta^{18}$ O correlations. This has particular implications for estimates of the effects of salinity and ice volume on  $\delta^{18}$ O records, which is the most common use an *El/Ca* ratio in belemnites. Such estimates must be made with care and trends rather than absolute values must be interpreted.

As discussed in the previous chapters the use of Mg/Ca palaeotemperature calculations for belemnites may not be appropriate. The Klein *et al.* (1996) equation was calibrated using the extant marine mussel *Mytilus trossulus* and was therefore considered here to be the most suitable equation for use on belemnites, since other palaeotemperature equations (e.g., those of Dwyer *et al.* (1995), Elderfield & Ganssen (2000) and Lear *et al.* (2002)) were calibrated using foraminifera and ostracods. It is acknowledged however, that McArthur *et al.* (2000) and Bailey *et al.* (2003) both used Mg/Ca palaeotemperature

equations derived from the above foraminifera and ostracod calibrations, even though, the justification for doing this is unclear. In fact, in neither study do the authors satisfactorily explain why such systematically distant taxa to the coleoid order Belemnitida are utilised, when a much closer related, taxon calibration (derived from the bivalve *Mytilus*) is available.

If the Lear et al. (2002) palaeotemperature equation (based on foraminifera) is applied to the Mg/Ca data presented in this study, for example for the Izhma River succession, then a calculated palaeotemperature range of 4.9 to 19.2°C and an average value of 12.2°C is generated. This can be compared to the Anderson & Arthur (1983)  $\delta^{18}$ O derived palaeotemperature range of 7.3 to 17.3°C (average 13.0°C) and the Klein et al. (1996) range of -4.5 to 6.7°C (average -0.9°C) for the same succession. Based on this data, it is clear that the Lear et al. (2002) calibration presents Mg/Ca derived palaeotemperatures closest to those of the  $\delta^{18}$ O calibration. It seems likely, that this is the reason that McArthur et al. (2000) and Bailey et al. (2003) selected this calibration rather than that of Klein et al. (1996) for their research since no other justification is given. Whether or not this is sufficient reason to select a calibration, especially given the taxonomic arguments aginst such a selction, is clearly debateably. In this study, the decision was taken that the use of foraminiferal or ostracod calibrations was not appropriate given the lack of taxonomic or ecological comparibility with belemnites. In order to consider these calibrations as appropriate, a much more convincing argument than seemingly suitable palaeotemperatures must be presented.

The Mg/Ca calculated palaeotemperatures generated here using the Klein *et al.* (1996) equation, commonly record sub-freezing values that could not have been recorded by belemnites (as they almost certainly would not have survived in such conditions). In addition, the  $\delta^{18}$ O composition of belemnite calcite is not expected to yield absolute values of palaeotemperature for two key reasons, firstly the  $\delta^{18}$ O<sub>seawater</sub> composition (on which the  $\delta^{18}$ O<sub>carbonate</sub> composition is dependent) can only be estimated and secondly, the  $\delta^{18}$ O

231

fractionation capacity of belemnites cannot be measured since the group is extinct. Despite belemnite Mg/Ca ratios being possibly independent of seawater composition, there is still an element of uncertainty with regards to the fractionation of Mg/Ca. Mg/Ca calculated palaeotemperatures must, therefore, not be considered as absolute values but as being descriptive of a trend, particularly where relatively low values are concerned. Immenhauser *et al.* (2005) questioned the validity of applying the Klein *et al.* (1996) temperature equation to fossilised skeletal calcites. They suggested that it may only be appropriate for temperatures in the range of 5-23°C where the temperature-Mg relationship is linear. In addition, they go on to suggest that the utility of Mg/Ca ratios may be limited by the ion regulating capability of the animals being considered.

If, as is commonly accepted, Mg/Ca ratios in biogenic calcite did reflect calcification temperature alone, (e.g., whilst  $\delta^{18}$ O reflects temperature plus a salinity and/or ice volume effect), then where both proxies are measured it should be possible to calculate relative changes in  $\delta^{18}O_{seawater}$ . This has very recently been attempted using Early Cretaceous (Berriasian-Hauterivian) belemnites from France and Spain (McArthur *et al.*, in press). Such a calculation however, requires equilibrium fractionation of Mg/Ca, which for belemnites at least is highly questionable (see above). Nevertheless, if we assume here that equilibrium fractionation has occurred, it is possible to consider the effects of fluctuations in  $\delta^{18}O_{seawater}$  on the  $\delta^{18}O_{carb}$  composition. Figure 10.2 shows calculated  $\delta^{18}O_{seawater}$  values for the Callovian-Hauterivian Izhma River succession. The average  $\delta^{18}O_{seawater}$  value of -4.9 ‰ is indicated so that relative fluctuations about that mean can be considered, rather than considering absolute values of  $\delta^{18}O_{seawater}$ , which are probably unrealistic given the sub-freezing palaeotemperatures generated from the Mg/Ca ratios.

At the base of the Izhma River succession where palaeotemperature estimates are relatively high, the  $\delta^{18}O_{seawater}$  values are relatively positive. Conversely, where a shift towards cooler temperatures is observed (in the Mg/Ca record) relative  $\delta^{18}O_{seawater}$  values switch to being relatively negative. The presence of more negative  $\delta^{18}O_{seawater}$  values

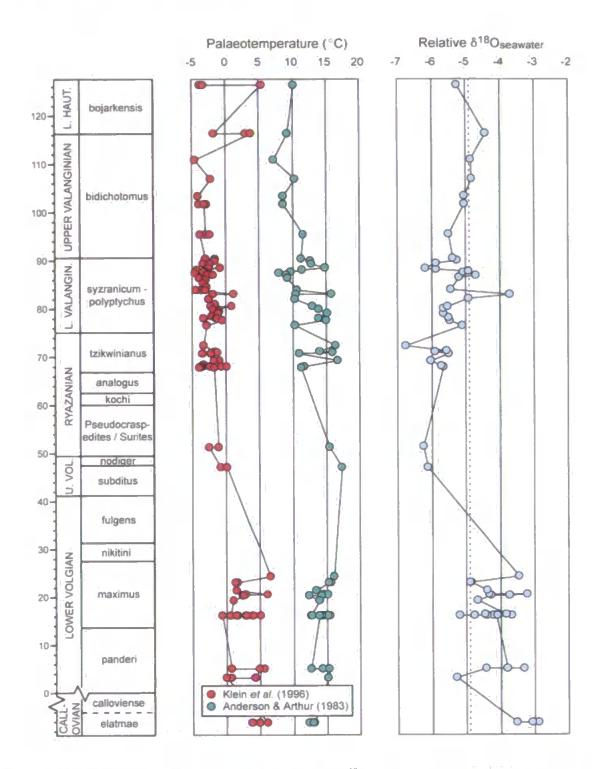


Figure 10.2 Calculated palaeotemperatures and relative  $\delta^{18}O_{seawater}$  values for the Callovian-Hauterivian Izhma River succession, Russia. Boreal (Russian) ammonite zones are illustrated. Scale is in metres.

would be consistent with either a period of freshening or of ice melt, both of which would introduce isotopically depleted water into the system. The problem with this is that an average 2 ‰ fall in  $\delta^{18}O_{\text{seawater}}$  composition would require a 4 ‰ freshening (according to the modified Railsback *et al.* (1989) and Woo *et al.* (1992) temperature-salinity model), which may be difficult to account for from freshwater input alone. The waning of ice-

sheets however, if of significant magnitude, may help to account for the  $\delta^{18}O_{seawater}$  change. The issue here is that the shift towards more negative  $\delta^{18}O_{seawater}$  values coincides with very cold palaeotemperatures if the Mg/Ca estimates are accepted. Even if the absolute palaeotemperature values are ignored and just the trend considered, the shift still coincides with a drop in temperature. Cold temperature values could be consistent with ice-melt if the melt was occurring locally but if it was occurring on a global scale such cold values are impossible. In addition, given the correlation between falling temperature and falling  $\delta^{18}O_{seawater}$  values it seems inconceivable that the relative shift in  $\delta^{18}O_{seawater}$  could be attributed to ice melt. In light of the problems associated with this model, it seems most unlikely that Mg/Ca ratios are faithfully recording temperature trends in belemnites.

Despite the quantity of elemental data presented in this study, which was generated from a number of locations as well as from a range of time periods, the usefulness of El/Ca data as a palaeoclimate proxy remains in doubt. In addition, no definite conclusions can be drawn with regards to the relative effects of environmental and physiological factors on the elemental ratios, nor can the observed Mg/Ca trends be convincingly related to palaeotemperature. Whilst this data does not rule out the use of El/Ca ratios as palaeotemperature proxies in certain circumstances, it does suggest that any interpretation of such data conducted in the future must be done with great care, at least until further research is conducted.

### 10.1.5. Carbon Isotopes

As discussed above, modern cephalopods are known to secrete their shells very close to isotopic equilibrium with seawater, although for the carbon isotope, a slight offset from equilibrium fractionation is not uncommon, with shells being slightly less enriched in  $\delta^{13}$ C than might be predicted (Wefer and Berger, 1991; Klein *et al.*, 1996; Bettencourt & Guerra, 1999; Geist *et al.*, 2005). Assuming that this offset is also present in belemnites and that the offset is consistent, it should not present a problem for the interpretation of

carbon isotope values or trends, since most carbon isotope values are presented relative to a belemnite standard (V-PDB).

Where belemnite derived  $\delta^{13}$ C records have been compared with temporally similar  $\delta^{13}$ C records generated from other marine carbonate material (e.g., bulk rock, foraminifera, other macrofossils etc.) similar trends have been observed (e.g., van de Schootbrugge, 2000; Gröcke *et al.*, 2005). This confirms that belemnites faithfully record a  $\delta^{13}$ C signal. Unlike oxygen isotope records, which are strongly influenced by temperature and therefore often by local conditions, carbon isotope curves record more global signals. The global  $\delta^{13}$ C seawater composition primarily reflects the distribution of global carbon between oxidised (carbonate, bicarbonate, carbon dioxide) and reduced (organic carbon) reservoirs (Jenkyns *et al.*, 2002). Distinctive excursions within the  $\delta^{13}$ C record can therefore be correlated to provide a high resolution carbon isotope stratigraphy.

This approach of matching curves with a distinctive shape has been carried out on pelagic carbonates (e.g., Lini *et al.*, 1992; Padden *et al.*, 2002) other marine carbonates (e.g., belemnites - Podlaha *et al.*, 1998) and between marine carbonates and terrestrial organic matter (e.g., Gröcke *et al.*, 2005). The major problems with such correlations however, are that biostratigraphic control on the correlated successions is often weak and that small, isolated successions with different stratigraphic zonal schemes and/or sedimentological features (e.g., condensed sections and hiatuses) are common subjects for correlation. Such splicing together of small, isolated records only introduces more noise and inaccuracy into an already noisy system. The initiation of the Valanginian positive carbon isotope excursion, for example, was described by Channell *et al.* (1993) as occurring in the *Pachydicranus* Zone (now the uppermost Valanginian *Furcillata* Zone or the lowermost Hauterivian *Radiatas* Zone (McArthur *et al.*, in press)). By comparison, however, the initiation of the same excursion was assigned by Hennig *et al.* (1999) to the *Campylotoxus* Zone, the uppermost ammonite zone of the Lower Valanginian. In addition, Gröcke *et al.* (2005) record the initiation of the Valanginian positive carbon isotope

excursion from plant material in the Crimean Submartini Zone, which they correlate with the Verrucosum Zone of Europe. McArthur et al. (in press) however, note that Crimean excursion occurs over just 1.2 m of sediment and immediately above a sandstone unit where ammonites are unusually uncommon. They, therefore, suggest that condensation or a hiatus is present in the Gröcke et al. (2005) succession and that the strata recording the real onset of the excursion may not even be present making further carbon isotope correlation difficult.

The problem of correlation is particularly prevalent where marine carbonate and terrestrial organic carbon records are correlated. The comparison of marine with terrestrial carbon isotope curves is essential to confirm that isotopic patterns are of a global origin rather than the result of local or diagenetic factors. To date, such correlations have only been carried out from geographically different successions. This study is the first to investigate marine carbonate and terrestrial organic  $\delta^{13}$ C records from the same succession and with samples collected simultaneously. This new approach eliminates any uncertainty associated with the correlation and allows conclusions about the relationship between the ocean and atmosphere systems to be drawn with confidence. The coeval marine and terrestrial  $\delta^{13}C$  records investigated here were synchronous throughout the Ryazanian-Hauterivian Boyarka River succession and much of the Callovian-Kimmeridgian Staffin Bay succession. This demonstrates for the first time without any correlation related uncertainty that the ocean-atmosphere system was strongly linked at these times. The Staffin Bay record also provides information about a potential decoupling of the oceanatmosphere system during the Callovian period. Presumably, either the marine or the terrestrial realm was being influenced by local factors at this time, although the nature of this influence needs further investigation.

# 10.2. Late Jurassic - Early Cretaceous Global Palaeoenvironment

### 10.2.1 Boreal Realm Data

The stable isotope and geochemical data presented in this study comprise the first high resolution investigation of the Late Jurassic-Early Cretaceous Boreal Realm (as defined by belemnites). A Callovian-Hauterivian compilation of the  $\delta^{13}$ C and  $\delta^{18}$ O data was generated in order to assess whether any long-term trends could be identified across the northern high latitude region (Fig. 10.3). In order to produce this compilation, the numerical age of each sample was estimated using the Gradstein *et al.* (2004) timescale.

The oxygen isotope compilation displays a considerable degree of natural variability, making the identification of long-term trends difficult but by no means impossible. The most negative  $\delta^{18}$ O values (-2.8 ‰) occur in the Lower Kimmeridgian, whilst the most positive  $\delta^{18}$ O values (2.8 ‰) occur in the Lower-Upper Ryazanian. In terms of global palaeotemperature, this equates to the highest palaeotemperatures (24°C) occurring in the Lower Kimmeridgian and the lowest palaeotemperatures in the Lower-Upper Ryazanian (2°C). Care must be taken with this approach however, because the warmest palaeotemperatures are recorded from the Helmsdale succession (at a palaeolatitude of ~45°N), whilst the coldest values are recorded from the Boyarka River succession (at a palaeolatitude of ~70°N), which may indicate that local environmental conditions have had some impact on the  $\delta^{18}$ O record.

Despite this limitation, the  $\delta^{18}$ O compilation provides significant evidence of predominantly warm conditions punctuated by cold episodes in the Late Jurassic and Early Cretaceous Arctic region. Oxygen isotope values exceeding 1 ‰ (which equates to ~ 8°C) are common in the Lower-Middle Oxfordian and in the Ryazanian-Lower Hauterivian intervals. For the Oxfordian, these values are almost certainly not an artefact of palaeolatitudinal differences because these positive values come from one of the lowest palaeolatitude sites (Staffin Bay). For the Ryazanian-Hauterivian interval, the observed

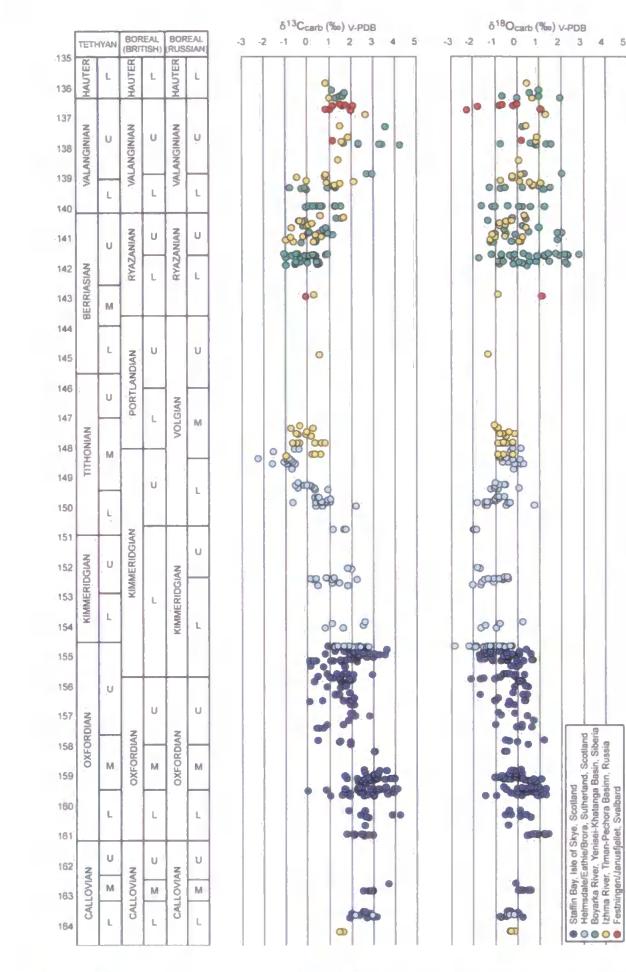
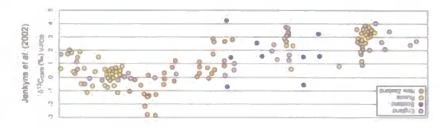


Figure 10.3 Callovian-Hauterivian compilation of  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  data derived from this study. Compilation was produced by estimating the numerical age of each sample. Scale is in Ma (after Gradstien *et al.* (2004)) and Tethyan, Boreal (British) and Boreal (Russian) timescales are illustrated.

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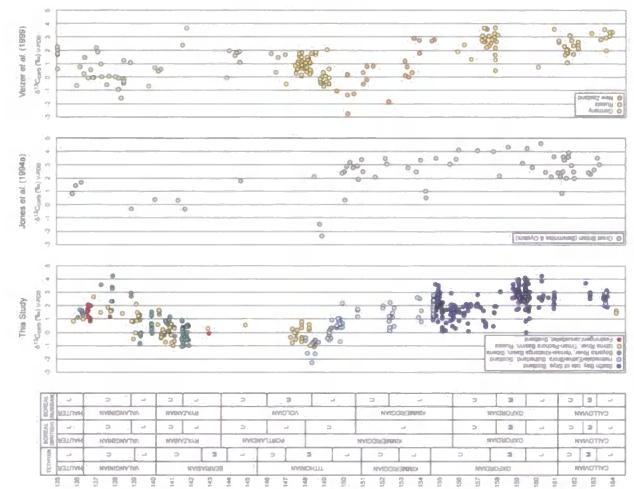
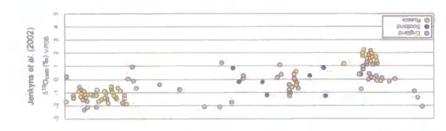


Figure 10.4a Callovian-Hauterivian compilation of  $\delta^{13}C_{carb}$  data derived from this study and compared with published data. Isotope curves are correlated by age based on conversion to the Gradstein *et al.* (2004) timescale. Stable isotope data is derived from well-preserved belemnites unless otherwise stated. Scale is in Ma (after Gradstein *et al.* (2004)) and Tethyan, Boreal (British) and Boreal (Russian) timescales are illustrated:

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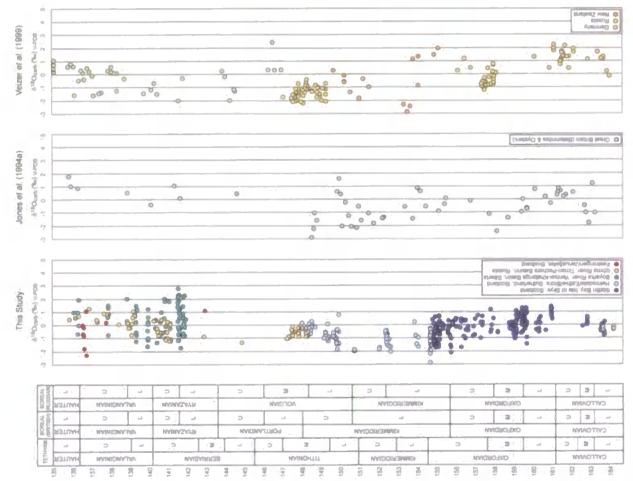


Figure 10.4b Callovian-Hauterivian compilation of  $\delta^{18}O_{carb}$  data derived from this study and compared with published data. Isotope curves are correlated by age based on conversion to the Gradstein *et al.* (2004) timescale. Stable isotope data is derived from well-preserved belemnites unless otherwise stated. Scale is in Ma (after Gradstien *et al.* (2004)) and Tethyan, Boreal (British) and Boreal (Russian) timescales are illustrated.

 $\delta^{18}$ O ratios are significantly higher than those observed from any of the other sites indicting that these values reflect genuinely lower palaeotemperatures (as low as 2°C). Despite the scatter present in the Boyarka River data for this interval a faint trend towards less negative  $\delta^{18}$ O values from the Ryazanian and into the Hauterivian can be observed. This is consistent with the more distinct cooling trend observed in the Izhma River data for the same time interval. Interestingly, the occurrence of potential dropstones in Svalbard coincides with the latter part of this cooling trend (in the Upper Valanginian) and the coldest palaeotemperatures recorded from the Izhma River (~ 7°C) are also coincident with the occurrence of glendonites on Svalbard, lending strong support to the concept of a high latitude cooling episode at this time.

The presence of cold conditions as observed from the record presented here is consistent with published works that have also identified cold episodes during the Callovian-Oxfordian, which is coincident with a eustatic sea level fall (e.g., Dromart *et al.*, 2003a, b; Lecuyer *et al.*, 2003) and the Valanginian (e.g., Price, 1999; Pucéat *et al.*, 2003; Kessels *et al.*, 2006). A cold episode during the Tithonian/Volgian (e.g., Price, 1999; Schudack, 1999) has also been postulated, although evidence for this event is not observed here. This, however, may be due to the sparsity of data from this time interval.

Distinctive long-term trends can also be identified in the Callovian-Hauterivian carbon isotope compilation (Fig. 10.3). The Callovian-Volgian interval witnesses a gradual shift from relatively positive  $\delta^{13}$ C values (exceeding 4 ‰ in the Oxfordian) to more negative values (-2.2 ‰). This is followed by a rapid excursion to more positive values (4.2 ‰) during the Valanginian and a return towards pre-excursion values in the Hauterivian. This pattern has also been identified in other Jurassic-Cretaceous global compilations (e.g., Jones *et al.*, 1994a; Podlaha *et al.*, 1998; Veizer *et al.*, 1999; Jenkyns *et al.*, 2002) (Fig. 10.4). In addition, elements of the overall pattern (e.g., the Oxfordian-Volgian/Tithonian fall in  $\delta^{13}$ C values and the Valanginian positive  $\delta^{13}$ C excursion) have also been observed in smaller scale studies and studies of isolated successions, both from

marine carbonate and terrestrial organic carbon records (e.g., Lini *et al.*, 1992; Weissert & Mohr, 1996; Weissert *et al.*, 1998; Bartolini *et al.*, 1999; Price *et al.*, 2000; van de Schootbrugge *et al.*, 2000; Cecca *et al.*, 2001; Padden *et al.*, 2002; Price & Gröcke, 2002; Gröcke *et al.*, 2003; Price & Mutterlose, 2004; Weissert & Erba, 2004; Gröcke *et al.*, 2005).

A comparison of the  $\delta^{13}$ C and  $\delta^{18}$ O data shows no consistent relationship between the two variables. The strongest relationship observed is that of the Valanginian Izhma River data, which reveal a positive correlation between  $\delta^{13}$ C and  $\delta^{18}$ O that can be explained by the 'Monterey Hypothesis,' where the significant burial of organic carbon rich sediments results in a fall in the concentration of atmospheric CO<sub>2</sub> and a subsequent drop in temperature.

The compilation of  $\delta^{18}$ O Boreal Realm data presented here confirms that cold episodes occurred in the Arctic region during the Late Jurassic and Early Cretaceous, most strikingly during the mid-Ryazanian *Kochi-Analogus* zones and the Late Valanginian *Bidochotomus* Zone but also during the Lower Oxfordian *Cordatum* Zone. The  $\delta^{13}$ C data confirm that the Arctic region faithfully records the same  $\delta^{13}$ C signature as observed in the Tethyan regions. These findings are significant in terms of understanding the Late Jurassic-Early Cretaceous Arctic region as well as global palaeoenvironments.

#### 10.2.2. Global Palaeoenvironmental Studies

Published palaeoenvironmental studies on the Late Jurassic and Early Cretaceous have tended to focus on the mid- to low latitudes or on the southern high latitudes, whilst studies focusing on the northern high latitudes are relatively fewer. The new data presented here address this knowledge gap and provide significant information with which to assess global palaeoclimate.

The data presented here are compared with those of similar published studies (i.e., those that concentrate on the stable isotope analysis of macroscopic (or large microscopic)

Age	Region (Estimated Palaeolatitude)	Organism	<sup>18</sup> O values	Temperature (*C)	Reference		
Valanginian - Barremian	Speeton, Yorkshire, England (40°N)	Belemnites	-2.12 to +0.79	9-21	McArthur et al. (2004)		
Valanginian - Hauterivian	Vocontian Basin, SE France (40°N)	Belemnites	-1.38 to +0.59	9-18 (12.7)	van de Schoolbrugge et al. (2000		
Berriasian - (Hauterivian)	Western Tethyan Platform (35*N)	Fish Teeth/Bone	+19.2 to +22.0 (PO4)	13-25 (19)	Pucéat et el. 2003		
Ryazanian - Hauterivian	Boyarka River, Siberia (70°N)	Belemnites	-1.71 to +2.83	2-19 (10.6)	This study		
Ryazanian - Upper Valanginian	Festningen/Janusfjellet, Svalbard (62*N)	Belemnites	-2.26 to +1.14	8-21 (13.0)	This study		
Upper Ryazanian - Middle Hauterivian	Speeton, Yorkshire, England (40*N)	Betemnites	-0.86 to +1.11	8-15 (11.4)	Price et al. (2000)		
Volgian - Hauterivian	Izhma River, Russia (60*N)	Belemnites	-1,32 to +1,27	7-17 (13.0)	This study		
Volgian - Valanginian	Yatria River, Siberia (62°N)	Betemnites	-2.26 to +1.34	7-21	Price & Mutterlose (2004)		
Tithonian	Volga Basin, Russia (45*N)	Belemnites	-2.11 to -0.58	14-21 (17.3)	Gröcke et el. (2003)		
Tithonian - Hauterivian	Germany (38°N)	Belemnites	-3.10 to +2.30	4-25	Veizer et al. (1999)		
Tithonian?	Santa Cruz, Argentina (40°S)	Betemnites	-2.00 to -1.60	19-20 (19.8)	Bowen (1961)		
Kimmerigian - (Berriasian)	James Ross Island, Antarctica (64*S)	Belemnites	-1.02 to -0.26	13-16 (14.6)	Ditchfield et el. (1994)		
Kimmeridgian - Tithonlan	Mallorca, Spain (30*N)	Belemnites	-1.00 to +0.04	12-16 (13.9)	Price & Seliwood (1994)		
Kimmeridgian	Cutch, India (33*N)	Belemnites	-0.59 to -0.40	13-15 (13.8)	Bowen (1966)		
Kimmeridgian	Subpotar Urals (55*N)	Belemnites		(20)	Zakharov et el. (2005)		
Kimmeridgian	Heimsdale, Sutherland, Scotland (45*N)	Belemnites	-2.84 to +0.78	9-24 (15.8)	This study		
Middle Kimmeridgian - Tithonian	Milne Land, East Greenland (50*N)	Belemnites	-1.91 to -1,13	17-20 (18)	Bowen (1966)		
Early Kimmeridgian	Hündsruck, Germany (38*N)	Belemnites	-1.18 to -0.91	16-17 (16.1)	Bowen (1961)		
Upper Oxfordian - Middle Tithonian	Kawhia Harbour, New Zealand (80*S)	Belemnites	-3.10 to +0.36	11-25 (17.8)	Gröcke et al. (2003)		
Oxfordian - Volgian	Russian Platform (55*N)	Belemnites		7-18	Riboulleau et al. (1998)		
Oxfordian - Tithonian	New Zealand (80°S)	Belemnites	-4.40 to +1.90	5-32	Veizer at al. (1999)		
Oxfordian - Tithonian	Falidand Plateau, South Atlantic (55°S)	Belemnites	-1,88 to -0.95	16-20 (17.6)	Price & Sellwood (1997)		
Oxfordian - Early Kimmeridgian	Scotland; Poland; Germany (40"N)	Belemnites	-1.88 to +0.81	9-20	Wierzbowski (2004)		
Oxfordian	Polish Jura Chain, Central Poland (40*N)	Brachlopods	-2.5 to +0.4	11-23	Wierzbowski (2002)		
Oxfordian	Polish Jura Chain, Central Poland (40°N)	Belemnites	-1.5 to +0.5	10-16	Wierzbowski (2002)		
Callovian - Barremian	Falkland Plateau, South Atlantic (55°S)	Belemnites	-2.22 to +0.08	12-21 (17.4)	Price & Gröcke (2002)		
Callovian - Volgian	Russia (55°N)	Betemnites	-2.30 to +2.20	4-22	Veizer et al. (1999)		
Callovian - Kimmeridgian	Staffin Bay, Isle of Skye, Scotland (45*N)	Belemrites	-2.07 to +1.43	7-21 (12.4)	This study		
Callovian - Oxfordian	Kachchh Basin, W India (33°N)	Belemnites	-2.17 to +0.28	11-21	Fürsich et el. (2005)		
Bathonian - early Kimmeridgian	E France; Switzerland (35*N)	Shark/Fish Teeth	+18.7 to +21.4 (PO4)	15-28 (21.3)	Dromart et el. (2003b)		
Bathonian - Callovian	Kachchh Basin, W India (33"N)	Brachlopods	-2.86 to -1.66	19-24	Fürsich et el. (2005)		
Bajocian - Valanginian	Kong Karls Land, Svalbard (62*N)	Belemnites	-0.97 to +1.64	5-18 (9.5)	Ditchfield (1997)		
Bajocian - Kimmeridgian	Poland; England (40°N)	Bivatves (aragonitic)		13-27	Matchus & Steuber (2002)		
Aalenian - Portlandian	Anglo-Paris Basin, France (35°N)	Shark/Fish Teeth	+18.5 to +22.3 (PO4)	21-29	Lecuyer et al. (2003)		

Table 10.3 Compilation of published Late Jurassic-Early Cretaceous  $\delta^{18}$ O and palaeotemperature data. All palaeotemperatures were calculated using the equation of Anderson & Arthur (1983) (except for PO<sub>4</sub> values - see respective references) and a  $\delta^{18}O_{seawater}$  value of -1%. Data is arranged according to age and data from this study is highlighted. (Please note where possible palaeotemperatures were recalculated using raw data.)

fossils). By considering such similar studies, direct comparisons can be drawn with regards to relative palaeoclimate. Table 10.3 shows the palaeotemperatures calculated from published literature as well as from the sites investigated here. Data from belemnites, bivalves, brachiopods and fish teeth/bone are included from a range of locations worldwide (including England, France, Germany, Switzerland, Poland, Spain, India, Russia, Greenland, Argentina, New Zealand and Antarctica). The majority of the published data are concentrated in the northern mid-latitudes between ~30 and 40°N. Calculated palaeotemperatures for this region are typically in the range of 15-25°C for the Late Jurassic and Early Cretaceous, although values as low as 8°C in the Lower Hauterivian (Price *et al.*, 2000) and as high as 29°C at the Bathonian-Callovian boundary (Lecuyer *et al.*, 2003) have also been recorded.

Palaeotemperatures calculated from southern high latitude locations (e.g., the Falkland Plateau, New Zealand and Antarctica) reveal a range from 11 to 25°C. The upper end of the range is certainly consistent with high latitude warmth, although, the lowest values may be consistent with the presence of occasional cold episodes. Even lower values are observed from the northern high latitudes, where palaeotemperatures between 2 and 24°C are recorded. Again, the higher palaeotemperature values are compatible with high latitude warmth, whilst the lowest values suggest that cold episodes may occur at times.

The lowest palaeotemperatures calculated from each of the sites investigated in this study varied from 2-9°C. Such values are consistent with the few northern high latitude studies that have been published, for example, Ditchfield (1997) recorded values as low as 5°C from the Tithonian-Valanginian of Svalbard, Price & Mutterlose (2004) recorded values down to 7°C from the Volgian-Valanginian of Siberia and Riboulleau *et al.* (1998) recorded temperatures as low 7°C from the Oxfordian-Volgian of the Russian platform. In terms of relative palaeotemperature, the evidence appears to be consistent with the northern high latitudes being on average ~7°C cooler than the mid-low latitudes during Late Jurassic and Early Cretaceous time.

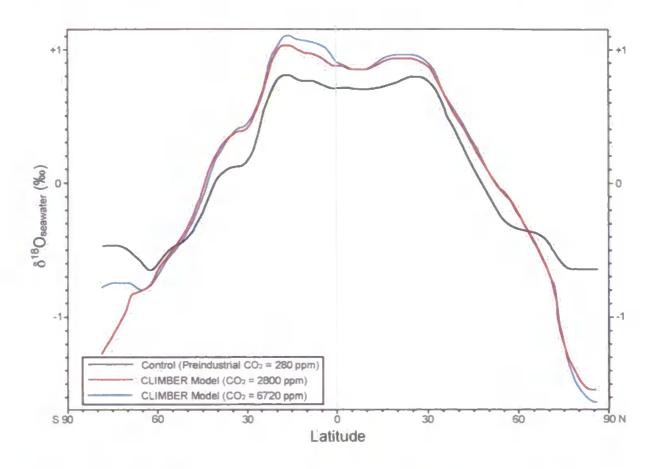


Figure 10.5 Latitudinal changes in  $\delta^{18}O_{seawater}$  in warm climates. Adapted after Roche et al. (2006).

Roche *et al.* (2006) used a coupled climate model to investigate the distribution of surface water  $\delta^{18}$ O composition under past warm climate conditions. One of the time periods considered in their research was the late Mesozoic greenhouse climate. Their results are shown in Figure 10.5. The latitudinal gradient produced by Roche *et al.* (2006) is broadly equivalent to that of the present day oceans for the mid- to low latitudes (e.g., Broecker, 1989; Zachos *et al.*, 1994), although for the high latitudes Roche *et al.* (2006) predict  $\delta^{18}O_{seawater}$  values approximately 0.5 ‰ lower than those of the present day. If the Roche *et al.* (2006) model is correct, the palaeotemperature difference between the low and high latitudes is likely to be even greater, since  $\delta^{18}O_{seawater}$  values in the mid-low latitudes (>70° palaeolatitude) are likely to be lower than -1 ‰ (Fig. 10.4), which would in effect raise low latitude temperature estimates and lower high latitude estimates. By substituting the standard  $\delta^{18}O_{seawater}$  estimate of -1 ‰ with the Roche *et al.* (2006) range of values for  $\delta^{18}O_{seawater}$  a change in latitudinal temperature gradient is observed when the data presented

in Table 10.3 for the Lower Kimmeridgian and Upper Valanginian is considered. These time intervals were chosen in order to illustrate the difference between a supposed warm period (the Lower Kimmeridgian) and cold period (the Upper Valanginian). Further subdivision of these time intervals (i.e., to ammonite zone level) was not possible due to a lack of published information.

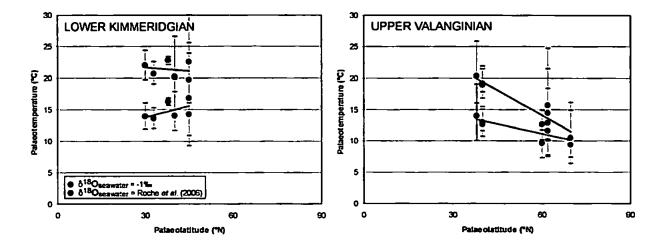


Figure 10.6 Calculated average palaeotemperatures for the Oxfordian and Valanginian periods. A  $\delta^{18}O_{seawater}$  value of -1 ‰ and the Roche *et al.* (2006)  $\delta^{18}O_{seawater}$  values are used. Only northern hemisphere locations and belemnite data were used.

Figure 10.6 provides an approximation of latitudinal differences in palaeotemperature for the northern hemisphere resulting from the different  $\delta^{18}O_{scawater}$ estimates. This model assumes a homogenous Earth surface and does not take into account regional factors that may influence palaeotemperature. Allowing for this limitation, the Roche *et al.* (2006) values for  $\delta^{18}O_{\text{seawater}}$  produce an increased temperature gradient for the Upper Valanginian data, with the offset between the calculated temperature values significantly smaller at higher latitudes. For the Kimmeridgian, the change in latitudinal gradient is less pronounced, although the relationship at this time is more difficult to assess owing to the limited latitudinal range of the data. The northern high latitude temperatures for the Upper Valanginian are on average approximately 10°C (at 70°N), although temperatures as low as ~6°C are recorded. During the Lower Kimmeridgian, the high latitude temperatures are estimated to be ~20°C (based on extrapolation of the trend line) using the Roche *et al.* (2006)  $\delta^{18}O_{seawater}$  latitudinal gradient. These significantly different high latitude palaeotemperature estimates suggest that both warm and cold conditions were present at the poles during different intervals of the Late Jurassic and Early Cretaceous.

The traditional view of continuously warm polar conditions during the Jurassic and Cretaceous greenhouse climate is still championed by many workers. For example. Jenkyns et al. (2004) recently extrapolated mid-Cretaceous temperatures in excess of 20°C for polar waters using the TEX<sub>86</sub> proxy. Such estimates of extreme polar warmth are also coincident with estimates for the tropics, only slightly warmer than those of the present day. This is especially true of the Late Cretaceous, where temperatures in excess of 15-20°C are commonly estimated for the poles (e.g., Huber et al., 1995; Huber, 1998; Jenkyns et al., 2004), whilst temperatures in the region of 33-37°C are postulated for the low latitudes (e.g., Clarke & Jenkyns, 1999; Norris et al., 2002; Steuber et al., 2005). The existence of such conditions however, poses a considerable problem, in that to date, the mechanism by which enhanced high latitude warming occurs without simultaneous warming in the tropics remains undefined. Sloan et al. (1995) summarised a number of mechanisms by which a low global temperature gradient might be achieved, including, an increase in the volume of warm deep/surface waters transported to the poles, increased high latitude albedo, increased cloud cover at high latitudes, cirrus cloud cover at low latitudes, or an expanded Hadley Cell. No definitive conclusion has yet been reached, although, the most commonly cited mechanism to account for such a situation is increased oceanic heat transport (e.g., Sloan et al., 1995; Huber & Sloan, 1999; Bice & Norris, 2002). The problem with this model is that increased poleward heat transport produces more active circulation in the oceans, which may be incompatible with the formation of black shales during Oceanic Anoxic Events (OAEs) as are recorded in the Cretaceous period. Black shale formation is commonly attributed to oceanic stagnation, caused by slow oceanic circulation and consequent anoxia (Wilson & Norris, 2001) and may therefore contradict the model of increasingly active ocean circulation. The distinctive

provinciality of marine faunas at this time may also indicate that particularly active circulation would be unlikely. It is probable that marine provinciality was controlled to some degree by temperature or salinity gradients and, therefore, may not be compatible with enhanced circulation.

If, as this study suggests, an enhanced global temperature gradient relative to that traditionally envisaged (e.g., Barron, 1983) is present during intervals of the Late Jurassic and Early Cretaceous, for example when cold conditions are present at the poles, then the need to invoke complicated and often poorly understood mechanisms is removed at these times. Present day summer sea surface temperatures range from approximately 0°C at the poles to 28°C at the equator, with the present day average global temperature gradient therefore being in the region of 0.31°C per degree of latitude. The palaeotemperature gradient calculated using the Roche et al. (2006)  $\delta^{18}O_{\text{seawater}}$  value and the data from this study was 0.26 for the Upper Valanginian, compared with a gradient of 0.10 for temperatures calculated using a  $\delta^{18}O_{seawater}$  value of -1 %. The data presented here is, therefore, consistent with a moderate global temperature gradient during cold episodes of the Late Jurassic and Early Cretaceous. In this situation, oceanic heat transport would not need to be significantly increased, which would be compatible with belemnite provinciality and the deposition of black shales. The global rise in temperatures therefore, could probably be accounted for primarily by increased atmospheric CO<sub>2</sub> levels, although differences in palaeogeography may have also had an influence. When warm conditions exist at the poles however (for example, in the Lower Kimmeridgian), a relatively reduced global temperature gradient may still exist.

If this model is applied to the Late Cretaceous, for which tropical palaeotemperature estimates in the region of 35°C are relatively common, then the newly calculated palaeotemperatures would be approximately 45°C (using a  $\delta^{18}O_{seawater}$  value of ~+1 ‰). This would also be consistent with a moderate global temperature gradient if polar temperatures in the region of 15-20°C are correct. Such high tropical values

however, may raise questions about the ability of calcifying organisms to live in these conditions and therefore also about the validity of the model. The Roche *et al.* (2006) data must therefore be utilised with care until further investigations can be carried out.

General Circulation Models (GCMs) have frequently been used in order to assess Cretaceous palaeoclimate (e.g., Moore *et al.*, 1992; Barron *et al.*, 1995; Price *et al.*, 1997; Poulsen *et al.*, 1999) and have often encountered difficulties modelling the extreme warmth at the poles and concomitant tropical temperatures in the region of 30-37°C. Barron *et al.* (1995) estimated that atmospheric carbon dioxide concentrations of approximately four times present day levels were required, together with a  $1.2 \times 10^{15}$  W increase in oceanic heat flux in order to best account for the greenhouse scenario. The model of Poulsen *et al.* (1999) however, produced temperatures that agreed well with the low latitude  $\delta^{18}$ O palaeotemperature estimates for the mid-Cretaceous but not the warm polar estimates. Perhaps the existence of an increased global temperature gradient for parts of the Late Jurassic and Early Cretaceous could help resolve some of the discrepancies encountered in the GCMs by removing the need to invoke such a substantially increased poleward transport of oceanic heat to warm the poles and to prevent the tropics from overheating.

Evidence for genuinely cold conditions during the Late Jurassic and Early Cretaceous is limited to several discrete intervals such as the Lower Oxfordian *Cordatum* Zone, the mid-Ryazanian *Kochi-Analogus* zones and the Upper Valanginian *Bidichotomus* Zone. At these times it is perhaps possible that the Late Jurassic-Early Cretaceous Earth system functioned in much the same way as it does today, with the formation of polar ice increasing the salinity and density of polar waters and therefore dense cold bottom waters originating in the Arctic Ocean region and influencing thermohaline circulation to drive global climate (assuming that the required depth was available in the Arctic Ocean to generate circulation). This is something that will need to be considered and investigated in future palaeoceanographic models. In addition, the presence of at least seasonal ice cover may have had an influence on the Earth's albedo as well as the distribution of fresh water. If this scenario is correct, the investigation of these cold intervals as a potential analogue with which to model future climate change is a very interesting prospect.

This research provides a significant compilation of northern high latitude Late Jurassic and Early Cretaceous data, which show that high latitude warmth was almost certainly the norm for this time. This warmth however, would have been punctuated by cold conditions during which limited polar ice may have formed. Perhaps the key characteristic of the Late Jurassic-Early Cretaceous high latitudes is climatic instability, which contrasts markedly with the low latitudes that are commonly believed to be much more stable. Previous research has provided snapshots of these conditions but this research for the first time provides a more comprehensive overview of this greenhouse climate. Strong evidence for both very warm and cold polar conditions is presented here suggesting that in the future, proponents of either warm or cold conditions will need to accept that both are likely to be a reality.

## **11. CONCLUSIONS**

The principal aim of this research was to investigate the nature of Late Jurassic and Early Cretaceous northern high latitude climates, principally via stable isotope and geochemical proxies as derived from belemnites and fossilised wood. This has been achieved and a considerable contribution to the understanding of Late Jurassic and Early Cretaceous climate has been made.

# 11.1. Summary of Site Specific Investigations

The major palaeoenvironmental findings for each of the sites investigated in this study are summarised below.

#### 11.1.1. Staffin Bay, Isle of Skye, Scotland

- Callovian-Kimmeridgian palaeotemperatures derived from the belemnite δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) were 6.7°C to 20.6°C (average 12.4°C). The highest palaeotemperatures were recorded in the Upper Oxfordian *Rozenkrantzi* Zone and the lowest palaeotemperatures in the Lower Oxfordian *Mariae-Cordatum* Zones.
- The  $\delta^{13}C_{org}$  data record a broad Lower-Middle Oxfordian positive carbon isotope excursion of ~5 ‰. This trend is also observed in the  $\delta^{13}C_{carb}$  data. This correlation indicates a strong coupling of the ocean-atmosphere system at this time and suggests that the total exchangeable carbon reservoir was affected. Such a relationship has never before been observed from a coeval marine and terrestrial record.
- The mid-Oxfordian negative carbon isotope excursions previously identified in the Tethyan regions are not recorded in the Staffin Bay data. These new data indicate that the Tethyan excursions may not represent fluctuations in the total exchangeable carbon

reservoir and, therefore, the fidelity of the methane hypothesis to account for this trend should be re-evaluated.

### 11.1.2. Helmsdale, Sutherland, Scotland

- Kimmeridgian palaeotemperatures derived from the belemnite δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) were 9.1 to 24.0°C (average 15.8°C). The highest palaeotemperatures were recorded in the Lower Kimmeridgian *Cymodoce* Zone and the lowest palaeotemperatures in the Upper Kimmeridgian *Elgans* Zone.
- The  $\delta^{13}C_{carb}$  record shows a distinctive long-term trend towards more negative values throughout the Kimmeridgian. This is likely to be associated with a sea-level fall during which  $^{12}C$  would be released by the weathering, erosion and oxidation of organic-rich sediments.
- The shift to low  $\delta^{13}$ C values during the Kimmeridgian is also recorded from the Tethyan region and the northern and southern hemispheres. The widespread occurrence of this event suggests that the total global carbon reservoir was affected.

## 11.1.3. Boyarka River, Yenisei-Khatanga Basin, Siberia

- Ryazanian-Hauterivian palaeotemperatures derived from the belemnite δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) were 2.1 to 19.0°C (average 10.6°C). Both the highest and lowest palaeotemperatures were recorded in the mid-Ryazanian *Kochi-Analogus* zones.
- An Upper Valanginian positive carbon-isotope excursion is identified in both the  $\delta^{13}C_{org}$ and  $\delta^{13}C_{carb}$  records. This trend is consistent with that observed in Tethyan carbonate successions and therefore indicates a strong coupling of the ocean-atmosphere system at this time and suggests that the total exchangeable carbon reservoir was affected.
- The Boyarka River  $\Delta\delta$  values may indicate a drop in atmospheric  $\rho CO_2$ . This is likely to be the result of enhanced organic carbon burial, which could lead to a drawdown of

 $\rho$ CO<sub>2</sub> and a period of cooling in the late Valanginian. The palaeotemperature record is consistent with a slight cooling event.

#### 11.1.4. Izhma River, Timan-Pechora Basin, Russia

- Callovian-Hauterivian palaeotemperatures derived from the belemnite δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) were 7.3°C to 17.3°C (average 13.0°C). A distinct fall in palaeotemperature is observed throughout the Valanginian period. This is consistent with previously published evidence for a cooling event during the Valanginian.
- The Late Valanginian positive δ<sup>13</sup>C excursion is also recorded here. The timing and duration of this excursion is consistent with that observed in the Boyarka River succession. The positive δ<sup>13</sup>C excursion occurs at a time of relatively low sea level in Russia and Siberia. The exposure and erosion of lowland areas and restricted ocean circulation (and therefore enhanced stratification) associated with a period of sea-level lowstand may account for increased rates of organic carbon burial.
- The most positive carbon isotope values coincide with the lowest palaeotemperatures. This could be explained by a fall in atmospheric CO<sub>2</sub> concentration and a subsequent drop in temperature as the result of a significant burial of organic carbon-rich sediments.

#### 11.1.5. Festningen & Janusfjellet, Svalbard

- The preservation of belemnites at this site is generally very poor.
- Ryazanian-Upper Valanginian palaeotemperatures derived from the belemnite δ<sup>18</sup>O record (using the Anderson & Arthur (1983) equation) were 7.7 to 21.4°C (average 13.0°C).
- Glendonites and outsized clasts were identified, lending support to the idea that cold conditions occurred in the northern high latitudes during the Early Cretaceous.

The δ<sup>13</sup>C data display a shift to more positive values from the Ryazanian and into the Upper Valanginian (of ~2 ‰). This shift is consistent with the timing of the Upper Valanginian positive carbon isotope excursion.

## 11.2. Wider Implications of Research

In addition to the findings outlined in the previous section, this research presented the opportunity to evaluate the use of belemnites as palaeoclimate indicators as well as to investigate Late Jurassic and Early Cretaceous global palaeoenvironmental conditions. The major conclusions drawn from this research are summarised below.

#### 11.2.1. Belemnites as Palaeoenvironmental Indicators

- Belemnite preservation must be assessed using a combined approach incorporating both geochemical and optical techniques.
- Significant natural variability is present in belemnite data, although the reason for this is
  unclear. It is likely to be the combined result of a number of factors including genusspecific differences in fractionation (this could neither be confirmed nor refuted here),
  ontogenetic differences in fractionation (again this could be neither confirmed nor
  refuted), seasonal temperature variability, migration and comparison with homogenised
  bulk rock records. Providing long term trends are interpreted rather than small scale
  fluctuations, natural variability is not a significant problem.
- Oxygen isotope data are assumed to reflect fractionation temperature together with a salinity/ice-volume effect. This is, however, assumed to be the most appropriate belemnite palaeotemperature proxy.
- It is not possible to determine whether the elemental/Ca data generated in this study were influenced primarily by environmental factors (e.g., temperature) or physiological factors (e.g., metabolic activity and growth rate).

- Mg/Ca ratios regularly generated sub-freezing palaeotemperatures. This suggests that the use of the Klein *et al.* (1996) equation may not be suitable for belemnites, especially at relatively low temperatures.
- Calculations of relative  $\delta^{18}O_{seawater}$  indicate that the Mg/Ca composition of belemnite calcite does not faithfully record temperature. This is based on the observation of a shift towards relatively negative  $\delta^{18}O_{seawater}$  values coincident with a fall in palaeotemperature.
- The problems associated with correlating  $\delta^{13}$ C records are eliminated here where a direct correlation between coeval marine carbonate and terrestrial organic carbon records from a given succession is possible. This confirms that the Jurassic-Cretaceous ocean-atmosphere system was strongly linked at times.

#### 11.2.2. Late Jurassic - Early Cretaceous Global Palaeoenvironment

- A Callovian-Hauterivian compilation of δ<sup>13</sup>C data for the Boreal Realm reveals relatively positive values in the Oxfordian, followed by a gradual shift to more negative values until the end-Volgian and a distinct positive carbon isotope excursion in the Valanginian. This confirms that the Arctic region records the same δ<sup>13</sup>C signature as is observed in the Tethyan regions.
- A Callovian-Hauterivian compilation of δ<sup>18</sup>O data for the Boreal Realm reveals evidence for warm polar conditions, punctuated by cold episodes during the Lower Oxfordian Cordatum Zone, the mid-Ryazanian Kochi-Analogus zones and the Upper Valanginian Bidichotomus Zone. This is consistent with published research. No Tithonian/Volgian cold episode was identified, although data were sparse through this interval.
- A comparison with published Late Jurassic-Early Cretaceous palaeotemperatures reveals a moderate global temperature gradient for the Upper Valanginian interval if

the standard estimate for  $\delta^{18}O_{scawater}$  of -1 ‰ is substituted with the  $\delta^{18}O_{scawater}$  estimates of Roche *et al.* (2006).

- The existence of a moderate global temperature gradient during cold episodes is contrary to the traditional view of greenhouse conditions, where extreme polar warmth is concomitant with temperatures similar to those of present day at the equator. No mechanism to account for such a scenario has ever been satisfactorily determined.
- The most commonly cited mechanism to account for a reduced thermal gradient is increased oceanic heat transport, although this may be incompatible with the formation of black shales and marine faunal provinciality.
- Throughout the Late Jurassic and Early Cretaceous high latitude warmth was almost certainly the norm. This warmth however, would have been punctuated by cold conditions during which limited polar ice may have formed. The key characteristic of the Late Jurassic-Early Cretaceous high latitudes is likely to be climatic instability, which contrasts markedly with the low latitudes that are commonly believed to be much more stable.
- During the cold episodes it is possible that the Earth's climate system functioned in much the same way as it does today. If this is the case, the Late Jurassic-Early Cretaceous interval represents an ideal analogue through which to investigate the nature of future climatic change.

## 11.3. Future Work

This study presents a significant amount of data with which to investigate the nature of Late Jurassic and Early Cretaceous northern high latitude palaeoclimates. It also highlights the areas where our current knowledge is limited and hence the areas that need to be addressed in order to resolve some of the uncertainties present here. The future work recommended as a result of this research falls into two key categories; firstly our

understanding of belemnite palaeoecology needs to be expanded and secondly additional high latitude data need to be examined.

Perhaps the most important element of future work is to further our understanding of belemnite palaeoecology by conducting high resolution investigations of modern analogues, namely Sepia officinalis and Spirula spirula. Preliminary work of this nature has been conducted by Rexfort & Mutterlose (2006), although significantly more data are In particular, the extensive investigation of aquaria specimens is required. needed. Analysis of genus-specific and ontogenetic differences in stable isotope and trace element fractionation must be focused on, in order to have any hope of truly understanding the limitations of belemnite data. Additional analyses of this nature must also be conducted on belemnite specimens so that comparisons can be drawn between the taxa. This requires the identification of belemnite rich horizons containing individuals belonging to either different genera or being of different ages. Work is currently being undertaken by John McArthur (University College London) to investigate genus-specific differences in belemnite fractionation using a deposit (of what is most likely fossilised Ichthyosaur vomit) containing abundant belemnite remains. The results of this research may provide information vital to furthering our understanding of belemnite fractionation.

In order to fully understand belemnite data it is also important to undertake further investigation into the nature of relative stable isotope and geochemical compositions of belemnites and other co-occurring organisms (e.g., brachiopods, benthic bivalves and ammonites). Preliminary work of this kind has been undertaken by several authors (e.g., Anderson *et al.*, 1994; Voigt *et al.*, 2003; Wierzbowski & Joachimski, 2006), although the results of such research have been very limited and desperately need expanding.

In addition to the required work on belemnite palaeoecology it is important to collect high resolution data from further high latitude sites (in both the northern and southern hemisphere). In particular, data should be sought from Greenland and Alaska

where very few studies have been conducted to date. If possible, attempts should also be made to investigate stratigraphically more extensive successions.

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307

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# **APPENDIX** 1

# SYSTEMATIC PALAEONTOLOGY

### **APPENDIX 1. SYSTEMATIC PALAEONTOLOGY**

### A1.1. Introduction

The present understanding of Boreal belemnite systematics has been derived largely from the work of Saks & Nal'nyaeva (e.g., 1964, 1966, 1967) and Gustomesov (1964, 1977, 1989). Their interpretation is followed here, although it is worth noting that there has been some considerable disagreement regarding the validity of certain belemnite genera (Doyle & Kelly, 1988) and subgenera (Dzyuba, 2005), particularly within the family Cylindroteuthididae. For example, the position of *Pachyteuthis* and *Acroteuthis* (which have been considered synonymous by several authors) is discussed by Doyle & Kelly (1988) and the status of the genus/subgenus *Simobelus* is considered by Dzyuba (2005). Whilst such problems are acknowledged, the following system (based largely on the work of Saks & Nal'nyaeva (1964, 1966) Gustomesov (1960, 1964) and Doyle & Kelly (1988) has been adopted for the family Cylindroteuthididae:

o Genus: Acroteuthis Stolley, 1911

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Subgenera: Acroteuthis Stolley, 1911; Boreioteuthis Saks & Nal'nyaeva, 1966; Microbelus Gustomesov, 1958

- Genus: Cylindroteuthis Bayle, 1878
   Subgenera: Cylindroteuthis Bayle, 1878; Arctoteuthis Saks & Nal'nyaeva, 1964
  - Genus: Lagonibelus Gustomesov, 1958 Subgenera: Lagonibelus Gustomesov, 1958; Holcobeloides Gustomesov, 1958
- Genus: Pachyteuthis Bayle, 1878
   Subgenera: Pachyteuthis Bayle, 1878; Simobelus Gustomesov, 1958

The systematic descriptions given below use the terminology outlined by Doyle & Kelly (1988) and Doyle (1990b) (Fig A1.1). Approximate size ranges are indicated by the terms small (<60 mm), medium (60-80 mm) and large (>80 mm). All figures are natural size (x1) and specimens have been photographed in outline (venter forward), right profile (venter to the left) and where appropriate, transverse views (orientated with venter down). Recorded ranges and distributions are taken from Saks & Nal'nyaeva (1964, 1966), Doyle & Kelly (1988) and Mutterlose (1988).

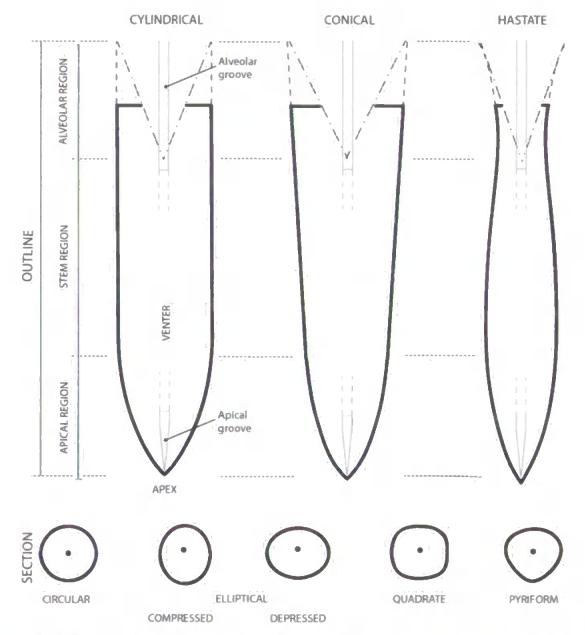


Figure A1.1 Morphological terms employed in the systematic descriptions of belemnite rostra. Adapted after Doyle & Kelly (1988) and Doyle (1990b).

## A1.2. Systematic Descriptions

Class CEPHALOPODA Cuvier, 1794 Subclass COLEOIDEA Bather, 1888 Superorder BELEMNOIDEA Hyatt, 1884 Order BELEMNITIDA Zittel, 1895 Suborder BELEMNITINA Zittel, 1895 Family CYLINDROTEUTHIDIDAE Stolley, 1919

#### Genus ACROTEUTHIS Stolley, 1911

Type Species: Belemnites subquadratus Roemer, 1836

**Diagnosis:** (After Doyle & Kelly, 1988) Medium to large size. Robust. Symmetrical, conical to cylindriconical outline. Profile asymmetrical with flat venter and often moderately inflated dorsum. Apex acute to moderately obtuse. Subquadrate and dorso-ventrally depressed in transverse section. Ventral apical groove short and indistinct, or long and well-defined. Phragmocone is ventrally displaced and penetrates one third to one half of the rostrum. Apical line is cyrtolineate.

Range: Recorded from Volgian to Barremian (Doyle & Kelly, 1988; Mutterlose, 1988).

**Distribution:** Widespread throughout the Boreal Realm (known from Northwest Europe, East Greenland, North Russia, Arctic Canada, North America, Siberia and Svalbard).

**Remarks:** There are three subgenera of *Acroteuthis: Acroteuthis* s. str., *A. (Boreioteuthis)* and *A. (Microbelus).* The differences between these subgenera are discussed separately below. *Acroteuthis* differs from *Pachyteuthis* in possessing a generally less inflated

dorsum and a (dorso-ventrally) depressed rather than (laterally) compressed transverse section (Doyle & Kelly, 1988).

#### Subgenus ACROTEUTHIS Stolley, 1911

Type Species: Belemnites subquadratus Roemer, 1836

**Diagnosis:** (After Doyle & Kelly, 1988) Robust, cylindriconical to conical *Acroteuthis*. Ventral apical groove short and indistinct. Subquadrate in transverse section.

Range: Recorded from Volgian to Barremian (Doyle & Kelly, 1988).

**Distribution:** Widespread throughout the Boreal Realm (known from Northwest Europe, East Greenland, North Russia, Arctic Canada, North America, Siberia and Svalbard).

**Remarks:** Acroteuthis s. str. is distinct from A. (Boreioteuthis), which is more cylindrical with a long and distinct ventral apical groove, and from A. (Microbelus), which is smaller, with weaker dorsal inflation and a more depressed transverse section (Doyle & Kelly, 1988).

#### Acroteuthis (Acroteuthis) acrei Swinnerton, 1936

Plate 9, Figures 2-3; Plate 10, Figures 1-2.

1936 Acroteuthis aceri Swinnerton, p.14, pl. 4, figs 7-8; pl. 5, figs 9-13.
1966 Acroteuthis (Acroteuthis) acrei Saks & Nal'nyaeva, p. 119, pl. 29, figs 1-3; pl. 30, fig. 1.

Material: Boyarka River, Lower Valanginian (*Klimovskiensis* Zone) [KH13; Loose A, KH13; Loose B, KH13; 3.45] and Upper Valanginian to Lower Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [KH6-7; Loose].

**Description:** Large and robust. Symmetrical outline, cylindrical to cylindriconical. Asymmetrical in profile, with flattened venter, moderately inflated dorsum and some flattening of lateral flanks. Apex acute to moderately obtuse, with short and indistinct lateral groove. Subquadrate and depressed in transverse section. Phragmocone ventrally displaced and penetrates up to one half of the rostrum.

Range: Valanginian (Saks & Nal'nyaeva, 1966).

**Remarks:** Very similar morphology to A. (A.) bojarke Saks & Nal'nyaeva. However, the apex of A. (A.) bojarke is more mucronate than that of A. (A.) acrei. The specimen shown in Pl. 10, Fig. 2 shares all of the characteristics of A. (A.) acrei mentioned in the description above, although it is significantly shorter than the other specimens assigned to this species (97 mm compared with 124-138 mm). Nevertheless it has been identified here as A. (A.) acrei as no other species with comparable features and of an appropriate age could be identified.

#### Acroteuthis (Acroteuthis) anabarensis (Pavlow, 1914)

Plate 8, Figures 2-4;

(A. (A.) cf. anabarensis - Plate 9, Figure 1.)

1914 Belemnites (Piesetrobelus) anabarensis Pavlow, p. 16, pl. 2, figs 1-3.

1966 Acroteuthis (Acroteuthis) anabarensis f. curta Saks & Nal'nyaeva, p. 103, pl. 24, fig. 4; pl. 25, figs 1-3. 1966 Acroteuthis (Acroteuthis) anabarensis f. sulcatiformis Saks & Nal'nyaeva, p. 103, pl. 24, figs 1-3; pl. 25, fig. 4.

1966 Acroteuthis (Acroteuthis) anabarensis f. typica Saks & Nal'nyaeva, p. 103, pl. 23, figs 1-4.

Material: Boyarka River, Lower Valanginian (*Stubendorffi* Zone) [KH18; 10.50]. Izhma River, Volgian (*Maximus* Zone) [PC2.6] and Upper Ryazanian to Valanginian

(Tzikwinianus to Polyptychus zones) [PC7.a2 B, PC7.c1].

**Description:** Large and robust. Symmetrical and conical to cylindriconical in outline. Asymmetrical profile, with flattened venter and weakly inflated dorsum. Apex is obtuse. Apical line weak, but exaggerated by extensive weathering. Subquadrate in transverse section (with flat ventral edge due to flattening). Phragmocone is ventrally deflected and penetrates half-way down the rostrum.

Range: Late Berriasian to Valanginian (Saks & Nal'nyaeva, 1966).

**Remarks:** The specimen shown in Pl. 9, Fig. 1 (A. (A.) cf. anabarensis) is morphologically similar to those specimens described here as A. (A.) anabarensis, however it is cylindrical rather than conical in outline and is Middle Volgian in age, which is younger than recorded examples of A. (A.) anabarensis.

#### Acroteuthis (Acroteuthis) arctica Blüthgen, 1936

Plate 7, Figure 5; Plate 8, Figure 1.

1936 Acroteuthis arcticus Blüthgen, p. 31, pl. 5, figs 4-5.

1966 Acroteuthis (Acroteuthis) arctica f. elata Saks & Nal'nyaeva, p. 95, pl. 20, figs 5-6; pl. 21, figs 1-3; pl. 22, figs 3-4.

1966 Acroteuthis (Acroteuthis) arctica f. typica Saks & Nal'nyaeva, p. 95, pl. 21, fig. 4; pl. 22, figs 1-2. 1988 Acroteuthis (Acroteuthis) arctica Doyle & Kelly, p. 25, pl. 9, figs 1-8.

Material: Boyarka River, Upper Ryazanian (*Meseshnikowi* Zone) and Lower Valanginian (*Klimovskiensis* Zone) [KH13; 4.35]. Izhma River, Upper Ryazanian to Valanginian (*Tzikwinianus* to *Polyptychus* zones) [PC7.a1].

**Description:** Large and moderately robust. Symmetrical and cylindriconical outline. Asymmetrical profile, with flattened venter and weakly inflated dorsum. Moderately acute apex, with indistinct apical groove. Transverse section elliptical and depressed. Phragmocone deflected towards venter and penetrates one third of rostrum.

Range: Late Volgian to Early Valanginian (Saks & Nal'nyaeva, 1966; Doyle & Kelly, 1988).

#### Acroteuthis (Acroteuthis) lateralis (Phillips, 1835)

Plate 10, Figure 3; Plate 11, Figures 1-3.

1835 Belemnites lateralis Phillips, edit. 3, p. 334, pl. 25, fig. 8.

1936 Acroteuthis lateralis Swinnerton, pp. 19, pl. 6, figs 3-9; pl. 7, figs 1-2; pl. 8, figs 1-2.

1966 Acroteuthis (Acroteuthis) lateralis Saks & Nal'nyaeva, p. 122, pl. 30, fig. 2; pl. 31, figs 1-3.

Material: Izhma River, Lower Valanginian (*Syzranicum* to *Michalskii* zones) [PC9a, PC9 GP22, PC9 GP24 A, PC9 GP24 B].

**Description:** Medium to large and very robust. Commonly broken between top of apical region and mid-stem. Symmetrical and cylindriconical to conical in outline. Distinctly asymmetrical in profile, with flattened venter and moderately to strongly inflated dorsum. Moderately acute apex, displaced ventrally. Short, generally indistinct ventral apical groove (although groove can be enhanced in poorly preserved specimens). Transverse section subcircular, except for ventral edge of section which is very straight, due to ventral flattening. Phragmocone strongly displaced towards venter, with deep penetration of the rostrum (up to one half of total length).

Range: Late Volgian to Berriasian of Russia (Saks & Nal'nyaeva, 1966). Valanginian of

the UK (Swinnerton, 1936).

**Remarks:** The specimen shown in Pl. 11, Fig. 3 was assigned to this species despite the lack of apical region for identification. The transverse section (in the stem region) is the correct shape and the specimen is of the same age as the others identified here as A. (A.) *lateralis*. This specimen is the largest specimen collected during this research, and A. (A.) *lateralis* is the most massive of the species identified here.

#### Genus CYLINDROTEUTHIS Bayle, 1878

Type Species: Belemnites puzosianus d'Orbigny, 1842

**Diagnosis:** (After Doyle & Kelly, 1988) Large and elongate. Symmetrical, cylindrical to cylindriconical outline. Profile, usually symmetrical with venter and dorsum equally inflated. Apex acute to very acute generally with short apical groove (mostly confined to the apex). Weakly to strongly compressed in transverse section. Some species have lateral lines. The phragmocone is moderately to strongly ventrally deflected and penetrates approximately one fifth of the rostrum. Apical line is cyrtolineate or goniolineate.

Range: Recorded from Bathonian to Hauterivian (Doyle & Kelly, 1988; Mutterlose, 1988).

**Distribution:** Widespread and common throughout the Boreal Realm (known from Northwest Europe, East Greenland, North Russia, Siberia, Svalbard, Arctic Canada, Alaska).

**Remarks:** There are two subgenera of *Cylindroteuthis*: *Cylindroteuthis* s. str. Bayle and *C.* (*Arctoteuthis*) Saks & Nal'nyaeva. The differences between these subgenera are discussed

separately below.

#### Subgenus CYLINDROTEUTHIS Bayle, 1878

Type Species: Belemnites puzosianus d'Orbigny, 1842

**Diagnosis:** (After Doyle & Kelly, 1988) Moderately elongate. Symmetrical and cylindrical in profile. Venter and dorsum weakly to moderately inflated. Apex acute, with well-developed ventral apical groove. Compressed and subquadrate in transverse section. Apical line cyrtolineate.

Range: Recorded from Bathonian to Valanginian (Doyle & Kelly, 1988).

**Distribution:** Widespread throughout the Boreal Realm in the Jurassic (Northwest Europe, East Greenland, North Russia, Siberia, Svalbard, Alaska) with numbers decreasing into the Cretaceous, when *C. (Cylindroteuthis)* became restricted to the Arctic Province (Stevens, 1973b; Doyle & Kelly, 1988).

# Cylindroteuthis (Cylindroteuthis) cuspidata Saks & Nal'nyaeva, 1964 Plate 4, Figure 8; Plate 5, Figures 1-3.

1964 Cylindroteuthis (Cylindroteuthis) oweni cuspidata Saks & Nal'nyaeva, p. 47, pl. 3, figs 1-8. 2004 Cylindroteuthis (Cylindroteuthis) cuspidata Dzyuba, p. 83, pl. 1, figs 1-2.

Material: Staffin Bay, Isle of Skye, Lower Callovian to Lower Kimmeridgian (*Koenigi* to *Cymodoce* zones) [SK4; 1.80, SK5; 4.70, SK6; 6.40, SK7; 20.25 A].

**Description:** Medium to large and elongate. Symmetrical and cylindriconical to cylindrical in outline. Symmetrical profile. Moderately acute to acute apex, with a short

and weak ventral apical groove (although this groove may be exaggerated in poorly preserved specimens). Subcircular to subquadrate in transverse section.

Range: Middle Oxfordian to Kimmeridgian (Saks & Nal'nyaeva, 1964).

**Remarks:** Saks & Nal'nyaeva (1964) named a new subspecies of *C. (C.) oweni*, resulting in the designations *C. (C.) oweni oweni oweni* and *C. (C.) oweni cuspidata*. These subspecies were later included within *C. (C.) puzosiana* (previously *C. (C.) oweni oweni*) and *C. (C.) cuspidata* (previously *C. (C.) oweni cuspidata*).

#### Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964

Plate 5, Figures 4-9.

1964 Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, p. 59, pl. 6, figs 1-6.
2004 Cylindroteuthis (Cylindroteuthis) lepida Dzyuba, p. 166, pl. 3, figs 3-4.

Material: Boyarka River, Lower to Upper Ryazanian (*Kochi* to *Meseshnikowi* zones) [KH17b; 1.35, KH17c; 1.50, KH17c; 2.55]. Staffin Bay, Isle of Skye, Lower Kimmeridgian (*Cymodoce* Zone) [SK6; 7.20, SK6; 7.40, SK6; 7.80).

**Description:** Medium to large and very elongate. Symmetrical and cylindrical in outline. Symmetrical profile. Some flattening of ventral flanks. Apex very acute, with long, but weak ventral groove (sometimes exaggerated by weathering, particularly in the Skye samples). Subcircular to subquadrate or elliptical (compressed) in transverse section. Shallow penetration of phragmocone.

Range: Volgian to Berriasian (Saks & Nal'nyaeva, 1964).

**Remarks:** C. (C.) lepida is very similar in appearance to L. (H.) sitnikovi Saks & Nal'nyaeva. L. (H.) sitnikovi is however, slightly less long and slender, with a more strongly developed ventral apical groove than C. (C.) lepida. Both species are present throughout the Volgian, although only C. (C.) lepida is known to continue into the Berriasian. For these reasons the specimens shown here were assigned to C. (C.) lepida.

Pl. 5, Figs 4, 6, 7 show specimens of C. (C.) lepida from the Isle of Skye. C. (C.) lepida has not been recorded from the Kimmeridgian, but these specimens have been assigned to this species as it is the closest match for the characteristics observed.

Pl. 5, Fig. 9 shows a juvenile specimen which has been tentatively assigned to this species. Although hastate in outline it is very elongate, with an acute apex and long, but faint apical groove. It occurs approximately 2 m below the other examples of C. (C.) *lepida* from the Boyarka River.

#### Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842)

Plate 4, Figures 1-7.

1842 Belemnites puzosianus d'Orbigny, pl. 16, figs 1-6.

1844 Belemnites oweni Pratt in Owen, p. 66, pl. 2, figs 3-4.

1964 Cylindroteuthis (Cylindroteuthis) oweni oweni Saks & Nal'nyaeva, pl. 1, figs 4-6; pl. 2, fig. 1.

1991 Cylindroteuthis (Cylindroteuthis) puzosiana Page & Doyle, p. 145, pl. 28, figs 1-4.

Material: Staffin Bay, Isle of Skye, Lower Callovian to Lower Kimmeridgian (*Koenigi* to *Cymodoce* zones) [SK3; 1.20, SK4; 11.50, SK5; 4.15, SK5; 4.35, SK6; 1.50, SK6; 6.55, SK8; 33.70].

**Description:** Large, elongate and slender. Symmetrical and cylindrical in outline. Symmetrical to subsymmetrical profile, with some flattening of venter. Moderately acute to acute apex that is slightly dorsally deflected (and particularly noticeable in juvenile specimens), with a short and weak ventral apical groove (although this groove may be exaggerated by weathering). Subcircular to elliptical (compressed) in transverse section.

Range: Middle Callovian to Kimmeridgian (Saks & Nal'nyaeva, 1964).

**Remarks:** This species is very similar to *C. (C.) cuspidata. C. (C.) puzosiana*, however, tends to be more elongate and cylindrical rather than cylindriconical.

The juvenile forms shown in Pl. 4, Figs 4-7 are here identified as C. (C.) cf. *puzosiana*. They share the known characteristics of the adult forms, however images of C. (C.) puzosiana juveniles are rarely available for comparison.

#### Subgenus ARCTOTEUTHIS Saks & Nal'nyaeva, 1964

Type Species: Cylindroteuthis septentrionalis Bodylevsky, 1960

**Diagnosis:** (After Doyle & Kelly, 1988) Elongate to very elongate. Cylindriconical to cylindrical outline. Venter and dorsum very weakly inflated. Uncompressed and subcircular or weakly depressed and elliptical in transverse section. Apical grooves absent or weakly developed. Goniolineate apical line.

Range: Recorded from Oxfordian to Hauterivian (Doyle & Kelly, 1988).

**Distribution:** This species is largely restricted to the Arctic Basin (Siberia, North Russia, Alaska, Arctic Canada, Svalbard). *C. (Arctoteuthis)* developed many new species in the Arctic Province during the Late Volgian, although these were confined to the east of the Urals (Stevens, 1973).

Remarks: The major distinguishing feature of C. (Arctoteuthis), compared with C.

(Cylindroteuthis), is the absence of a well-developed apical groove.

#### Cylindroteuthis (Arctoteuthis) harabylensis Saks & Nal'nyaeva, 1964

Plate 3, Figures 2-3.

1964 Cylindroteuthis (Arctoteuthis) harabylensis Saks & Nal'nyaeva, p. 80, pl. 15, figs 1-3; pl. 16, figs 1-2.

Material: Boyarka River, Valanginian to Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [KH1-4; 4.10, KH14; 4.30].

**Description:** Medium and elongate. Symmetrical and cylindriconical in outline. Slightly to moderately flattened venter and slightly inflated dorsum. Acute apex with short apical groove (confined to apical region). Subcircular and weakly depressed in transverse section.

Range: Valanginian to Early Hauterivian (Saks & Nal'nyaeva, 1964).

#### Cylindroteuthis (Arctoteuthis) pachsensis Saks & Nal'nyaeva, 1964

Plate 2, Figure 5; Plate 3, Figure 1.

1964 Cylindroteuthis (Arctoteuthis) pachsensis Saks & Nal'nyaeva, p. 76, pl. 11, fig. 1; pl. 12, fig. 4.

Material: Boyarka River, Upper Valanginian to Lower Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [KH1-4; Loose, KH1-4; 21.40].

**Description:** Large and elongate (although relatively robust for *Cylindroteuthis*). Symmetrical and cylindrical to cylindriconical in outline. Symmetrical profile, with slightly to moderately flattened venter. Acute apex with short apical groove that is often exaggerated by weathering. Transverse section subcircular and weakly depressed.

Range: Early Hauterivian (Saks & Nal'nyaeva, 1964).

#### Cylindroteuthis (Arctoteuthis) porrectiformis Anderson, 1945

Plate 1, Figures 1-3; Plate 2, Figures 1-2.

(C. (A.) cf. porrectiformis - Plate 2, Figure 3.)

1945 Cylindroteuthis porrectiformis Anderson, p. 988, pl. 9, fig. 3.

1964 Cylindroteuthis (Arctoteuthis) porrectiformis Saks & Nal'nyaeva, p. 77, pl. 12, figs 1-3; pl. 13, figs 1-2. 2004 Cylindroteuthis (Arctoteuthis) porrectiformis Dzyuba, p. 86, pl. 4, figs 1-5.

Material: Boyarka River, Lower to Upper Ryazanian (Kochi to Meseshnikowi zones) [KH16; 0.90, KH16; 2.45; KH16; 2.80, KH17b; 1.55, KH17c; 2.75]. Izhma River, Lower Valanginian (Syzranicum to Michalskii zones) [PC9; GP24 C].

**Description:** Large and very elongate. Symmetrical and cylindrical in outline. Symmetrical profile. Acute to moderately apex with a generally short apical groove, although this is sometimes extended by weathering. Transverse section compressed and elliptical.

Range: Middle Volgian to Early Berriasian (Saks & Nal'nyaeva, 1964).

**Remarks:** Pl. 2, Fig. 3 shows a specimen that is very like *C. (A.) porrectiformis* in appearance. However this specimen is Valanginian in age, and *C. (A.) porrectiformis* is not known from this time.

#### Cylindroteuthis (Arctoteuthis) cf. subporrecta Bodylevsky, 1960

Plate 2, Figure 4.

1960 Cylindroteuthis subporrecta Bodylevsky, p. 194, pl. 47, fig. 5.
1964 Cylindroteuthis (Arctoteuthis) subporrecta Saks & Nal'nyaeva, p. 73, pl. 10, figs 4-5.
1966 Cylindroteuthis (Arctoteuthis) subporrecta Saks & Nal'nyaeva, p. 203, pl. 40, fig. 1.

Material: Boyarka River, Valanginian to Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [KH1-4; 13.00].

**Description:** Large and elongate. Symmetrical and conical to cylindriconical in outline. Profile symmetrical. Very acute apex with a short apical groove that is extended by weathering. Subcircular and slightly depressed in transverse section.

Range: Early Hauterivian (Saks & Nal'nyaeva, 1964).

**Remarks:** This species is represented here by a single, poorly preserved specimen. It is very similar in appearance to *C. (A.) subporrecta* as illustrated in Saks & Nal'nyaeva (1966). However, the Saks & Nal'nyaeva (1966) specimen is very long and elongate (reaching ~225 mm in length). This specimen has been broken off in the stem region. It is, therefore, impossible to estimate how long this specimen would have been and whether it would have reached the length of *C. (A.) subporrecta*. It is also similar in appearance to *C. (A.) porrectiformis*, although the apex is perhaps too acute and the transverse section slightly the wrong shape (slightly depressed rather than elliptical and compressed) to assign this specimen to that species. It has therefore been assigned tentatively to *C. (A.) subporrecta*, which is known to occur in Russia at the appropriate time.

#### Genus LAGONIBELUS Gustomesov, 1958

Type Species: Belemnites magnificus d'Orbigny, 1845

**Diagnosis:** (After Doyle & Kelly, 1988) Medium to large and elongate. Symmetrical and cylindrical to cylindriconical in outline. Symmetrical in profile and weakly inflated, with central, moderately acute apex. Some taxa have a flattened venter. Depressed and subquadrate to elliptical in transverse section. Moderate to strong ventral apical groove, may continue into stem region (where it broadens substantially). Phragmocone penetrates up to one quarter of the rostrum.

Range: Recorded from Callovian to Hauterivian (Doyle & Kelly, 1988; Mutterlose, 1988).

**Distribution:** This genus is common in the Boreal-Arctic Province (Siberia, North America, North Russia).

**Remarks:** There are two subgenera of *Lagonibelus*: *Lagonibelus* s. str. and *L. (Holcobeloides)*. The differences between these genera will be described separately below. *Lagonibelus* can be distinguished from *Cylindroteuthis* by a generally less slender form and more strongly developed apical groove.

#### Subgenus LAGONIBELUS Gustomesov, 1958

Type Species: Belemnites magnificus d'Orbigny, 1845

**Diagnosis:** (After Doyle & Kelly, 1988) Elongate and cylindrical to cylindriconical outline. Symmetrical and weakly inflated profile, with flat venter. Depressed and quadrate in transverse section. Moderate apical groove.

Range: Recorded from Oxfordian to Hauterivian (Saks & Nal'nyaeva, 1964; Doyle & Kelly, 1988).

**Distribution:** This subgenus is common in the Boreal-Arctic Province (Siberia, North America, North Russia).

#### Lagonibelus (Lagonibelus) gustomesovi Saks & Nal'nyaeva, 1964

#### Plate 7, Figure 4.

(L. (L.) cf. gustomesovi - Plate 7, Figure 3.)

1964 Lagonibelus (Lagonibelus) gustomesovi Saks & Nal'nyaeva, p. 99, pl. 18, figs 1-2; pl. 22, figs 1-4; pl. 23, fig. 1.

Material: Boyarka River, Lower Ryazanian (Kochi to Analogus zones) [KH16; Loose]. Izhma River, Upper Ryazanian to Valanginian (Tzikwinianus to Polyptychus zones) [PC7.a2 A].

**Description:** Large and elongate. Symmetrical and cylindrical outline. Symmetrical profile, with slightly flattened venter and weak dorsal inflation. Apex moderately obtuse, with a short, indistinct ventral groove. Transverse section subcircular.

Range: Late Volgian to Berriasian (Saks & Nal'nyaeva, 1964).

**Remarks:** The specimen shown in Pl. 7, Fig. 4 was broken off in the stem region. There is no evidence of the alveolus in transverse view and so this specimen must be a minimum of three quarters of the total specimen length.

Pl. 7, Fig. 3 shows a specimen of a very similar morphology to that shown in Pl. 7, Fig. 4, although this specimen is slightly shorter than might be expected for an example of

#### Subgenus HOLCOBELOIDES Gustomesov, 1958

Type Species: Belemnites beaumontianus d'Orbigny, 1842

**Diagnosis:** (After Doyle & Kelly, 1988) Medium to large and cylindrical outline. Symmetrical profile, weakly inflated. Depressed, elliptical to quadrate in transverse section. Strong, deep and long apical groove, extending into stem region.

Range: Callovian to Late Volgian (Saks & Nal'nyaeva, 1964; Doyle & Kelly, 1988).

**Distribution:** This subgenus is common in the Boreal-Arctic Province (Siberia, North America, North Russia).

**Remarks:** L. (Holcobeloides) and L. (Lagonibelus) are distinguished primarily by the strength of the apical groove. The groove of L. (Holcobeloides) is stronger, deeper and longer than that of L. (Lagonibelus).

#### Lagonibelus (Holcobeloides) memorabilis (Gustomesov, 1964)

Plate 6, Figure 1.

1964 Cylindroteuthis (Lagonibelus) memorabilis Gustomesov, p. 134, pl. 5, figs 4-5.
1964 Lagonibelus (Holcobeloides) memorabilis Saks & Nal'nyaeva, p. 120, pl. 27, figs 4-6; pl. 22.

Material: Izhma River, Middle Volgian (Panderi Zone) [PC3a B].

**Description:** Large and elongate. Symmetrical and cylindriconical in outline. Symmetrical and cylindrical profile, with flattened venter. Very long and deep ventral groove, extending through the stem and broadening and shallowing towards the alveolar region. Transverse section is elliptical (depressed) to subquadrate. Phragmocone penetrates approximately one fifth of rostrum.

Range: Late Kimmeridgian to Middle Volgian (Saks & Nal'nyaeva, 1964).

Remarks: The specimen shown here is missing the apical region of the rostrum.

#### Lagonibelus (Holcobeloides) rosanovi Gustomesov, 1960

Plate 7, Figures 1-2.

1960 Lagonibelus (Holcobeloides) rosanovi Gustomesov, p. 195, pl. 45, figs 1-2.
1964 Lagonibelus (Holcobeloides) rosanovi Gustomesov, p. 130, pl. 5, figs 1-3.
1964 Lagonibelus (Holcobeloides) rosanovi Saks & Nal'nyaeva, p. 115, pl. 25, figs 4-5.

Material: Izhma River, Middle Volgian (Maximus Zone) [PC2.11 C, PC2.11 F].

**Description:** Large and elongate. Symmetrical and conical outline. Symmetrical profile, with slightly flattened venter. Very acute apex, with very strong, deep and long ventral groove extending through the stem region until the alveolus. Transverse section reniform in stem region (due to depth of groove) and subquadrate at alveolar region.

Range: Middle Volgian (Saks & Nal'nyaeva, 1964).

**Remarks:** *L. (H.) rosanovi* is very similar to the species *L. (H.) sitnikovi*, which is of a similar age; both species are recorded from the Volgian. The criteria used to separate the species here are as follows. *L. (H.) rosanovi* is generally longer, but less slender and more conical than *L. (H.) sitnikovi*.

#### Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964

Plate 6, Figures 2, 4-7.

(L. (H.) cf. sitnikovi - Plate 6, Figure 3.)

1964 Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, p. 122, pl. 28, figs 1-5.

Material: Izhma River, Middle to Upper Volgian (*Maximus* to *Pseudocraspedites / Surites* zones) [PC2.4, PC2.11 A, PC2.11 B, PC2.12 B, PC4a]. Boyarka River, Lower Ryazanian (*Kochi* to *Analogus* zones) [KH16; 1.15].

**Description:** Medium to large. Symmetrical and cylindrical to cylindriconical outline (although juvenile forms are weakly hastate). Symmetrical profile, with slightly flattened venter. Very acute apex, with strong and deep ventral groove extending from apex to alveolus (groove is very faint or possibly absent at apex tip). Transverse section reniform in stem region (due to depth of groove) and subcircular at alveolar region.

Range: Volgian (Saks & Nal'nyaeva, 1964).

**Remarks:** The apparent absence of the ventral groove at the apex tip of some specimens might suggest that these specimens should belong to a different genus e.g., *Belemnopsis* rather than *Lagonibelus*. However, unlike *Belemnopsis* these specimens do not possess a reniform transverse section at the alveolar end and (apart from the juvenile forms) are not hastate.

Pl. 6, Fig. 3 shows a poorly preserved specimen, which has been identified as L. (H.) cf. sitnikovi. The specimen shares the same characteristics as the other L. (H.) sitnikovi specimens identified here. It is however, from the Lower Ryazanian, whilst L. (H.) sitnikovi has only been identified in the Volgian. The poor preservation prevents an accurate identification.

#### Genus PACHYTEUTHIS Bayle, 1878

Type Species: Belemnites excentralis Young & Bird, 1822

**Diagnosis:** (After Doyle & Kelly, 1988) Medium to large and robust. Outline symmetrical and conical to cylindriconical. Profile is either symmetrical with a central apex, or asymmetrical with a flat venter and ventrally deflected or recurved apex. Ventral apical grove is short and sometimes difficult to distinguish. Moderately compressed and subquadrate or elliptical in transverse section. Phragmocone penetrates one half to two thirds of rostrum. Apical line cyrtolineate.

Range: Recorded from Aalenian to Hauterivian (Doyle & Kelly, 1988; Mutterlose, 1988).

**Distribution:** This genus is common throughout the Boreal Realm (Northwest Europe, East Greenland, North America, Siberia, North Russia, Svalbard).

**Remarks:** There are two subgenera of *Pachyteuthis*: *Pachyteuthis* s. str. and *P.* (Simobelus). The differences between these subgenera will be discussed separately below. *Pachyteuthis* is easily distinguishable from *Cylindroteuthis* and *Lagonibelus*, which are both elongate with little or no inflation of the rostrum.

#### Subgenus PACHYTEUTHIS Bayle, 1878

Type Species: Belemnites excentralis Young & Bird, 1822

**Diagnosis:** (After Doyle & Kelly, 1988) Symmetrical and conical outline. Symmetrical or subsymmetrical profile with an acute central apex. Compressed and subquadrate or elliptical in transverse section.

Range: Recorded from Aalenian to Hauterivian (Doyle & Kelly, 1988).

**Distribution:** This subgenus is common throughout the Boreal Realm in the Jurassic (Northwest Europe, East Greenland, Siberia, North Russia, Svalbard). It is restricted to Siberia and Svalbard from the Early Cretaceous (Doyle & Kelly, 1988), with some endemic species known from Svalbard (Stevens, 1973b).

**Remarks:** The main identifying characteristic that distinguishes *P. (Pachyteuthis)* from *P. (Simobelus)* is a symmetrical profile. *P. (Pachyteuthis)* is symmetrical in profile, whilst *P. (Simobelus)* is asymmetrical with a flat venter and dorsal inflation.

Pachyteuthis (Pachyteuthis) acuta Saks & Nal'nyaeva 1966 (after Blüthgen, 1936) Plate 12, Figures 2-3. (P. (P.) cf. acuta - Plate 12, Figure 4)

1936 Acroteuthis johnseni var. acuta Blüthgen, p. 32, pl. 5, figs 9-10.
1966 Pachyteuthis (Pachyteuthis) acuta Saks & Nal'nyaeva, p. 36, pl. 5, figs 3-5; pl. 6, fig. 1.

Material: Izhma River, Middle Volgian (Maximus Zone) [PC2.11 D, PC2.11 E, PC3 B].

**Diagnosis:** Large and robust. Outline, symmetrical and cylindriconical. Subsymmetrical profile, with slightly flattened venter and some dorsal inflation. Central, moderately acute apex, with short, but distinct ventral groove. Transverse section subquadrate to elliptical (compressed).

Range: Late Volgian to Berriasian (Saks & Nal'nyaeva, 1966).

Remarks: P. (P.) acuta is morphologically very similar to P. (P.) apiculata. The species

have been divided here primarily on the robustness of the rostrum. P.(P.) acuta is slightly more robust than P.(P.) apiculata and has a slightly less acute apex.

Although this species has not been described in the Middle Volgian (it is only reported from the Upper Volgian onwards), specimens are here assigned to this species, as *P. (P.) acuta* is the closest match for the specimens.

The specimen shown in Pl. 12, Fig. 4 (*P.* (*P.*) cf. *acuta*) is slightly shorter and stouter than the other specimens of *P.* (*P.*) *acuta*.

#### Pachyteuthis (Pachyteuthis) apiculata Saks & Nal'nyaeva, 1966

Plate 14, Figures 2-3.

1966 Pachyteuthis (Pachyteuthis) apiculata Saks & Nal'nyaeva, p. 33, pl. 6, fig. 2; pl. 8, figs 1-3.
2004 Pachyteuthis (Pachyteuthis) apiculata Dzyuba, p. 96, pl. 10, figs 4-5.

Material: Izhma River, Middle Volgian (Maximus Zone) [PC2.8, PC2.12 A].

**Description:** Large and robust (although quite slender for *Pachyteuthis*). Outline, symmetrical and cylindrical to cylindriconical. Subsymmetrical profile, with slightly flattened venter and some dorsal inflation. Central, acute apex, with short, but distinct ventral groove. Transverse section subrounded to subquadrate.

Range: Volgian (Saks & Nal'nyaeva, 1966).

#### Pachyteuthis (Pachyteuthis) excentralis (Young & Bird, 1822)

Plate 13, Figures 1-4.

(P. (P.) cf. excentralis - Plate 14, Figure 1.)

1822 Belemnites excentralis Young & Bird, edit. 2, p. 275, pl. 14, fig. 4; pl. 15, figs 2, 7.

1964 Pachyteuthis (Pachyteuthis) excentrica Gustomesov, p. 158, pl. 12, figs 1-3.

1966 Pachyteuthis (Pachyteuthis) excentralis Saks & Nal'nyavea, p. 45, pl. 10, figs 1-3; pl. 12, figs 1-2.
2004 Pachyteuthis (Pachyteuthis) excentralis Dzyuba, p. 90, pl. 10, figs 6-7; pl. 11, fig. 1.

Material: Staffin Bay, Isle of Skye, Lower Oxfordian to Lower Kimmeridgian (*Mariae* to *Cymodoce* zones) (SK1; 50.00, SK5, 2.70; SK5, 5.70, SK6; 4.50, SK7; 16.90].

**Description:** Large and robust rostrum. Symmetrical and cylindriconical outline. Asymmetrical in profile, with flattened venter and weakly inflated dorsum. Some flattening of lateral flanks on several specimens. Moderately acute to acute central apex, with very short and weak apical groove (sometimes indistinguishable). Transverse section subquadrate to elliptical (compressed).

Range: Oxfordian to Kimmeridgian (Saks & Nal'nyaeva, 1966).

**Remarks:** *P.* (*P.*) excentralis has a very similar form to that of *P.* (*P.*) explanata. These species are both known from throughout the Oxfordian and Kimmeridgian of the Boreal Realm. *P.* (*P.*) explanata is generally slightly shorter and more robust than *P.* (*P.*) excentralis and has a more conical outline.

#### Pachyteuthis (Pachyteuthis) cf. explanata (Phillips, 1865)

Plate 16, Figures 6-7, 9.

1865 Belemnites explanatus Phillips, p. 128, pl. 36, fig. 96.

1964 Pachyteuthis (Pachyteuthis) explanata Gustomesov, p. 163, pl. 14, figs 2-6.

1966 Pachyteuthis (Pachyteuthis) explanata Saks & Nal'nyaeva, p. 42, pl. 7, figs 1-5.

2004 Pachyteuthis (Boreioteuthis) explanata Dzyuba, p. 104, pl. 15, fig. 4; pl. 16, figs 1-3, 5, 6.

### Material: Staffin Bay, Isle of Skye, Lower Oxfordian to Lower Kimmeridgian (Cordatum

to Cymodoce zones) [SK1; 60.20, SK3; 5.20, SK3; 5.80].

**Description:** Medium and robust (although relatively slender for *Pachyteuthis*). Outline symmetrical and cylindriconical. Profile subsymmetrical with slightly flattened venter and some flattening of lateral flanks. Acute apex, deflected dorsally. Apical groove short and indistinct. Transverse section is elliptical (compressed).

Range: Oxfordian to Early Volgian (Saks & Nal'nyaeva, 1966).

**Remarks:** The specimens shown here are relatively young specimens and are, therefore, difficult to identify with confidence, as very few published images of comparable specimens exist.

#### Pachyteuthis (Pachyteuthis) cf. ingens Krimholz, 1929

Plate 12, Figures 1.

1929 Pachyteuthis ingens Krimholz, p. 126, pl. 44, figs 1-3.

1966 Pachyteuthis (Pachyteuthis) ingens Saks & Nal'nyaeva, p. 59, pl. 11, fig. 1; pl. 12, fig. 3; pl. 13, figs 1-3.

2004 Lagonibelus (Lagonibelus) ingens Dzyuba, p. 129, pl. 7, figs 1-2; pl. 8, fig. 4.

Material: Izhma River, Upper Volgian (Pseudocraspedites / Surites Zone) [PC4].

**Description:** Large and robust. Symmetrical and cylindriconical in outline. Subsymmetrical profile, with flattened venter. Apex missing, however short indistinct ventral groove identifiable towards base of stem region. Transverse section subcircular (but with flat ventral edge due to ventral flattening). Range: Kimmeridgian to Early Volgian (Saks & Nal'nyaeva, 1966).

**Remarks:** This specimen (Pl. 12, Fig. 1) has been tentatively assigned to P. (P.) ingens due to the length and robustness of the stem region of the rostrum. P. (P.) ingens is one of very few belemnites to reach this size. P. (P.) ingens however is not known from the Upper Volgian. Positive identification is impossible without the apical region.

#### Pachyteuthis (Pachyteuthis) panderiana (d'Orbigny, 1845)

Plate 14, Figure 4; Plate 15, Figures 1-3.

1845 Belemnites panderianus d'Orbigny, p. 423, pl. 30, figs 1-11.

1964 Pachyteuthis (Pachyteuthis) panderi Gustomesov, p. 159, pl. 11, figs 1-4.

1966 Pachyteuthis (Pachyteuthis) panderiana Saks & Nal'nyavea, p. 30, pl. 4, figs 2-4.

2004 Pachyteuthis (Pachyteuthis) panderiana Dzyuba, p. 92, pl. 10, figs 1-3; pl. 13, fig. 5.

Material: Staffin Bay, Isle of Skye, Lower Oxfordian to Lower Kimmeridgian (*Mariae* to *Cymodoce* zones) [SK1; 47.10, SK5; 3.90, SK5; 8.10, SK6; 2.40].

**Description:** Large and elongate. Symmetrical and conical to cylindriconical outline. Profile asymmetrical, with slight ventral flattening and dorsal inflation. Apex moderately to very acute and either central or ventrally displaced. Short indistinct apical groove. Subrounded in transverse section.

Range: Oxfordian to Early Kimmeridgian (Saks & Nal'nyaeva, 1966).

Remarks: This species shows considerable morphological variation (as recorded by Gustomesov (1964) and Saks & Nal'nyaeva (1966)), from conical forms with a very acute apex to shorter, cylindrical forms with a less acute apex.

#### Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936)

Plate 15, Figures 4-6; Plate 16, Figures 1-3.

(P. (P.) cf. subrectangulata - Plate16, Figures 4-5)

1936 Acroteuthis subrectangulatus Blüthgen, p. 35, pl. 6, figs 10-11.

1966 Pachyteuthis (Pachyteuthis) subrectangulata Saks & Nal'nyaeva, p. 39, pl. 6, figs 3-6.

Material: Boyarka River, Lower Valanginian (*Klimovskiensis* to *Stubendorffi* zones) [KH13; 2.30, KH18; 7.10]. Izhma River, Upper Valanginian to Lower Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [PC5 C, PC5 D, PC6.2, PC10a A, PC10a B].

**Description:** Medium to large rostrum. Symmetrical and cylindrical to cylindriconical outline. Symmetrical in profile, but with a slightly flattened venter. Apex central and moderately acute, with a short and indistinct ventral groove. Subquadrate to elliptical and compressed in transverse section. Phragmocone deflected towards venter.

Range: Berriasian to Early Hauterivian (Saks & Nal'nyaeva, 1966).

**Remarks:** Several species have similar characteristics to *P.* (*P.*) subrectangulata e.g., relatively small specimens of *A.* (*A.*) anabarensis, *A.* (*A.*) arctica and *P.* (*P.*) acuta. However the specimens shown here were assigned to the species *P.* (*P.*) subrectangulata on the basis of robustness *P.* (*P.*) subrectangulata is slightly less stout than the others) and their transverse sections, which, if slightly elliptical, are generally compressed rather than depressed (as in *A.* (*A.*) anabarensis, *A.* (*A.*) arctica and *P.* (*P.*) acuta).

#### Pachyteuthis (Pachyteuthis) troslayana (d'Orbigny, 1850)

Plate 16, Figures 8, 10-11.

1850 Belemnites troslayanus d'Orbigny, p. 43.

1966 Pachyteuthis (Pachyteuthis) troslayana Saks & Nal'nyaeva, p. 50, pl. 9, figs 5-8.

2004 Pachyteuthis (Boreioteuthis) troslayana Dzyuba, p. 102, pl. 14, fig. 5; pl. 15, figs 1-3.

Material: Staffin Bay, Isle of Skye, Upper Oxfordian to Lower Kimmeridgian (*Regulare* to *Cymodoce* zones) [SK5; 5.70 B, SK6; 1.90, SK7; 1.10].

**Description:** Medium and relatively slender (for *Pachyteuthis*). Symmetrical and cylindrical to cylindriconical outline. Profile subsymmetrical, with slight flattening of venter. Acute apex, with slight dorsal deflection. Short ventral apical groove. Subrounded in transverse section.

Range: Kimmeridgian (Saks & Nal'nyaeva, 1966).

#### Pachyteuthis (Pachyteuthis) sp. indet.

Plate 16, Figures 12.

Material: Lower Ryazanian of the Boyarka River (Kochi to Analogus zones) [KH16; 1.25].

**Description:** Medium rostrum. Symmetrical and cylindriconical outline. Subsymmetrical profile. Apex moderately obtuse (although this could be the result of extremely poor preservation). Presence and extent of apical line uncertain. Transverse section subcircular.

Remarks: Although the specimen in Pl. 16, Fig. 12 is very poorly preserved it is possible

to ascertain that it is most probably a young specimen of *P. (Pachyteuthis)*. It is too short and robust to belong to either *Cylindroteuthis* or *Lagonibelus*, but appears to be less robust than *Acroteuthis*. It has little (if any) dorsal inflation so it has been assigned here to *P. (Pachyteuthis)* rather than *P. (Simobelus)*.

#### Pachyteuthis (Pachyteuthis) sp. indet. juv.

Plate 17, Figures 9-10.

Material: Izhma River, Upper Ryazanian to Upper Valanginian (*Tzikwinianus* to *Bidichotomus* zones) [PC5 A, PC7.c2].

**Description:** Short and robust. Symmetrical and subcylindrical to weakly hastate in outline. Profile symmetrical and cylindrical, with flattened venter. Apex acute and central, with a very short and indistinct ventral groove. Elliptical (depressed) in transverse section.

#### Genus SIMOBELUS Gustomesov, 1958

Type Species: Belemnites breviaxis Pavlow, 1892.

**Diagnosis:** (After Doyle & Kelly, 1988) Symmetrical and conical outline. Asymmetrical profile, with flat venter and ventrally displaced or recurved apex, often mucronate (with a sharp point). Subquadrate in transverse section.

Range: Recorded from Oxfordian to Hauterivian (Doyle & Kelly, 1988).

**Distribution:** This subgenus is common throughout the Boreal Realm (Northwest Europe, East Greenland, Arctic Canada, Siberia, North Russia, Svalbard). Some endemic species

#### Pachyteuthis (Simobelus) cf. breviaxis (Pavlow, 1892)

Plate 17, Figure 3.

1892 Belemnites breviaxis Pavlow, p. 67, pl. 8, fig. 7.

1964 Pachyteuthis (Simobelus) breviaxis Gustomesov, p. 174, pl. 16, figs 2-4.

1966 Pachyteuthis (Simobelus) breviaxis Saks & Nal'nyaeva, p. 65, pl. 14, figs 5-6; pl. 15, fig. 1; pl. 19, fig. 4.

2004 Simobelus (Simobelus) breviaxis Dzyuba, p. 110, pl. 16, fig. 4; pl. 17, figs 1-3.

Material: Staffin Bay, Isle of Skye, Upper Oxfordian to Lower Kimmeridgian (*Regulare* to *Baylei* zones) [SK7; 20.25 B].

**Description:** Short and robust. Symmetrical and conical in outline. Asymmetrical profile, with flattened venter and some slight lateral compression. Acute apex, deflected dorsally and with a short and indistinct lateral groove. Elliptical (depressed) in transverse section. Phragmocone deflected ventrally.

Range: Middle Oxfordian to Kimmeridgian (Saks & Nal'nyaeva, 1966).

**Remarks:** Only one juvenile specimen of this species was recorded, making a positive identification difficult.

#### Pachyteuthis (Simobelus) curvula Saks & Nal'nyaeva, 1966

Plate 17, Figures 1-2, 4.

1966 Pachyteuthis (Simobelus) curvula Saks & Nal'nyaeva, p. 84, pl. 7, fig. 6; pl. 8, figs 4-7.

1988 Pachyteuthis (Simobelus) cf. curvula Doyle & Kelly, p. 32, pl. 7, figs 10-12; pl. 8, figs 1-2.

Material: Boyarka River, Upper Ryazanian (*Meseshnikowi* Zone) [KH17b; Loose A, KH17b, Loose B, KH17c; 3.40].

**Description:** Medium and robust rostrum. Symmetrical and conical outline. Profile asymmetrical, with flattened venter (especially in apical region) and moderately to strongly inflated dorsum. Apex is ventrally displaced and mucronate. No distinguishable apical groove. Subrounded to subquadrate in transverse section. Phragmocone displaced towards venter.

Range: Berriasian (Saks & Nal'nyaeva, 1966).

#### Pachyteuthis (Simobelus) insignis Saks & Nal'nyaeva, 1966

Plate 17, Figure 5.

1966 Pachyteuthis (Simobelus) insignis Saks & Nal'nyaeva, p. 73, pl. 17, figs 2-4; pl. 19, fig. 3. 2004 Simobelus (Simobelus) insignis Dzyuba, p. 121, pl. 18, fig. 1; pl. 21, figs 1-6.

Material: Izhma River, Middle Volgian (Panderi Zone) [PC3a A].

**Description:** Medium rostrum. Symmetrical and conical outline. Asymmetrical profile, with some flattening of venter. Strongly flattened laterally. Moderately acute apex with short and indistinct ventral groove. Subquadrate and compressed in transverse section.

Range: Volgian (Saks & Nal'nyaeva, 1966).

# Suborder BELEMNOPSEINA Jeletzky, 1965

Family BELEMNOPSEIDAE Naef, 1922

#### Genus BELEMNOPSIS Bayle, 1878

Type Species: Belemnites bessinus d'Orbigny, 1942.

**Diagnosis:** (After Page & Doyle, 1991) Small to medium, slender and elongate. Outline symmetrical and hastate (sometimes weakly hastate). Cylindrical profile with acute apex. Depressed and reniform (kidney-shaped) in transverse section. Deep ventral groove, emanating in alveolar region and broadening towards apex. Very shallow penetration of phragmocone.

Range: Recorded from Toarcian to Valanginian (Mutterlose, 1988).

**Distribution:** This genus is widespread in the Indo-Pacific region from the Aalenian (Africa, India, Indonesia, New Zealand, Australia, Antarctica). Only recorded in the Boreal and Mediterranean regions until the Middle Oxfordian (Mutterlose 1988).

**Remarks:** Both *Belemnopsis* and *Lagonibelus* possess a long and deep ventral groove. They are easily distinguished, however, as the groove in *Belemnopsis* is present in the alveolar region and dies out towards the apex, whilst the reverse occurs in *Lagonibelus*.

#### Belemnopsis cf. depressa (Quenstedt, 1848)

Plate 17, Figure 6.

1848 Belemnites depressa Quenstedt.

1991 Belemnopsis depressa Page & Doyle, p. 148, pl. 29, figs 3-4.

367

Material: Staffin Bay, Isle of Skye, Lower to Upper Callovian (Koenigi to Lamberti zones) [SK4; 10.50].

**Description:** Medium, elongate rostrum. Symmetrical and weakly hastate in outline. Cylindrical profile with acute apex. Strong and deep ventral alveolar groove, extending through stem region and shallowing towards the apex (where it disappears). Subquadrate and reniform in transverse section.

Range: Callovian (Page & Doyle, 1991).

**Remarks:** This specimen is very similar morphologically to *B. depressa*, although perhaps with a slightly more acute apex, and slightly weaker hastate form (however this may be within the variability of the species). *B. depressa* is common in the Middle Callovian of the Oxford Clay (e.g., Wiltshire and Cambridgeshire).

#### Genus HIBOLITHES Montford, 1808

Type Species: Hibolithes hastata Montford, 1808.

**Diagnosis:** (After Doyle & Kelly, 1988) Small to large, slender and elongate. Symmetrical and hastate in outline and profile. Maximum inflation in apical region, from which flanks converge towards the alveolus. Acute, obtuse or rounded apex. Normally circular in transverse section. Prominent ventral alveolar groove (does not reach apex). Phragmocone penetrates up to one fifth of the rostrum. Apical line is ortholineate.

Range: Recorded from Bajocian to Aptian (Doyle & Kelly, 1988; Mutterlose, 1988).

Distribution: This genus is common in the Tethyan Realm (South and Central Europe,

East Africa, Antarctica, South America, Australasia and India), with some Boreal Realm incursions (particularly in the Early Cretaceous) (Mutterlose, *et al.* 1983).

**Remarks:** The flanks of *Hibolithes* converge strongly towards the alveolus, whilst those of *Belemnopsis* do not. *Belemnopsis* also has a much stronger and deeper alveolar groove than *Hibolithes*. This strong groove gives *Belemnopsis* its reniform appearance in transverse section, compared with the generally circular transverse appearance of *Hibolithes*. *Belemnopsis* is therefore easily distinguished from *Hibolithes*, by shape and alveolar groove.

#### (?)Hibolithes sp. juv.

Plate 17, Figures 7-8.

Material: Staffin Bay, Isle of Skye, Lower to Middle Oxfordian (Cordatum to Tenuiserratum zones) [SK2; 2.80, SK8; 39.40].

**Description:** Small and slender rostrum. Symmetrical and hastate outline. Symmetrical and weakly hastate in profile, with a bulbous stem and apical region. Apex is central and acute. Faint alveolar groove present in the specimen shown in Pl. 17, Fig. 8 (does not extend past the middle of the stem region), but absent in the smaller specimen. Elliptical (depressed) in transverse section.

**Remarks:** These obviously juvenile forms have been assigned to the genus *Hibolithes* on the basis of their hastate form, and in the case of the specimen illustrated in Pl. 17, Fig. 8 evidence of a faint alveolar groove. It is impossible to confirm the identify of these specimens beyond genus level due to their small size (< 34 mm). However it is worth noting that *H. hastata* (Montford) is frequently recorded from the Upper Callovian and

Lower Oxfordian of the Oxford Clay (e.g., Cambridgeshire).

### Belemnite gen. et sp. indet. juv. 1

Plate 17, Figure 11.

Material: Izhma River, Middle Volgian (Maximus Zone) [PC2.3].

**Description:** Small and robust. Symmetrical and cylindrical in both outline and profile. Flattened venter, plus some flattening of lateral flanks. Apex acute and slightly deflected ventrally. Short and indistinct ventral apical groove. Transverse section subquadrate to elliptical (compressed).

**Remarks:** This species is possibly a juvenile of *P. (Pachyteuthis)* based on the following features: The rostrum is robust and symmetrical in profile, with a short and indistinct apical groove and a slightly compressed transverse section.

Belemnite gen. et sp. indet. juv. 2

Plate 17, Figure 12.

Material: Izhma River, Upper Ryazanian to Valanginian (*Tzikwinianus* to *Polyptychus* zones) [PC7.c8].

**Description:** Small and robust rostrum. Outline symmetrical and cylindriconical to conical. Profile symmetrical and conical. Apex moderately obtuse (probably due to poor preservation). Transverse section subcircular with a flat ventral edge (due to flattening of the venter).

**Remarks:** The robust rostrum with flattened venter and depressed transverse section suggest that this specimen may be an *Acroteuthis* juvenile.

#### Belemnite gen. et sp. indet. juv. 3

Plate 17, Figure 13.

Material: Izhma River, Middle Volgian (Panderi Zone) [PC3 A].

**Description:** Small and moderately robust to elongate rostrum. Outline and profile both symmetrical and cylindrical. Flattened venter. Acute central apex with short and indistinct ventral apical groove. Lateral grooves present. Transverse section elliptical (depressed).

**Remarks:** This specimen is too slender to be *Acroteuthis*, although it may be *Pachyteuthis* or *Cylindroteuthis*. The presence of distinct lateral grooves may suggest that this is a *Cylindroteuthis* juvenile. This is possibly the same species as that shown in Pl. 17, Fig. 16 (Belemnite gen. et sp. indet. juv. 6).

### Belemnite gen. et sp. indet. juv. 4

Plate 17, Figure 14.

Material: Izhma River, Upper Valanginian to Lower Hauterivian (*Bidichotomus* to *Bojarkensis* zones) [PC10].

**Description:** Small and robust. Symmetrical and hastate in outline. Profile asymmetrical and hastate. Maximum inflation at base of stem region. Apex strongly recurved. No ventral groove (apical or alveolar) identifiable. Faint lateral grooves present. Elliptical (depressed) in transverse section.

371

**Remarks:** This form is similar in appearance to the juvenile form of *Mesoteuthis tiungensis* (Saks). However, *M. tiungensis* has only been recorded from the Toarcian in Russia (Saks & Nal'nyaeva, 1975).

#### Belemnite gen. et sp. indet. juv. 5

Plate 17, Figure 15.

Material: Staffin Bay, Isle of Skye, Upper Oxfordian (Serratum to Regulare zones) [SK10; 12.70].

**Description:** Small and slender. Symmetrical and weakly hastate in both outline and profile. Maximum inflation at apical region. Acute central apex, with very short and faint ventral groove. Circular in transverse section.

**Remarks:** This specimen is too slender to be *Acroteuthis*, although it may be a *Pachyteuthis* or *Cylindroteuthis* juvenile. Due to the slenderness of the specimens *Cylindroteuthis* seems the more likely determination.

### Belemnite gen. et sp. indet. juv. 6

Plate 17, Figure 16.

Material: Izhma River, Middle Volgian (Maximus Zone) [PC2.14].

**Description:** Very small rostrum. Outline, symmetrical and subcylindrical to very weakly hastate. Profile cylindrical. Acute apex. No ventral groove visible. Transverse section subcircular.

**Remarks:** This is possible the same species as the specimen shown in Pl. 17, Fig. 13. Both specimens are from the Middle Volgian of the Izhma River.

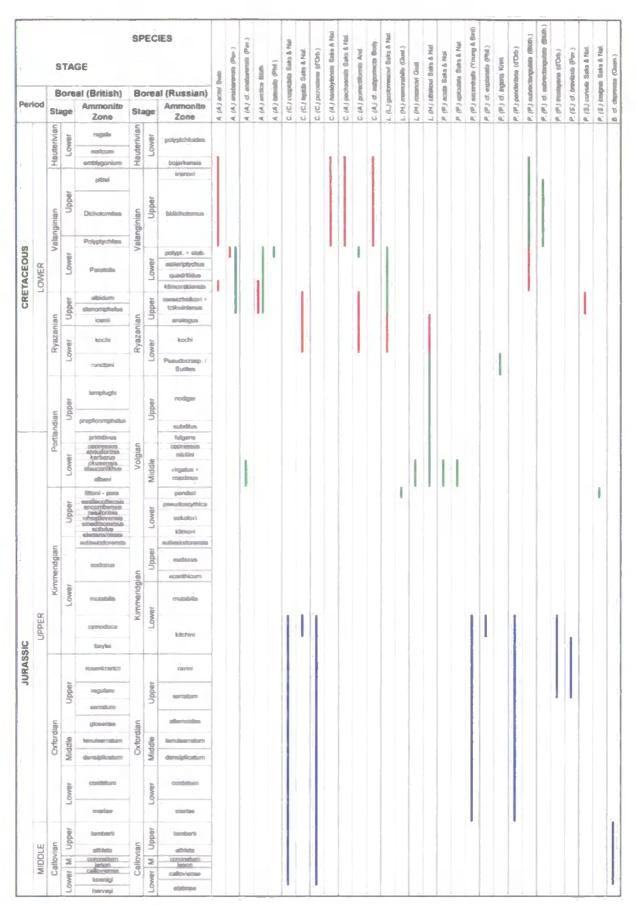


Figure A1.2 Stratigraphical and geographical ranges of the belemnite species recorded in this study. Key to colours: Staffin Bay, Isle of Skye (blue); Boyarka River, Yenisei-Khatanga Basin, Siberia (red); Izhma River, Timan-Pechora Basin, Russia (green).

# PLATES A1-17

All figures are natural size (x1) and specimens have been coated with ammonium chloride. Specimens have been photographed in outline (venter forward), right profile (venter to the left) and where appropriate, transverse views (orientated with venter down). Specimen numbers prefixed by the letters KH, PC and SK refer to specimens collected from the Boyarka River, Izhma River and Staffin Bay respectively. Specimens from Helmsdale (HL) and Svalbard (FS and JS) were not suitable for inclusion here.

## PLATE A1.

1. Cylindroteuthis (Arctoteuthis) porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile, (c) transverse section. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River, Siberia. (KH 16; 0.90)

2. Cylindroteuthis (Arctoteuthis) porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile, (c) transverse section. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River, Siberia. (KH 16; 2.45)

3. Cylindroteuthis (Arctoteuthis) porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH 17c; 2.75)

# PLATE A1



## PLATE A2.

Cylindroteuthis (Arctoteuthis) porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH 17b; 1.55)

2. Cylindroteuthis (Arctoteuthis) (?)porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River, Siberia. (KH 16; 2.80)

3. Cylindroteuthis (Arctoteuthis) cf. porrectiformis Anderson, 1945. (a) ventral outline, (b) right profile, (c) transverse section. Lower Valanginian, Syzranicum to Michalskii Zone material, Izhma River, Russia (PC9; GP24 C)

4. Cylindroteuthis (Arctoteuthis) cf. subporrecta Bodylevsky, 1960. (a) ventral outline, (b) right profile. Upper Valanginian or Lower Hauterivian, *Bidichotomus* to *Bojarkensis* Zone material, Boyarka River, Siberia. (KH1-4; 13.00)

5. Cylindroteuthis (Arctoteuthis) pachsensis Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian,
Bidichotomus to Bojarkensis Zone material, Boyarka River, Siberia. (KH 1-4; 21.40)

# PLATE A2



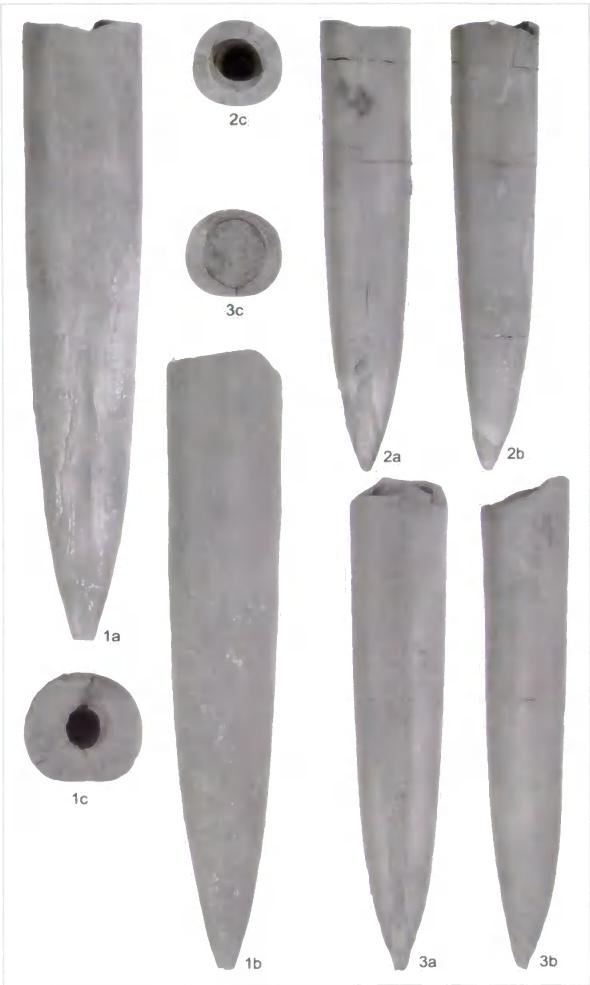
## PLATE A3.

Cylindroteuthis (Arctoteuthis) pachsensis Saks & Nal'nyaeva, 1964. (a) ventral outline,
 (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian,
 Bidichotomus to Bojarkensis Zone material, Boyarka River, Siberia. (KH 1-4; Loose)

2. Cylindroteuthis (Arctoteuthis) harabylensis Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian, Bidichotomus to Bojarkensis Zone material, Boyarka River, Siberia. (KH 1-4; 4.30)

3. Cylindroteuthis (Arctoteuthis) harabylensis Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian, Bidichotomus to Bojarkensis Zone material, Boyarka River, Siberia. (KH 1-4; 4.10)

# PLATE A3



## PLATE A4.

1. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 6.55)

2. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile, (c) transverse section. Callovian, Koenigi to Lamberti Zone material, Staffin Bay, UK. (SK4; 11.50)

3. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile, (c) transverse section. Lower or Middle Oxfordian, Cordatum to Densiplicatum Zone material, Staffin Bay, UK. (SK3; 1.20)

4. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile. Lower Kimmeridgian, *Baylei* to *Cymodoce* Zone material, Staffin Bay, UK. (SK5; 4.15)

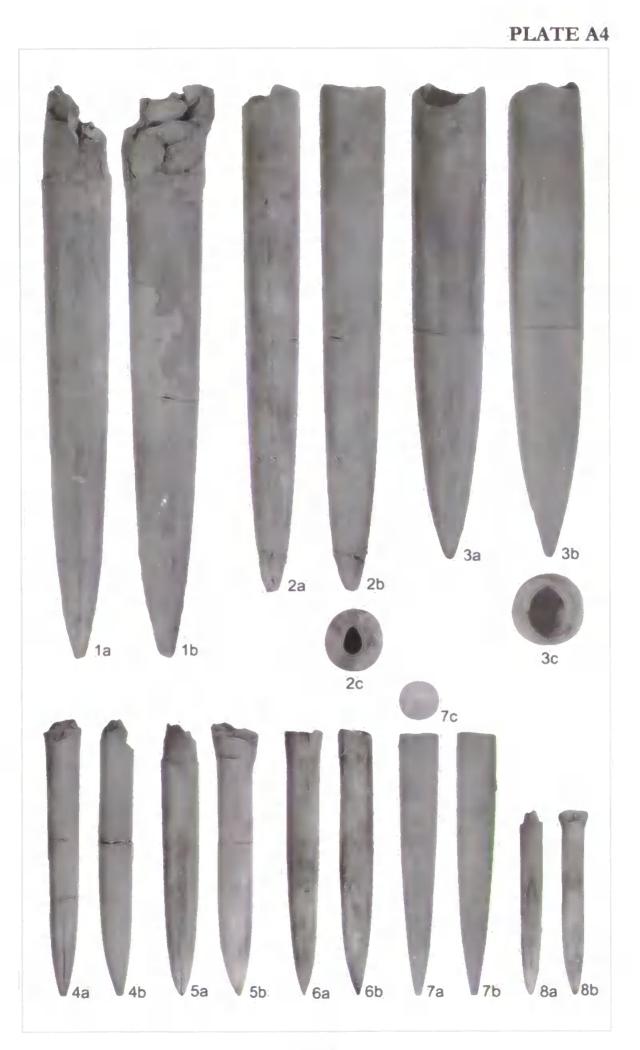
5. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile. Lower Oxfordian, Cordatum Zone, Staffin Bay, UK. (SK8; 33.70)

6. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 1.50)

7. Cylindroteuthis (Cylindroteuthis) puzosiana (d'Orbigny, 1842). (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, *Baylei* to *Cymodoce* Zone material, Staffin Bay, UK. (SK5; 4.35)

382

8. Cylindroteuthis (Cylindroteuthis) cuspidata Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile. Upper Oxfordian or Lower Kimmeridgian, Regulare to Baylei Zone material, Staffin Bay, UK. (SK7; 20.25 A)



#### PLATE A5.

1. Cylindroteuthis (Cylindroteuthis) cuspidata Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 6.40)

2. Cylindroteuthis (Cylindroteuthis) cuspidata Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Callovian, Koenigi to Lamberti Zone material, Staffin Bay, UK. (SK4; 1.80)

3. Cylindroteuthis (Cylindroteuthis) cuspidata Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile. Lower Kimmeridgian, *Baylei* to Cymodoce Zone material, Staffin Bay, UK. (SK5; 4.70)

4. Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile, (c) transverse section. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 7.40)

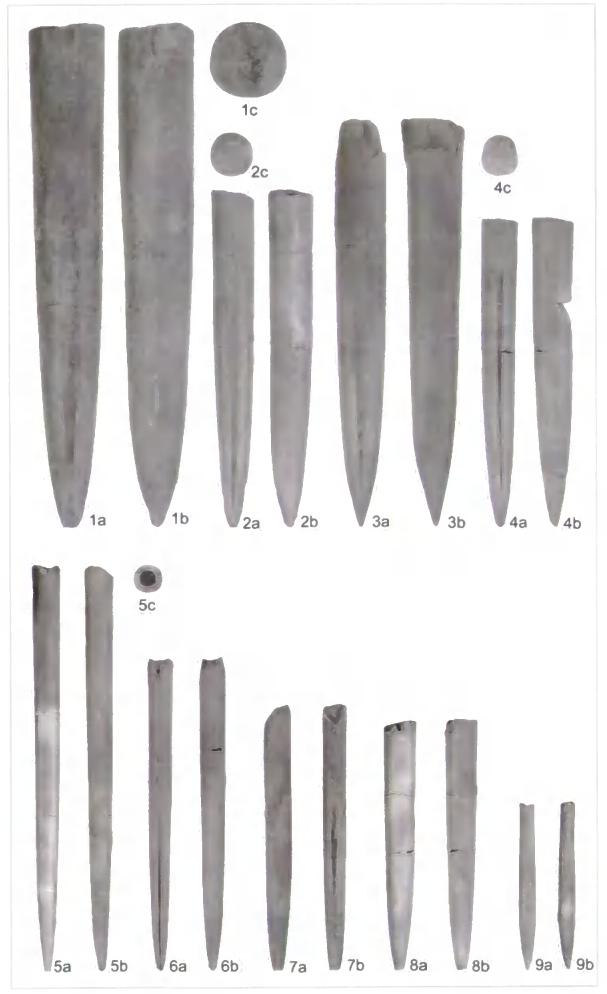
5. Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile, (c) transverse section. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH17c; 2.55)

6. Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 7.80)

7. Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 7.20)

8. Cylindroteuthis (Cylindroteuthis) lepida Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH17c;
1.50)

9. Cylindroteuthis (Cylindroteuthis) (?)lepida juv. Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH17b; 1.35)



Lagonibelus (Holcobeloides) memorabilis (Gustomesov, 1964). (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Panderi Zone, Izhma River, Russia. (PC3a B)

2. Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.12 B)

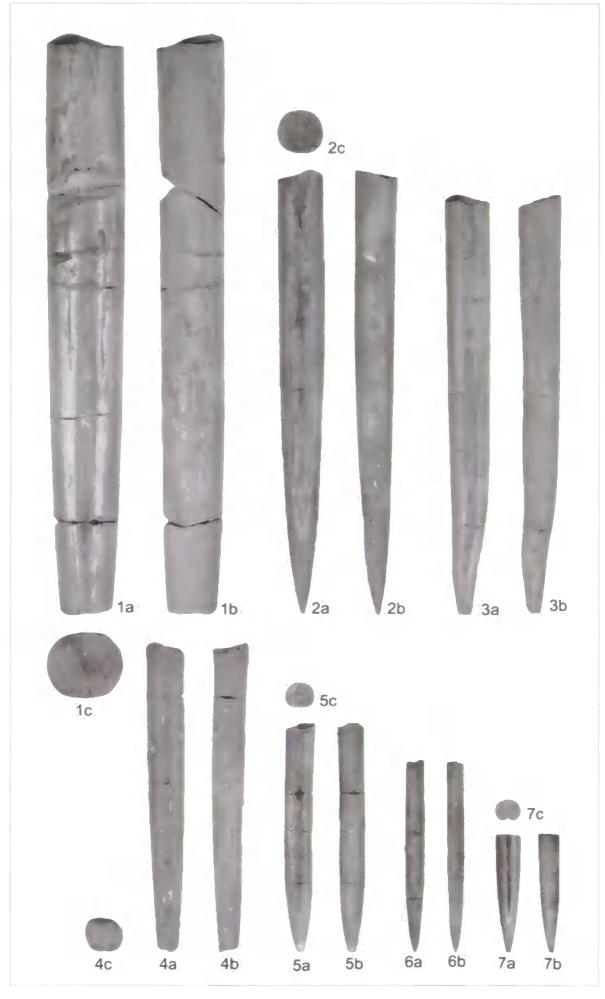
3. Lagonibelus (Holcobeloides) cf. sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River,
Siberia. (KH16; 1.15)

4. Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.11 B)

5. Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Upper Volgian, Subditus Zone, Izhma River, Russia. (PC4a)

6. Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.11 A)

7. Lagonibelus (Holcobeloides) sitnikovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.4)



### PLATE A7.

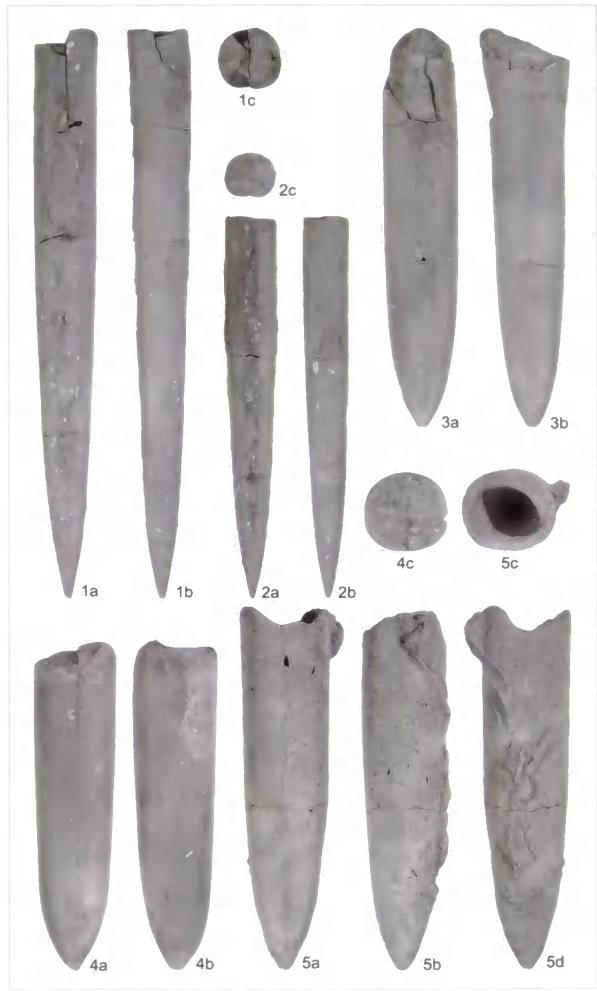
1. Lagonibelus (Holcobeloides) rosanovi Gustomesov, 1960. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.11 F)

2. Lagonibelus (Holcobeloides) rosanovi Gustomesov, 1960. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.11 C)

3. Lagonibelus (Lagonibelus) cf. gustomesovi Saks & Nal'nyaeva, 1964. (a) ventral outline, (b) right profile. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.a2 A)

4. Lagonibelus (Lagonibelus) gustomesovi Saks & Nal'nyaeva, 1964. (a) ventral outline,
(b) right profile, (c) transverse section. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River, Siberia. (KH 16; Loose)

5. Acroteuthis (Acroteuthis) arctica Blüthgen, 1936. (a) ventral outline, (b) right profile,
(c) transverse section, (d) dorsal outline. Lower Valanginian, Klimovskiensis Zone,
Boyarka River, Siberia. (KH13; 4.35)



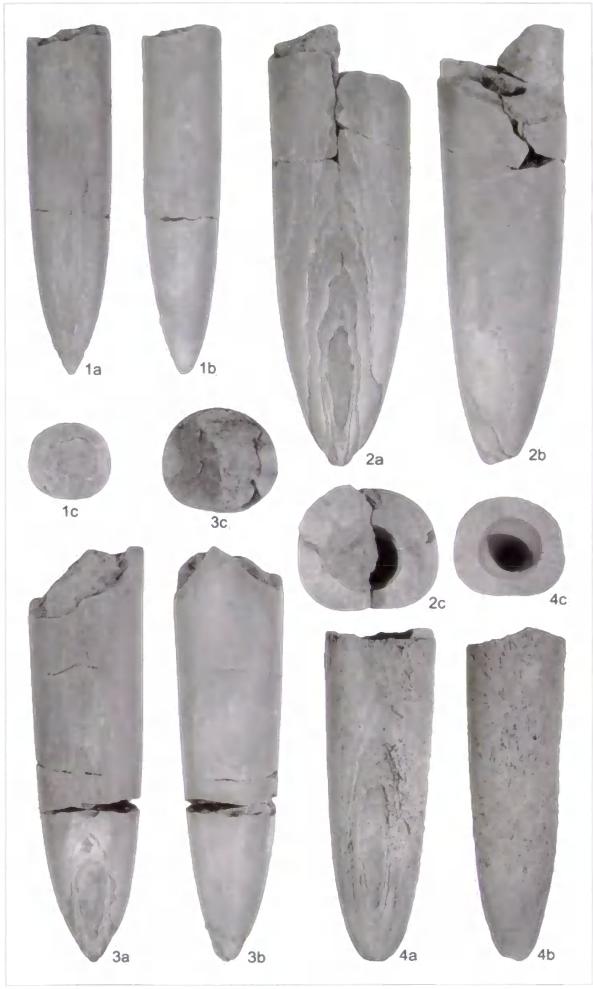
#### PLATE A8.

Acroteuthis (Acroteuthis) arctica Blüthgen, 1936. (a) ventral outline, (b) right profile,
 (c) transverse section. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.al)

2. Acroteuthis (Acroteuthis) anabarensis (Pavlow, 1914). (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.a2 B)

3. Acroteuthis (Acroteuthis) anabarensis (Pavlow, 1914). (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.c1)

4. Acroteuthis (Acroteuthis) anabarensis (Pavlow, 1914). (a) ventral outline, (b) right profile, (c) transverse section. Lower Valanginian, Stubendorffi Zone, Boyarka River, Siberia. (KH18; 10.50)

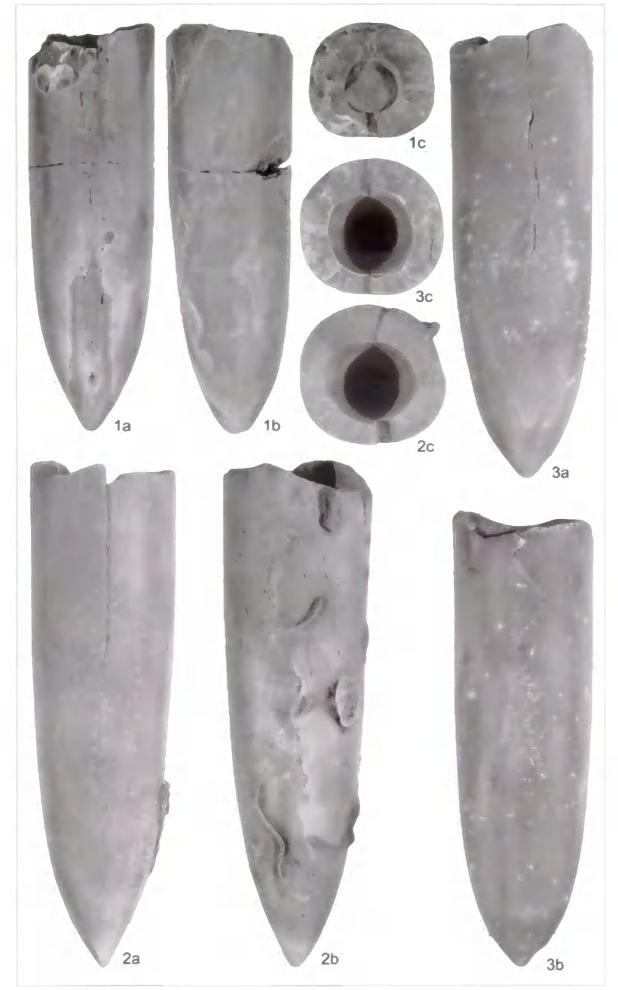


### PLATE A9.

 Acroteuthis (Acroteuthis) cf. anabarensis (Pavlow, 1914). (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.6)

2. Acroteuthis (Acroteuthis) acrei Swinnerton, 1936. (a) ventral outline, (b) right profile,
(c) transverse section. Lower Valanginian, Klimovskiensis Zone, Boyarka River, Siberia.
(KH13; Loose A)

3. Acroteuthis (Acroteuthis) acrei Swinnerton, 1936. (a) ventral outline, (b) right profile,
(c) transverse section. Lower Valanginian, Klimovskiensis Zone, Boyarka River, Siberia.
(KH13; Loose B)



### PLATE A10.

Acroteuthis (Acroteuthis) acrei Swinnerton, 1936. (a) ventral outline, (b) right profile,
 (c) transverse section. Lower Valanginian, *Klimovskiensis* Zone, Boyarka River, Siberia.
 (KH13; 3.45)

2. Acroteuthis (Acroteuthis) acrei Swinnerton, 1936. (a) ventral outline, (b) right profile,
(c) transverse section. Upper Valanginian or Lower Hauterivian, *Bidichotomus* to *Bojarkensis* Zone material, Boyarka River, Siberia. (KH6-7; Loose)

3. Acroteuthis (Acroteuthis) lateralis (Phillips, 1835). (a) ventral outline, (b) right profile,
(c) transverse section. Lower Valanginian, Syzranicum to Michalskii Zone material, Izhma River, Russia. (PC9 GP24 A)

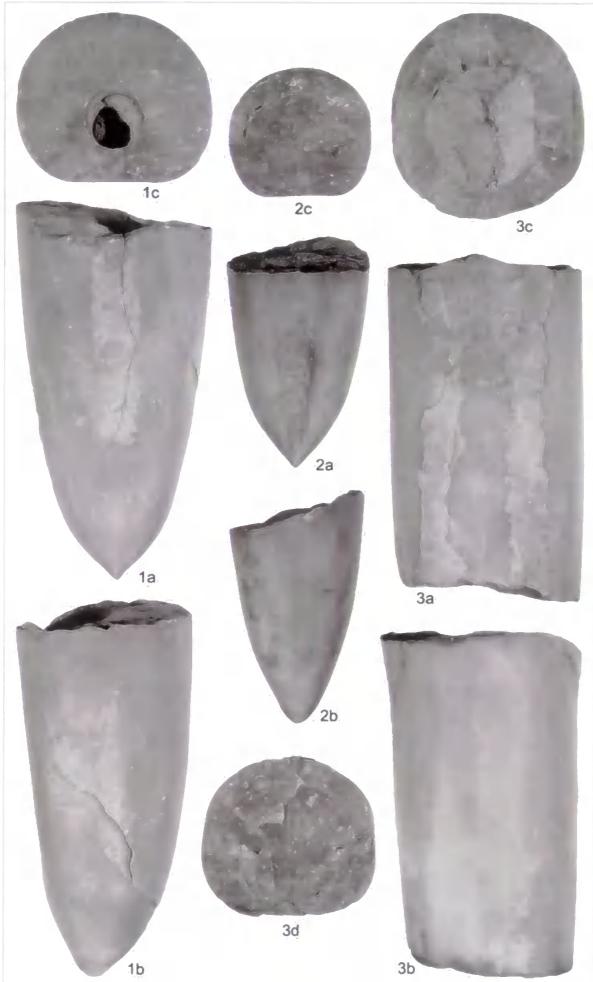


### PLATE A11.

 Acroteuthis (Acroteuthis) lateralis (Phillips, 1835). (a) ventral outline, (b) right profile,
 (c) transverse section. Lower Valanginian, Syzranicum to Michalskii Zone material, Izhma River, Russia. (PC9 GP24 B)

2. Acroteuthis (Acroteuthis) lateralis (Phillips, 1835). (a) ventral outline, (b) right profile,
(c) transverse section. Lower Valanginian, Syzranicum to Michalskii Zone material, Izhma River, Russia. (PC9 GP22)

3. Acroteuthis (Acroteuthis) lateralis (Phillips, 1835). (a) ventral outline, (b) right profile,
(c) alveolar transverse section, (d) stem transverse section. Lower Valanginian,
Syzranicum to Michalskii Zone material, Izhma River, Russia. (PC9a)



### PLATE A12.

1. Pachyteuthis (Pachyteuthis) cf. ingens Krimholz, 1929. (a) ventral outline, (b) right profile, (c) stem transverse section. Upper Volgian, Pseudocraspedites / Surites Zone, lzhma River, Russia. (PC4)

2. Pachyteuthis (Pachyteuthis) acuta Saks & Nal'nyaeva 1966. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.11 E)

3. Pachyteuthis (Pachyteuthis) acuta Saks & Nal'nyaeva 1966. (a) ventral outline, (b) right profile. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.11 D)

4. Pachyteuthis (Pachyteuthis) cf. acuta Saks & Nal'nyaeva 1966. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Panderi Zone, Izhma River, Russia.
(PC3 B)



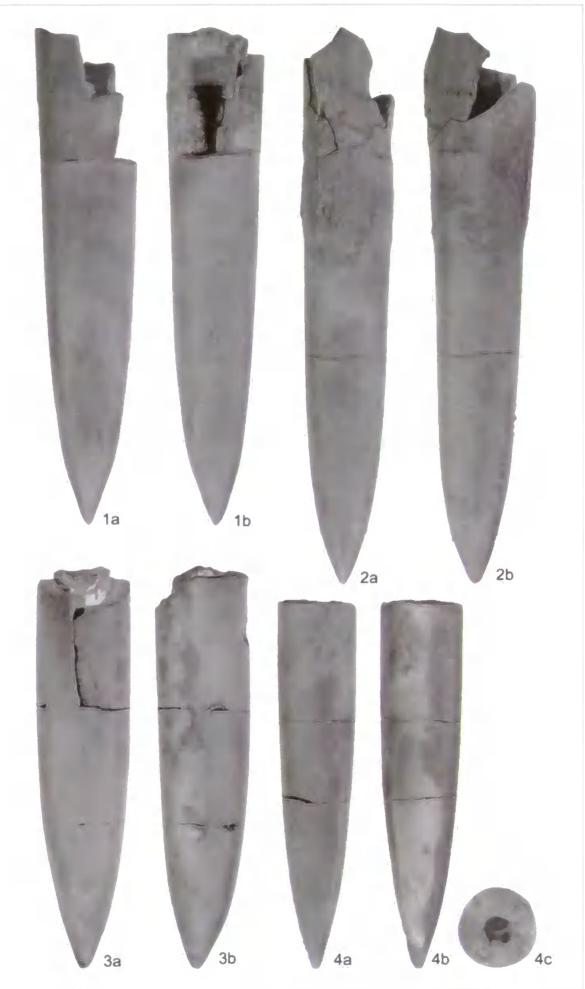
#### PLATE A13.

1. Pachyteuthis (Pachyteuthis) excentralis (Young & Bird, 1822). (a) ventral outline, (b) right profile. Upper Oxfordian or Lower Kimmeridgian, Regulare to Baylei Zone material, Staffin Bay, UK. (SK7; 16.90)

2. Pachyteuthis (Pachyteuthis) excentralis (Young & Bird, 1822). (a) ventral outline, (b) right profile. Lower Kimmeridgian, Baylei to Cymodoce Zone material, Staffin Bay, UK. (SK5; 5.70)

3. Pachyteuthis (Pachyteuthis) excentralis (Young & Bird, 1822). (a) ventral outline, (b) right profile. Lower Oxfordian, Mariae to Cordatum Zone material, Staffin Bay, UK. (SK1; 50.00)

4. Pachyteuthis (Pachyteuthis) excentralis (Young & Bird, 1822). (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, *Baylei* to *Cymodoce* Zone material, Staffin Bay, UK. (SK5; 2.70)



#### PLATE A14.

Pachyteuthis (Pachyteuthis) cf. excentralis (Young & Bird, 1822). (a) ventral outline,
 (b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 4.50)

2. Pachyteuthis (Pachyteuthis) apiculata Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.8)

3. Pachyteuthis (Pachyteuthis) apiculata Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Maximus Zone, Izhma River, Russia. (PC2.12 A)

4. Pachyteuthis (Pachyteuthis) panderiana (d'Orbingny, 1845). (a) ventral outline, (b) right profile, (c) transverse section. Lower Oxfordian, *Mariae* to *Cordatum* Zone material, Staffin Bay, UK. (SK1; 47.10)



#### PLATE A15.

1. Pachyteuthis (Pachyteuthis) panderiana (d'Orbingny, 1845). (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, Baylei to Cymodoce Zone material, Staffin Bay, UK. (SK5; 8.10)

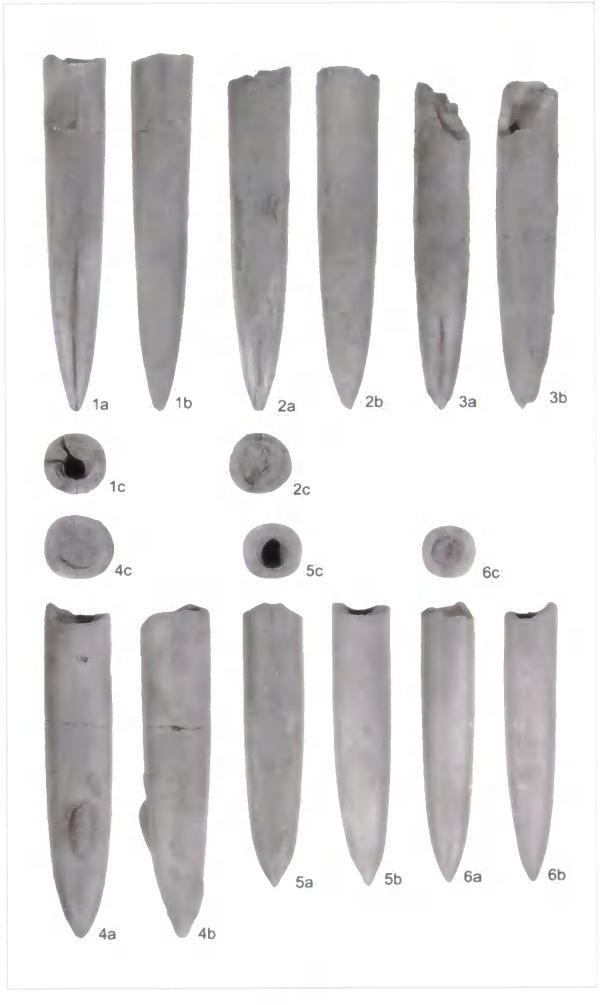
2. Pachyteuthis (Pachyteuthis) panderiana (d'Orbingny, 1845). (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, *Baylei* to *Cymodoce* Zone material, Staffin Bay, UK. (SK5; 3.90)

3. Pachyteuthis (Pachyteuthis) panderiana (d'Orbingny, 1845). (a) ventral outline, (b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 2.40)

4. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Lower Valanginian, Klimovskiensis Zone, Boyarka River, Siberia. (KH13; 2.30)

5. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian, Bidichotomus to Bojarkensis Zone material, Izhma River, Russia. (PC10a A)

6. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian, Bidichotomus to Bojarkensis Zone material, Izhma River, Russia. (PC10a B)



#### PLATE A16.

1. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian, Bidichotomus Zone, Izhma River, Russia. (PC5 D)

2. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian, Bidichotomus Zone, Izhma River, Russia. (PC5 C)

3. Pachyteuthis (Pachyteuthis) subrectangulata (Blüthgen, 1936). (a) ventral outline, (b) right profile, (c) transverse section. Lower Valanginian, Stubendorffi Zone, Boyarka River, Siberia. (KH18; 7.10)

4. Pachyteuthis (Pachyteuthis) cf. subrectangulata (Blüthgen, 1936). (a) ventral outline,
(b) right profile, (c) transverse section. (?)Upper Valanginian, (?)Bidichotomus Zone,
Izhma River, Russia. (PC6.2)

5. Pachyteuthis (Pachyteuthis) cf. subrectangulata (Blüthgen, 1936). (a) ventral outline,
(b) right profile, (c) transverse section. Upper Valanginian, Bidichotomus Zone, Izhma River, Russia. (PC5 B)

6. Pachyteuthis (Pachyteuthis) cf. explanata (Phillips, 1865). (a) ventral outline, (b) right profile, (c) transverse section. Lower or Middle Oxfordian, Cordatum to Densiplicatum Zone material, Staffin Bay, UK. (SK3; 5.80)

7. Pachyteuthis (Pachyteuthis) cf. explanata (Phillips, 1865). (a) ventral outline, (b) right profile, (c) transverse section. Lower Oxfordian, Mariae to Cordatum Zone material, Staffin Bay, UK. (SK1; 60.20)

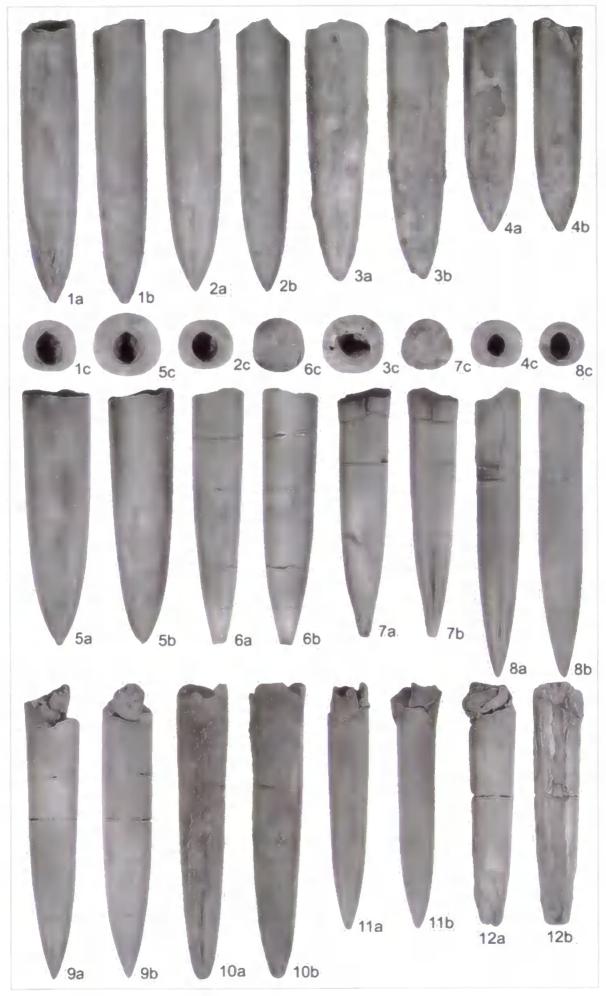
8. Pachyteuthis (Pachyteuthis) troslayana (d'Orbigny, 1850). (a) ventral outline, (b) right profile, (c) transverse section. Lower Kimmeridgian, Baylei to Cymodoce Zone material, Staffin Bay, UK. (SK5; 5.70 B)

9. Pachyteuthis (Pachyteuthis) cf. explanata (Phillips, 1865). (a) ventral outline, (b) right profile. Lower - Middle Oxfordian, Cordatum to Densiplicatum Zone material, Staffin Bay, UK. (SK3; 5.20)

10. Pachyteuthis (Pachyteuthis) troslayana (d'Orbigny, 1850). (a) ventral outline, (b) right profile. Lower Kimmeridgian, Cymodoce Zone, Staffin Bay, UK. (SK6; 1.90)

11. Pachyteuthis (Pachyteuthis) troslayana (d'Orbigny, 1850). (a) ventral outline, (b) right profile. Upper Oxfordian or Lower Kimmeridgian, Regulare to Baylei Zone material, Staffin Bay, UK. (SK7; 1.10)

12. Pachyteuthis (Pachyteuthis) sp. indet. (a) ventral outline, (b) right profile. Lower Ryazanian, Kochi to Analogus Zone material, Boyarka River, Siberia. (KH16; 1.25)



### PLATE A17.

1. Pachyteuthis (Simobelus) curvula Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH17c; 3.40)

2. Pachyteuthis (Simobelus) curvula Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian, Meseshnikowi Zone, Boyarka River, Siberia. (KH17b; Loose A)

3. Pachyteuthis (Simobelus) cf. breviaxis (Pavlow, 1892). (a) ventral outline, (b) right profile. Upper Oxfordian or Lower Kimmeridgian, Regulare to Baylei Zone material, Staffin Bay, UK. (SK7; 20.25 B)

4. Pachyteuthis (Simobelus) curvula Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian, *Meseshnikowi* Zone, Boyarka River, Siberia. (KH17b; Loose B)

5. Pachyteuthis (Simobelus) insignis Saks & Nal'nyaeva, 1966. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, Panderi Zone, Izhma River, Russia. (PC3a A)

6. Belemnopsis cf. depressa (Quenstedt, 1848). (a) ventral outline, (b) right profile, (c) transverse section. Callovian, Koenigi to Lamberti Zone material, Staffin Bay, UK. (SK4; 10.50)

7. (?)*Hibolithes* sp. juv. (a) ventral outline, (b) right profile. Lower Oxfordian, *Cordatum* Zone, Staffin Bay, UK. (SK8; 39.40)

8. (?)*Hibolithes* sp. juv. (a) ventral outline, (b) right profile. Middle Oxfordian, *Densiplicatum* to *Tenuiserratum* Zone material, Staffin Bay, UK. (SK2; 2.80)

9. Pachyteuthis (Pachyteuthis) sp. indet. juv. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.c2)

10. Pachyteuthis (Pachyteuthis) sp. indet. juv. (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian, Bidichotomus Zone, Izhma River, Russia. (PC5 A)

11. Belemnite gen. et. sp. indet. juv. 1. (a) ventral outline, (b) right profile, (c) transverse section. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.3)

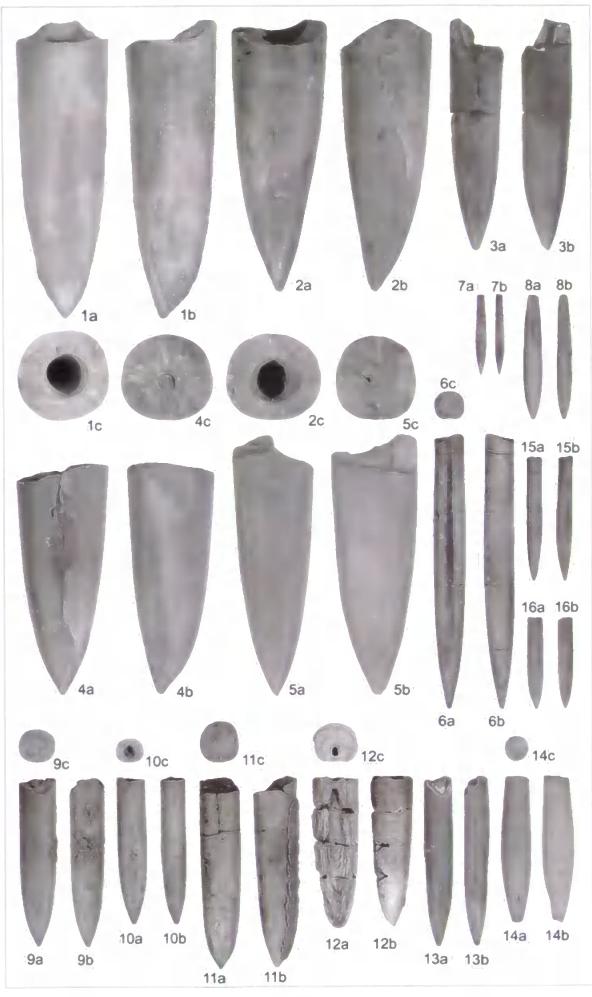
12. Belemnite gen. et. sp. indet. juv. 2. (a) ventral outline, (b) right profile, (c) transverse section. Upper Ryazanian or Valanginian, *Tzikwinianus* to *Polyptychus* Zone material, Izhma River, Russia. (PC7.c8)

13. Belemnite gen. et. sp. indet. juv. 3. (a) ventral outline, (b) right profile. Middle Volgian, *Panderi* Zone, Izhma River, Russia. (PC3 A)

14. Belemnite gen. et. sp. indet. juv. 4. (a) ventral outline, (b) right profile, (c) transverse section. Upper Valanginian or Lower Hauterivian, *Bidichotomus* to *Bojarkensis* Zone material, Izhma River, Russia. (PC10)

15. Belemnite gen. et. sp. indet. juv. 5. (a) ventral outline, (b) right profile. Upper Oxfordian, *Serratum* to *Regulare* Zone material, Staffin Bay, UK. (SK10; 12.70)

16. Belemnite gen. et. sp. indet. juv. 6. (a) ventral outline, (b) right profile. Middle Volgian, *Maximus* Zone, Izhma River, Russia. (PC2.14)



# **APPENDIX 2**

# **DATA TABLES : BELEMNITES**

ETAI 2220 (AJH)				80.12	112	1250.68	870		99 9 	991	122	00 0	96'61	PC 57	21.0	69 +92	19 909	302021-50	2+0	60.0-	Ţ	٤	Wjeatleyen	E. Kimm,	1A 8 (414) 85
	——-			1582	212	19 9011	000		YO 62	79,2	18 62	000	SUOZ	13.61	48.24	1422 222	100031	16 8/996Z	220	152.		2	Wheedleyen	E. Khnm.	47 HL4: 7.8
6971 8120 PTH				30.36	812	12:0601	000		69'21	66.1	EP'11	000	51 02	18 992	92.1	15.128	57 298	12 699/6Z	62 0	29.1-			Wheetleyen	E. Kimm.	A 7 (A.H. BA
				91'1Z	SI'Z	95 0971	000		99'Z	771	20.81	000	51 44	19521	28.11	86.6701	1014.39	59 C 1990C	95'0	62.1-		<u> </u>	US/SESUV/	E, Kimm,	48 HL4 8 D
i-	x	- <u>x</u>	x	1902	96'1	1215 28	100		28°C	99'1	12'61	000	82.61	28'17	51'20	98'282	1244 80	12 892 982	551	82'0		Pachy.	Wheedleyen	E, Kimm,	44 HF4: 8 C
				81 00	511	01.7841	110		NC'S	75'2	96.96	000	27 61	S1'2Z	078	82.8701	111830	302219 IB	110	1.34		2	Wheetleyen	. Кітт.	43 HL4: 6 B II
HIT4: 0515 1465				82'10	96'1	1328 38	62'0	1	90'01	09°C	51.63	000	15'61	65 <sup>-</sup> 62	16.91	22 0901	1053.63	275214 42	62.0	24.1.			Wheelleyen	. Kmm. 3	42 114 9 91
2071 SZ 10 'PTH				21.83	572	120951	210		27 7	3.60	51.63	000	SPEZ	20.02	59'2*	181181	122111	363002.00	89.0	8+0-			Wheatleyen	E. Kimm.	4 9 PTH 19
				90'27	282	26.5101	000		42.44	10'5	92'65	000	41'38	20.016	10.97	08 6722	190201	16 09/911	0.00	741		L	bolzzia.A	. мтін . Э	28 HF4 4 V
				54 81	05'1	28.1011	000		CO 7	08.1	12.8	00 0	13.26	65.61	62.01	191211	99 969	215701.30	SZ'V	<b>CB.1</b>			boizzituA	E, Kimm.	11 8 C 1+TH ZC
HF4: 0130 1383				51.12	513	87 9951	000		92'9	201	10'2	00 0	92.02	52'01	12.20	28 6111	C6 299	310203121	02.1	08'1-			bolesi huA	. Kimm,	28 HF4 2 B I
HIT# 0000 1580				EZ'IE	58'1	1343 43	280		38.2	5 09	92.8	000	177.61	11.11	80'ii	00 6201	65 629	363645 36	61'1	<u>78'1-</u>		<u> </u>	botasinuA	E, Kimm,	36 HL4; 3 A
				30.60	510	89.4411	000		91'2	3.38	91.9	000	20.03	99'12	54.19	1333 98	82.168	ISTETSEDE	870	C9'1-			<b>eleden</b> M	E. Kimm,	34 HF4' J B
7/21 CZ00 PTH				59'10	5.00	154213	29.1		69 5	597	50.7	000	10.61	38'50	99'61	9E 7201	26 696	66 8¥5/6Z	69.1	<u></u>		<u> </u>	eiliden M	ב. ולנחח.	A CALIFIC
9001 9995 2714				24.64	76'1	1482.57	91.1	<u> </u>	77 C	3 99	10.0	000	52 02	Z¥'Z	23 51	1204.66	1220.84	20.122362	20.1	62.1.		2	enxopn3	E, IQmm,	¥2.01H 20
HT3' 8843 1004				91'62	502	1230.60	000		22.0	96'1	77 7	000	102	94 SZ	189	98 2 90 1	60,909	S9 96906Z	102	89.1-		2	eurobu3	E. Kimm,	31 Kr3/1 V
				22 20	511	90 2821	000		<b>/9</b> '\$1	91.4	61.21	9 <b>7</b> S	51 63	65 ¥S	94'65	90 16/1	POEISI	350831 83	0.36	19.5		Ľ	ເປັນ	E, Kimm,	30 HLID: 27.60 B
				50 12	5.04	1153.04	460		8278	512	96'1	000	90 OZ	9 <b>7</b> S	31.37	92 048	52 629	536629 29	597	92'0		٤	Ū.	. Kimm, 3	A 08.72 , d1 JH 95
				18 67	SIZ	98 9921	512		3.10	69.2	65'61	000	91 SZ	96.11	12 6C	09 22211	100011	39713962	51.1	82.0			<u>c</u> ym	.mmbi.3	A 08 05 ;dr.1H 85
				21.82	208	20 112 I	000		51'21	96'1	99°Z	000	51.02	Z9 Z7	95'21	IT ZZZ	66 206	282304 85	555	57.1.		ć	<u>cym</u>	E, Kimm.	27 HL15 13 60
				09.91	528	01 6/9	<b>Z9</b> 0		16.14	545	18'90	000	67.02	¥6'90¥	ZP 92	1812181	PS'162	202312 03	57.0	92°F		د -	Q	E, Kimm.	26 HE 10 3'10 DI
				69'61	202	97.718	000	· · · · · ·	19 52	10 €	28.82	000	54'91	17,805	20.85	20 0281	51 9901	16'12196Z	11.1	18.5.		2		, nmbi, 3	26 HL 16, 3, 10 DI
				19.95	5.28	01.1211	01.0		is s	727	65 C	000	85.81	82°0Z	78 OS	11226	59 228	202178.52	191	191		Ĺ	<del>ري</del> سرع	, mmD4 , 3	24 HF1P 3'10 C
				19,26	5.18	1138 32	0.31		1192	IS'C	14'38	000	87.0Z	52 511	68 67	ZIZISI	1211.84	26 S1206Z	1271	<u>.</u>		٤	<u> </u>	. Kimm, 3	23 HF1P 3108
				12.12	5 39	1322.20	000		Z9'+	5.60	87.4	000	51.02	91'97	92'81	19'5761	1213.73	18.07219S	18.0	28.0-		- 2	<del>د</del> /س	E, Kimm.	22 HL16, 3.10 A
				86.91	502	1194.63	000		19722	<u>\$7.</u> C	81.6	00 0	3E 12	69 57	95'+1	28 2 101	22.1201	66 949 <b>+0</b> 0	07.1	20		č	CYm C	E, Kimm,	02.AL1; 4.70
				18.93	22	71 6711	000	· [	<u>11 S</u>	OS C	99 S	62.19	21.12	34.01	67 OZ	02 9261	108.0001	306431.56	06'1	28.0-		č	<u> </u>	E, Kimm,	50 HF1: 4 00 B
r				10.81	511	1180 43	000		90°C	ST.C	EB.1	000	99.81	11.74	29'91	62.8161	1160.94	302171.75	151	CZ 1-		2		E, Kimm,	IA 00.5 [1 H 81
				20.81	30.5	61 8121	00'0		21'21	05'0	3'40	000	18.03	09 EZ	1574	61 06Z I	11.8801	29 925+62	89.1	21.1.		ć	<u> </u>	, Kimm, .a	N 00 * 11H 91
				20.12	500	65'1011	000		10.11	92 C	18.0	00.0	06.81	19.64	89 CZ	1056.24	96716	57 257/62	1.28	180		6	<u>ē</u> u	E, Kimm,	A 01 S 11H 11
				25 01	5 23	LOOLZI	000		51.15	21.2	10.8	000	19.52	11990	13.36	20 698	19:008	SI 962206	5'42	81.S.		- L	U U	E. Kimm,	8 03'1 11'H 81
				29 81	3.08	IZ PSII	000	·	18,33	CZ C	213	000	62.61	59.92	09.01	01,0001	090 23	00'111962	SP'I	00.1.		4	C/w	. кита, Э	A 09.1 ; LUH 81
				12:07	5.68	21'6911	3 50	1	92'>	89.5	77'7	000	18:59	82 82	CI 901	26 9811	97 6911	67 ELPEIE	27.1	-5.84		Ĺ	<u>ت</u> س	. Kimm.	02°1°11H 91
t				59 W	212	1263.44	000		20.02	91.5	20'+	000	12.02	31'88	SPSI	907901	17.158	30,748095	5'48	-1.38		6	ω. Ο / μ	E. Kimm,	13 HT1 110
				15.16	51.2	29:0011	000	1	60'5	3.96	00.7	000	08.61	<u> 19 6</u> 2	59.61	6C 6911	92,878	11.195652	09'1	DE 1-		4	<u>سر</u> ع	. Kimm, 3	15 HT1: 0108
	×	- E	X	31.72	22	98 2901	000		16.8	10.6	16.11	000	62.02	52.62	60 S1	970211	95.728	22 61 SZOC	204	09'I-		2		. MmDI , 3	10201174
				17.65	212	1333 28	000		20 0	61°C	213	000	92'61	12.10	1545	90,9001	19108	15.990665	282	05'1-		2	<u> </u>	, мту, 3	10 HT 1: 0 20 C
				69 00	60 Z	87 6911	000	· I — —	05'91	00°C	80.8	000	09.61	35'42	SPEL	23.029	60 669	200366.20	91.2	25.1-			ີ່ໜູ	. Kimm,	9 05 0 1 TH 6
				1182	213	151021	000	T	56°05	3'30	13.53	000	60 02	<b>330 8</b> 8	97,71	ES ZIOI	29 906	30.270000	282	<u>8</u> 2.		4	ພາວ	. nmbi .a	UV 05 0 1 1 1 8
				50 GZ	212	1205.79	000		39.6C	3.37	CT.8	0000	19.61	CZ ISZ	IZSI	<b>39 0011</b>	1024 38	18.1100000	305	91.5.		4	<u> </u>	., Kūmm,	M 050 11H 1
ŀ				95'17	524	1132,221	000		99	90'#	<b>Z9</b> 6	00.0	17.05	37.48	12.64	09 6291	69 626	316133 86	291	96 1			с) ш(Э	E. Kima.	6 HTI 0 20 C
		<u> </u>		22.92	518	19'9011	02.0		51.8	28.0	13.24	0.00	ZL'61	67 OC	80.04	81.14021	¥8 SZOI	76.CT878S	28.1	20°1-			<u>ш(</u> э	. Ката.	PHF1 030 BU
		1		18 MC	31.5	00.8011	000		15.5	99 C	8E 6	000	30 OZ	6Z 71	SP 01	07 SZZ I	21.985	217.6255000	66'1	Ê1'1-			Q		18 000 INH P
		i	i	12.71	503	191211	000	<u> </u>	51.0	3 83	29.01	000	<u>78</u> .61	85 8i	12.02	1541.69	89 9011	300464.36	C8'i	95.0-			<u> </u>	. Kimin,	A 05.0 ; 1.1H 5
t		<u>                                     </u>	i	22.63	5 50	89 OCZ I	000		ZC ¥	5.66	62 <sup>°</sup> 9	00.00	20 22	6Z 0C	15.35	<b>C9.10</b> 6	82 ¥20	310264.41	222	280-			<u>ш</u> о	E, Kimm,	3 HL1: 0.10 B
······				10 TC	518	ZE 0/01	60 0		58 11	13	3.42	00.0	19.65	147.24	10 52	57 6671	Z9 9601	262+2200	92 1	26.1			<u>ر) س</u> ري	. ແານນະ.ອ	1 HL1; 0.10 A
Comments	Citrin Citrin	MBS8	10	<u>vz</u>	Ĩŭ	51	Q d	N	L MN	l n	ee Be		INT IA	63	K_	BW	L <sup>6</sup> N	1 *S	- 2 <sup>4</sup> 8	0 <sub>6</sub> 0	Photo	sund	enož .mA	egA	io. Gample No.

.

·····				90 SZ	544	671901	000	1 1	643	74	5#2	000	6E CZ	94.44	61 6Z	29 9091	1154 05	5369308 24	1211	80.1		<u>ب</u> ٨	elidenum	ר גושש	98 EV1 - 1 00
	- <u>-</u>	- <u></u>	<u> </u>	61'61	77	/8 9901	10		201	LY Z	10.1	000	112	EL'BZ	97.81	151251	1003 22	30,862,15	971	091	·		elidanM	רי אושי	05 1 · 1 20
	<u> </u>	<u> </u>		12'00	5.35	29 618	220		82.2	52.1	1.35	000	89 ZZ -	30.50	08.52	99 959	05.181	89 CC/ZOC	987	210		<u> </u>		Callovian	8 91H 96
				52.15	5'43	81.208	121		11.6	08'1	00'i	000	ETEZ	92.82	19.5.61	92 611	82413	20102 32	516	10 0			Koonig	Cellovan	11 V 97H 96
HTP: 8060 0329				97 67	543	02 628	000		65.5	991	80.1	000	SVIVZ	37.20	úж	119611	PS'299	203245 81	518	0.44	·		Koeujāj	Cellovian	1 V 97H 96
2991 6910 914		<b></b>		87.81	1972	68 9661	100		9 44	<u>28</u> '1	11.8	000	55°ZZ	22.80	25.11	07 6/5	1/ 2011	87.7A20C	96.2	29 5	<u> </u>		Rot-Friton	ר גרוי-ב המי	A 22 , 31H CE
2891 0810 -9 IA				97 91	5 38	12/2011	1000		115	ZI'E	979	000	92 22	10.02	90.61	98 0001	07.168	202/02 64	92.0	0.12			Rot-Fillon	F KI'E BAL	83 HFE' 51 B
9591 9410 'STH				11.81	5.46	87-2911	000	·I	96.7	60 C	61.8	000	55.90	12.54	00.0	98'129	10 909	11.7727200	000	61 0		<u> </u>		F KI'E 694	VIZ STHIE
				12'61	102	EN SEZI	000		<del>K</del> 2	98'1	89 51	000	64.CZ	29°52	00.0	12.162	C9 6/9	306360 86	0*0-	120			Rot-Faton	L KI E Por	8 02 'SIH 06
EC91 0210 STH		<u> </u>		11.54	5.38	697671	000		576	H8'I	3.64	000	2012	01.6	000	<b>298 24</b>	1592 (23	205602.87	690	910			Rot-Fatori	L KI E Por.	4 02 '91H 68
SZ91 1910 STH				51 23	5'40	99 2 901	000			3.55	91'0	000	86 62	81.81	28'12	99.078	56 926	302028 54	19'1-	82.0			Rot-Faton	T KI'E LOL	¥ 61 '97H 88
				07'12	ip'z	1320.38	000		21'S	ez c	05.0	000	55.55	12.92	14.24	28 028	57 5201	306615.33	527	40			Rot-Fatori	1900 3- DI T	8 81 'SIH 18
				PI'SI	00°Z	62'1811	000		10.02	98'1	897	000	SS ZZ	15 65	000	10 809	89.922	69 ¥1620C	190	61.0	<b>∖</b>		Moth T-soft	L KI LE PORT	8 4 BL (97H 98
				1021	5.33	89 0611	1000		99'21	518	97 9	000	2172	C6 0	000	00909	20 7/9	C6 115/0C	280	120			Post-Fetoni	1 KO - E 641	1 4 81 ,204 88
HT2' 0121 1950				06.91	533	1540.83	000		05.8	61.2	22.6	<u>000</u>	51'31	ZFCL	-	97 689	ET 5H6	206943.00	1011	990			NOT - NOT	POJ 3- DI 1	8 21 514 18
				NC.81	627	512021	000		520	EL'P	5.64	000	51'20	69 8	02'11	86 78/	15 008	12 692/06	690	0.28			Rot-Fatori	L KU, E Por.	¥ /1 '97H 88
HT2: 0444 1815				12.15	80 Z	90 0571	000		22.8	19.1	<u>Д'01</u>	000	18 61	65'95	96.01	<b>N8.72</b>	67 2111	76 00C96Z	080	210			Rot-Fatoni	FIN E LA	8 91 'STHIZE
				12.91	308 200	17 8051	000	·	GG 7	66.1	<u>120.</u>	000	58'81	13.04	50.15	6875/	1129 8211	582581.20	990	62 0	┨────┨			L KI E POL	1 V 91 STH 10
				09 51	81.5	99.621	- <u>600</u> -	·	000	GZ 1	29.7	000	51.30	85 62	92.9	67.118	82,8501	81 262852	65'1'	61.0	II		Rot-Fatoru	1 KI - E 64	1 V 91 197H 08
HL5; 0438 1608				92.61	5.39	99 2971	000	·	89.01	10'2	08.6	000	19'12	60.031	95.9	52 464	100013	301916.05	11.14	28.0		Pacity.	Pectinatus	1404 3- DI 1	V SL STH 44
9951 9010 'STH	<u> </u>	-		29'61	3.30	18 8921	000	·	21.85	SZ C	85'9	000	61.22	51'88	0001	19 6001	51'8011	82 951605	120	210			Pectinetus	L KI E POL	14 19
HF2: 000 1200				185	54.5	67 8771	200	·	54 23	21.1	85 02	000	54.31	PE'SP	9192	LS PCCZ	21 1671	305148 25	69 0	86.0			enjeujoed	LIQ.E Por	V CI STH 0/
2551 2800 STH				05'1	572	1428.44	110		90'*	121	20 51	000	51.66	20 25	197	010021	PE 698	309225900	000	190			HUD/Ped		19 HIZ 15 B B
				22 57	5 23	21.8111	000		60'7	92'1	05'9	000	11.02	16 91	19.91	987521	95 8/8	19198100	91.0	280	}	2	100-L/PRI	L KI E Por	1912 1381
				67'60	552	12:19:1	000	· i	90'SI	597	59.01	000	16.22	504 54	11.62	SZ 1091	1300.61	10'212/62	1210	80			HUG/POC	L KI E Por	13 HIS 12 A
1951 1800 STH				ZP BC	552	221221	000	·	009	00 0	101	000	8912	ITTE	ez ez	115/02	52 8151	300830 00	150	80	<u> </u>		HUDIESTON		811 514 24
						697571	000	·	20 61	671	ZS'91	000	97'IZ	50.051	29 21	99 808	97 0101	300 # 29000	110	250			hudiestoni		VIL'STH IA
8151 1800 SJH				28.43	222	109 06Z I	000	·	10001	19.5	25 01	000	1502	25'11	51.52	91 2221	09 996	303026.05	120	680			Hudiestoni	L KI E Por	ILOL STHOL
				81.05	81,5				5951	66.2	16'92	000	22 02	10 961	51 22	19 6001	22.1111	92 +26900	65 0	22.0		;	Hingjestoui	HAN BERN 1	101 STH 69
2151 8200 514			<u>×</u>	59.62	5.16	18 0821 10 2971	000		29.21	00 0	00.6	000	82.02	45.70	57 87	99 6222	97 /ZS1	10 02/962	570	101				100 B 101	86'514
				41'45	202		000		59 57	199'1	195	000	59'41	01.15	160	99.812	80 919	11 67CB/Z	100	80 0				10d 3 (X 1	67 HL5, 8 A
HLS: 070731H				54 58	88.1	1122 20	800	·	28'27 26'2	201	00 59	000	195.61	1911	2121	09 508	61'289	19 8/1800	580	140			Hudleston!	104 3 1N 1	88'SIH 89
				36.21	107	197361	000	·	202	5 00	15.34	000	50 43	57 59	59.92	PZ'9811	69 9901	304228 69	800	0211			Hudicaton	T KI'E LOL	¥8'STH 99
1151 0750 1541				25.64	506 202	00'2+21	2000	-	291	5.02	84.2	000	04 02	68 9	0091	EP'PC11	02 6001	11.052005	150	850		-Yrtang	Wheatleyen	TIN E 64	87:214
		×	×	31'41	E1.5	92'1901	000		01.2	512	62 C	000	09 61	68.8	31'00	1240.16	1065 64	20000000	870	090			URADINEOUAA	1 10 E 60	11 A 7 2.2.14 60
				97.20	107	19'1ZC1	1770		1991	SIZ	900	000	50 61	96.9	HOZZ	909121	92 0601	305120110	10.0	050	I		MANDON DA	AH 3 DI 1	IAT SUH SO
				92.11	501	05'1121	000		512	12.1	09.9	000	59.61	12.91	ere .	54.916	16191	12 916900	90'1	100	I		Weenesum	PA B- DI 1	89 91H 09
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	<b></b>			08'21	520	1404.04	6>0	-1	21.9	995.0	115	000	1102	68 51	51'99	6> 0801	1320.68	02 957/00	190	980		- e	Wireadoyen	- KO - E 64-	8 C 'SIH 99
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·				20'13	60 Z	89 6191	80	·	80.8	62.1	51'48	00 0	89'61	11.6>	11.61	61 0+6	92 9601	205225 68	180	82.1.		2	Westleyen	E, Kimm,	80 HI4 88
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E. Ryaz	E. Ryaz	E. Ryaz,	E, Ryaz,	E Ryaz	E. Ryaz	E. Ryaz,	E. Ryaz	E. Ryaz.	E. Ryaz.	E. Ryaz	E Ryaz,	E. Ryaz	E. Ryaz	E. Ryaz,	E. Ryaz,	E, Ryaz.	E, Ryaz,	E, Ryaz,	E, Val.	E, Val	E. Val.	E, Vat.	E, Val,		E, Val.	L, Val,		Val, Haur,	Val. Haut,	Val, Haud.	ValHaua,	Val, Haur,	Val-Haua.	Val Hau	Val,-Hau				Kann I	L. Kimm,	L. Ktmm.	r. Kimm.	L Kimm.	L Kima,	r Kinn.	L. Kimm,	L. Kimm,	L. Kimm.	L. Kimm.
H kocS an	H koc. S.an	H koc, San	H koc. S.an.	H.koc,-S.en.	H.koc, S.an,	Hitoc,-S.an,	Hitoc. S.an.	H kocS.an.	H koo,-S.an	H.koc,-S.an,	H koc. 8.an	H too, S.an	H.kcoS.en,	H.kocS.an.	H kocS.an	H.kocS.an.	H kocS.an.	H.kocS.an.	N.KEmov.	N klimov.	N.Kimov,	N.k@mov.	N kilmov,	N. KEIMOV,	N klimov,	D bidichot	D bidichat.	D bid,-H boy.	D.bid,-H.boy.	D. bid, -H. bay.	D bid . H boy	D.bid,-H.boy	D.bidH.boy.	D bidH boy.	D bid,-H boy.	D.bidH.boy.		Muabilis	Mutabilis	Mutabilis	Mutability	Mutabilis	Maabib	Mutability	Mutabilla	Mulability	Mutabilis	Mutabilis	Mutabills
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498	87	4.31	7.31	388	4.98	508	4.56	12	4	5,19	8.24	4.78	4.45	08	8	8	8	8	08	8	8	8	8	8	8	8	8	8	8	ŝ	08	8	0.00	80	08	00		8	8	8	8	8	8	8	8	8	8	8	8
2 48	8	2.42	1.88	2.08	2.08	1.07	2.73	2,48	1.93	222	200	2.02	2.53	2.61	2.04	1.71	1.75	2.76	1.47	Ę.	- 92	1.78	1.75	1.70	2.08	<u>.</u>	2.18	1.98	1.65	1.25	2,66	E	1.44	1.68	1,50	18		14 88	36.16	3.70	3.57	3.76	1.75	3.28	3.26	2.26	4.07	2.73	38
1	1.81	- 58	0.88	10	-		1.10		8	1.28		1	1.7		50	1.8	0.08	100	000	1.00	0.88	0.15	0,10	- 88	5	0.77	0.39	0.9	8	1.87	1.2	1.08	0.0	0.86	0.98	1.24		1,18	Q	2.83	3,28	2.58	2.36	2,45	2.63	1.2	, <b>6</b>	38	2.81
30 73	8.ZZ	3.92	597	19.85	19.62	6.26	5,71	9.98	12.60	18,40	822	4.83	14.43	12.87	11.7	6 80	8,43	8.83	8.76	11,95	7.80	4.58	6.39	0.03	802	4.51	7.80	10.10	12.39	10.47	149.99	38 82	12.65	7.71	809	3.45		3 82	3.95	333	3.34	2.68	38	5 53	5.75	2.38	835	3.65	3.90
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<b>I</b>			1	1131 33		1	T			1	÷	ī	T	1						-	1481,50	1361.03	1	1308.89		1342.30		<b>—</b>	T	1207.03	1214 34	1336,12	1429.28	1363.50	1339.47	1344,84		1222.81	1219.19	1336.00	1234.80	1482.59	1480.38	1271.84	1235,11	1203 20	1290.25	1160 64	1201.18
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					SS 2>	10 +	20 9001	8C 5Z		02.9	60.2	532	87 6	25 83	58.91	20'21	01.050	92,168	STRICOLC	900-	65.0-		- ODIA	(¿) x8W ()	- (L) - (ADA	189 bC5 31
					20'27	05 6	07198	0021		REZ.	12.8	52'1	60.6	72'17	61.81	81.8	99 696	92 968	302939 68	05'0-	81.0-		quoter	(¿) xwu ()	- (c) 000A	101 bC5 1 B
					11.12	29'1	27 798	997		79.1	26'1	86'1	81.1	2911	69'2	00 0	68 0001	686.33	251275.65	023	-0.64		-quoter	(¿) xưu (j	(¿) ·@ioA	198 PC2.1 A
۱ <u> </u>					98.41	677	823 36	051		89 61	52.5	991	29 7	\$9.61	26'8	18'81	91'169	97 2/9	561565'14	87'1	92.0		Cylindro.		E, Callov,	188 bC1: 8
· <u> </u>			—		18.21	555	72752	571		<u>207</u>	5.68	1951	29-1	28.71	81.7	00 0	17 666	192.63	S68065.18	871	0.12		Pachy.	C. clutmae	E. Callov.	194 BCI! VI
·	95001	- <u>x</u> -	<u></u>		16 61	5.84	07'612	02.1		91'2	100	EP'1	25'1	50 CZ	223	5.55	108241	89 184	09 996262	991	15.0		Pachy.	C.elamae	E. Callov.	183 BC1! M
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					53.40	578	59'168	117		21-11	3.24	18.1	16'1	<b>78 62</b>	95'51	000	195 528	11111	585410 45	090	60		- opra	P. studen.	E. Val.	192 KHI8 10 20 B
·					66'61	2 63	159101	584		06'11	875	522	89 S	21 60	24.51	000	91 2/9	56'6//	296956 96	110	22 1.		Arcto.	P,stuben.	. (N).	109 01 BIHNISI
J					85.62	110	C9'108	687		105	11'0	1.40	28'1	SI'12	82.8	000	99.159	01.488	208312 00	20	120		Pachy.	P,stuben,	E. Val.	190 KHI9 110
·	Sudda ni				12.34	90'5	109011	697		CP'S	3.68	191	1 20	22	C8 8	000	08 109	20 858	LY 0//052	1.34	02.0-				72437	188 KHIJC' 3'40
·	Configuration of				54 20	592	82.428	500		1540	5.69	95'1	291	69 72	19'11	000	95 872	10.657	90 #8:8/Z	210	120		C/man.		726/37	188 KHIZC 1'CO
					105 SZ	200	82'5221	95'1		10'2	572	573	192	50 72	96.7	85'6	85928	1517121	87 996622	98.0-	12.1-		Cylindro,	H KOC, -3.80.	E, Ryaz,	187 KH16, 2,40
. <u> </u>			·		29.95	222	1003 37	112		90'8	121	18.1	271	06 02	52.6	00.0	05'112	123 651	99 94C69Z	0.55	52'0-		C/µquo'	H KOC. S. DI.	E. Ryaz.	188 KHIG 1'22
					10.12	524	10001	84.0		91.9	512	917	90 +	11 OZ	08'2	59'+	129861	PC 8511	20111182	150	110		C/Trate	118.8-, 303.H	E. Ryaz.	188 KH18 1'13
			<b> </b>		11.00	500	02.0701	985	ł	<u>67.6</u>	500	5 20	172 C	88'12	69.8	60 VC	100+001	152.43	284884 E8	580	570		Chinato	H KOC5.07.	E, Ryaz.	194 KHIG 0'80
		<u> </u>	<u> </u>		10725	27.2	57 0211	890		678	07'1	191	100	21.23	96'01	00 0	59 96Z	SZ 169	59 Z8/68Z	92.0	19'1-		Arcto.	NOWIN	E, Val.	183 KH13 4 32
I					10 22	212	1062.45	ar	1	14.81	891	95'1	89'1	05'K	08'61	00.0	452.03	57 109	336489 04	90.0-	90 0		Pachy.	N ICINOV.	E, Val.	195 KH13' 5'30
					32'46	82.5	1003 63	000		91 GE	500	92'i	00'1	51.26	15.61	00 0	69'1221	1118 33	10'127182	00'1	20 0		Chindro	D DKI H POX	ValHaut.	181 KHI-4' 31'40
					57 22	81.5	90.1361	000		90 61	5 38	22'1	82.1	18 22	11.9	18.81	67 5601	13.1001	588848 23	5.22	210		Cylindio.	D PRI 'H PON'	IneH- Iev	118 KH1-4'30
		. <u></u> .			54'40	100	21 0221	52		10.14	514	191	1.54	50 SZ	99.6	000	12574	1003 36	205114 35	3.30	<b>15</b> 1		Cylindro.	D PIQ H PON	N#NV	ROL'P PHIN BLL
1					29 92	3.38	05'1811	EZ C		55.0	513	59.1	00 C	9972	12 00	00 0	10101	89 + 56	596941'84	343	101		Cylindro.	D PICT +H POX	ValHaur,	101'9 '9" HX LLL
ļ			<b> </b> i	<u> </u>	98 90	01.5	11.2+11	101		Z9 C	5.46	10.2	1.54	80 52	10.01	00.0	22 2001	12 066	81 29996Z	OZ I	86'0	1	"quotien	P,stuben.	E' AºI'	176 KH16, 27,00
					09.90	21.5	101021	727		28.51	991	201	105 +	54 BB	0Z C1	000	15'195	95'112	07.788100	<u>α</u> .ι	12.0		<u>۱</u> ۷.	P, stuben.	E. Val.	176 KH18, 11, 20
		·			51.69	30.6	27 268	411		8.92	52	52 1	513	21 92	08.8	00 0	111125	99 1ZL	202623-82	58 0	67'1		Contribució	P, stuben.	. vai.	114 KHIB 10.80
ļ					62'21	987	16.1801	5007		517Z	12.2	191	20 1	10 12	8.24	87 6	19'219	89756	3018335'14	100	61'1		5	P, etuben.	E' A91'	173 KH18, 2.85
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			_ <u>*</u>	<u> </u>	9592	568	195211	ez c	·}	101	82.2	212	89 Z	1272	9Z 9	8+ Z+	10 6921	08 5251	58 61 5282	10.0	120	<b>—</b>	Cylindro.	B. meaes.	้ระไม้ๆ	121 KHI12 328 1
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·				- <u>x</u> -	20 20	5.66	ZPZEII	67 6	·	21'C	191	5.63	1959	51 42	109	50 10	185 281	07.969	09 519162	210	950	1	C/man.	. eoeom.8	70/87	09'0 PLINX 891
I			I	<u> </u>	92.07	5.60	20 9211	285		27.5	521	181	188	1102	72.6	000	29 889	11'096	70 957962	60 0	190		'quođej	.eseom.B	70/87	108 KH112P 1'02
					59 60	582	PC 828	1.44	╂────	61 C	291	25'1	0.8	52'12	16'2	000	87 209	0+916	20100301	28 0	ī9'ī		<u>Sotoriny</u> 2	B.means,	'ze/8'1	187 KH175, 1,75 8
I		·	- <u>x</u> -	x	68 OC	μz	1056.22	07.1	1	21'5	67'1	59'1	277	2022	90.8	26.61	9C 029	87,789	303880.43	590	500	1	<u>Sorbrity</u> D	B.moses,	78/27	182'1 '921Hx 881
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			1	I	31'00	212	51 2901	687	†	95°C	201	28.1	181	51'89	<u>97.8</u>	000	94.489	36.216	303993 92	61'1	80.0-		C/Undro.		, Ser A.J	183 KHI12P 1'52
			í——	1	PL'Z	512	1183730	188	1	+5.1	121	18.1	987	28.15	25.9	150	2.782	92.188	26 05/600	62.0	29.1		C/mano	B.meses.		182 KH11291
		t	×	<u> </u>	30.05	5.80	ET.8851	19.1	1	52.5	1Z 1	C8.1	159	22.22	02.8	00 0	60 65/	20 689	314877.65	62.0	12.0		Cylindro.		, Ryaz,	A 02.0- 161 KH1781
		t	<u> </u>	1	39'12	5.60	119811	222		91'5	57.5	50.9	687	16.22	<u>17,</u> 8	91 CZ	12.1221	1220 82	310306.96	SZ 0	-1`0		CYINGIO	្រះលខោយ ម៉	<u>รญชา</u>	160 KH176 -1,00 F
			1	1	22.00	64.2	116.1811	EZ.1	1	SI'P	197	542	16.6	88 22	65.8	70.57	02 9261	1548.39	308430 55	20	61'1-		Cylindro.	. eacam.G	, Kyaz,	100'1- 921HX 891
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			1	·	12.15	5.66	21'1601	295	·	00 C	231	19.1	18.5	89.61	<b>29</b> 9	80.71	CZ 598	ZZ 969	07.870716	<b>96</b> 0	0.00		1-(C2)-M	H KOCS.BR.	E, Ryaz,	186 XH16 3.60
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				29.62	222	89'6PC1	51.1	i		3.85	890	000	PP 61	62.01	62 51	SC 192	05.417	310352 66	25'1	201		COMMAD	,100,9-,Wa.N	E' Asi	387 608 018
	x	×	x	<u>u</u> w	511	1361,60	000	I		12.7	99.0	000	19 61	11 8	000	21.123	CS 9/9	20 228515	x	x		Arcto.	100.4 . W # N	E. Val.	283 PC9, G18 B
				1872	SIZ	00 1051	000	<b> </b>	82.2	10.1	21'1	000	67 61	<u>Ш</u> е	190	**5 43	06'#601	203205 01	92'I	<u>67.0</u>		Pacity	NO & NON	E, Val.	281 6C8 C18 V
·				12.71	027	<u>79 9621</u>	000		1112	QC 7	0.84	000	81'61	81.8	25.5	229 622	00 524	310229 50	x	*		- Aroad	NAM P DOL	E. Val.	580 PC9, G17 B
				19:23	212	PZ PICI	10 31		60 2	6C 7	180	687	92 61	85.6	6972	322 51	10 191	200003 22	1.37	02'0		- Aused	New P. pol.	E' A'9	1219 600 611 I
}				0072	91'2	597661	000		197	9272	160	000	11.81	99°II	000	52'117	01 005	304158 38	x	x		2010001	100 G. V. W.	E' AN'	378 PC9, G16
				31.54	551	81 0201	650		0.02	00'5	55'1	180	62 61	39.65	80.0	282 90	12 909	59 969ZIC	x	x			IOU - WEN	E. Val.	<u>211 66' CI2</u>
				10.81	504	1450 24	000		98'1	111	<u></u>	98'1	77 81	11.6	000	17 657	60 198	08 951ZIC	;	x		- Auron	100.4. N . N		316 bC8' CI40
	×	<u> </u>	X	50.00	<u>500</u>	98 6921	000			97.7	280	000	19 61	6911	99 9	501'00	012.76	207973.95	<del>اي</del>	x		Pacity	100 G . 1/9 N	E' AN'	219 BC8' GI4 B
			<b></b>	60.02	5.24	1320.84	000			01.5	121	000	22'21	190	000	17217	90 919	58 592/05	<u> </u>	<b>.</b>		- Aurea	IDd d WWW	E. Val.	314 PC9 CI4 MI
	- <u>x</u>	<b></b>		19'1Z	112	24.0461	000		999 52	197	62'I	021	19.33	34,16	28'61	329.650	12 624	210210 67	65'0	0.36			Nay P. Do	E. Val.	513 6C8' CI4 M
			<u> </u>	1916	<u> </u>		<u></u>	ł	55 50		<u> – – – – – – – – – – – – – – – – – – –</u>		~			~			<u> </u>	<u> </u>			100 G- X = N	E. Val.	- 609, 013
			<b>—</b> —	28 51	5.10	CO VEZI	00 0		89'5	98 7	SZ 0	199	25 81	91.6	000	255 86	07'191	200428 43	17-	x		- 2	Nay -P. pol.	E. Val.	315 6C8 C13 B
		<u> </u>	<u> </u>	82.82	01.5	92 6911	000		50.7	2.83	220	9.38	67 61	29.6	08.9	1Z 609	61.708	311118.64	225	100		<u> </u>	Nev. P. pol.	E. Val.	511 PC8, G12 A
			┨────	2	010	ac 0851	1000	<u> </u>	302				-		<u> </u>	~ ~ ~	-						IDD	E. Val.	- bc8' CII
			<u> </u>	El'OZ	520	69 9121	92.0		50'80	S1'9	20'1	10'2	01 61	65'07	00 0	87 017	82.057	2102492010	19'1	0.43		- ODA	100 d . WIN	E' AN'	110 PC8. GIO
			I				20			<u> </u>		<u> </u>	1		<u> </u>				-			<u> </u>	100.4-1(e.N	E' AN	60 604 ~
			I	1972	5.06	19'1001	000		98.8	<u>/5 9</u>	88'0	3.85	¥2'61	14.38	000	96'175	25.528	303514 ED	x	x		VICIO	100 4 W 1N	E. Val.	263 bC8' C9
			<b> </b>	59.92	612	61'20+1	000		58.92	87.9	081	09 7	01'02	02.74	15.01	00 69/	56 726	201202 22	x	x		VICIO	100 4-WSN	E. Val.	11 20 '60d 852
		- <u>x</u> -	<b></b>	20 22	112	1488.30	100	·	80.6	10.1	68 1	60.01	58.02	13.20	91.0	484 30	18 6/8	90 9/090C	100	20	I		New P. DOL	E' \NI	120 '60d 192
			<u> </u>	19.02	518	EP PZEI	000	·	34.44	95'2	29'1	1279	11.61	21'901	000	10 525	109.168	312120 28	020	670		- ODIA	N ey-P pol	E. Val.	\$88 bCB' CG
J			<b> </b>	99'61	572	12'1001	<u>ar.</u>		00 0Z	89'Z	82'1	111	50.02	28 91	110	21.100	91.928	215181'40	×	x		- Auped	Ney Ne N	E. Val.	589 bC8' C2
			I	51.52	520	6Z 8ZZ 1	000	·	5 48	82.8	109.1	69 CI	99 81	2+6	51 35	19 665	82+28	2036832.33	220	820	1	N	100 - K . N	E, Val.	581 bC3' CH
				51.68	227	122503	000	·	81'2	10.0	291	108 8	92 02	126	000	21.667	51'202	11100/05		<u> </u>	·		100 d WS N	E' AN	263 bC8' C3
			<b> </b>	8572	5'18	92'9521	000	┨────	51 90	90 01	1051	1581	27 61	10989	189	69 5/5	28 959	19 529900	i	ļ.—			100.9. W. N	E' AN	285 bC8' C3 8 8
		<b>├</b> ───	┞───	09'61	51.5	CZ SZZI	000	┨────	25.91	85 01	21-1	62'51	09.02	38.35	160	18'119	60 619		1000	150			IDD - Man	E' A¤'	201 LCB' CS B1
	- <u>x</u> -	<u> </u>	- <u>x</u>	1191	57.5	1416.36	000	·}	88	10.11	291	09.91	68'61	1/ 98	807	39 160	91.172	2152215	X	1	<b> </b> -		NSY -P. DOL	E. Val.	500 6C8' C3 V
			<u> </u>	08.61	5.18	96.1361	120		6, 22	12.00	181	1951	72'61	61.85	<u>11.6</u>	65'979	29 558	310331-33	100	<u>110</u>	ł	Arcto.	100 - W 8 N	E. Val.	263 PC9, G1
	· ·	—		19 72	527	09 5811	000		69 101	13 00	05'1	19'91	11 OZ	25.115	13.64	12 582	92'091	11.680110	x	x		· ~	100 9-1121 \$	124 - 43 1	268 PC7.c12
								-l		~			·[			-	-			ļ.——	1	<u> </u>	. 100.97151.8	101.14	119,739
		<u> </u>	<b> </b>	09.81	522	22 2251	000		92'92	21'51	02'1	14.94	20'85	69 CZZ	000	432 CR	05.701	99 695IIC	1	x	<u>├ ──</u>	Chiped	. IOQ. 9- XIZI. 2	184.481	267 PC7.c10
·			┨────			-	1	<u>↓</u>				~	-	-		-	-		-		× -	<u> </u>	Log. 9- Jizi 2	L RX+ Val	89'ZOd ~
		I		191	5.24	126921	000	·I	101	SI'ZI	52'1	96.41	02.02	06.6	000	25 680	62'512	99 66C60C	x	×	<u> </u>	Pacity.	Ind G- NIZI S	121.14	266 PC7.c7 8
·	- <del>x</del>	- x		00 91	5 28	71.1951	000	·/	100	102	UT1	11 01	16 02	578	68 1	19 165	95 669	208249.64	62.0	21'1-	·	Pactry.	Jod 4- XIZI S	LEV-VAL	268 PC7.c71
	<u> </u>	<u>-</u>	<u> </u>	90 62	528	1518 24	000	<u>+</u>	91'01	12.62	1.62	50.8	27.23	15.60	000	60 6/5	69 6/9	64 975805	81.0	98.0	1	~~~	Jog 9 . xist 6	144-141	282 PC7.c6
	<u> </u>	I	I	026	19+	PC 6001	540	21.5	80.01	000	111	000	CV ZV	NC.81	000	17 095	21842	112289 PM	1	1	1	<b>,</b>	1		~
		I	ł	26 67	2/ +	00 +001	890	020	125.01	000	SI'I	000	59.6>	62 61	000	CZ 999	12.417	311566336	1	1	1	·	<b>1</b>		·
	—	ł	1	02.87	11.1	1011.38	29 00	111	10.44	000	91.1	89 1	99.05	29 61	000	91'929	18 BPL	320475 09	99 0	150	1	Arcto	. log. 9 xist. 8	124.481	261 PC7.c5
			ł	99.9*	191	1012 02	9C 12	92 9	18.5	00.0	691	000	43.90	69.81	000	99 987	IT'IZZ	200289900	x	×	1	Pachy	100.9.JIS	184.481	260 PC7 c4 8
	- <u>x</u> -	- x		15'57	191	19 1001	45 20	189	15.6	00'0	001	000	20 95	15.61	201	378.12	11.201	21.88281E	51'0-	520	I	Pachy.	. 100, 9XIS), 8	184.481	249 PC7,c4 A
			<u> </u>	69 51	99'9	27 6601	31 00	91'#	12'9	00.0	55'T	00 0	01.29	07.61	0011	99'LZS	1221122	12'972900	×	<b>A</b>	i	Pachy	.100.93121.8	ר אי יאשו	348 PC7.c2 II
		L	L		T			<b>1</b>	<u> </u>		1	1		-	-	-				A					

ſ.	336	336	334	ម្ព	:	ž	ar a			İ.	329	328	327	12	ž	ž	32	32	126	32	319	۲	12	١Ľ	12	214	١,	2	312		[]	2	5	ទ្ធ	<u>چ</u>	g	ğ	ğ	۲	g	벐	301	ij	23	2	297	280	296	204
	02.1 CNS	6 SIC: 0 85			2 SK3, 0.10	1 SK2 4.55	0 SK2 4.40	SK2 3.30	SK2	SK2 2.20	SK2: 2.15	SK2, 2.00	1 SK2 1,80	ន្ត	-		SKZ	2 SIC2		SIC 2		SK2 0 65	SK2, 0.45	202	SK1:	ISK1:	SK1; 60.20	SK1: 52.50	_	SK1: 50.00	SK1; 47,10	SK1: 48 60						-			SK1: 4 00	PCIO B							
1.50	1.20	085	SK3; 0.25 B	SK3; 0.25 A	0.10	4.53	-	3.30	260	2.20	2,15	2.00	1,80	SK2, 1,50 C	SK2, 1,50 B	SK2, 1.50 A	SK2, 1,30 B	SK2 1.30 A	1.25	SIC2; 1.05 B	SK2, 1.05 A	8	0.45	SK2; 0.00 A	SK1; 68,70	68.30 A	80.20	52.50	52.30	50.00 0	47,10					SK1: 5.90 C	SK1; 5.90 B	SK1: 5.90 A	SK1: 4,50 B	SK1: 4.50 A	8	B	A	A			325 8	_	PC9, G25 AI
E-M. OM.	E-M. Od.	E-M, Orf,	E.M. Orf.	E-M. Od.	E-M. Orf.	M, OM	M, OX.	M. Oxf.	M. 04	MON	M.Q.	M, Orr	M OT	M. Orf,	M, OM	M. 02	M, OH,	M, Orf.	M. Od	M. Orf.	M. OM	M. 01.	M. OX	M. 01.	E, 011.	<u>г</u> . Од	E. O.1.	E, 011.	E. Orf.				E. 0x1,	E. Oxi		Г. 92	Р. 91	E, 011	e. <b>0</b> x1.	F. 011	E. 011	L, Val, Ha.		L Val, Ha	L. Val,-Ha.	E, Val,			E. Val
Cor-Den	Cor-Den	Cor-Den	Cor-Den	Cor-Den	Cor-Den	Den-Ten	Den-Ten	Den-Ten	Don-Tan	Don-Ten	Den-Ten	Den-Ten	Den-Ten	Don-Ten	Den-Ten	Den-Ten	Den-Ten	Den-Ten	Den-Ten	Den-Ten	Den-Ten	Den-Ten	Dan-Ten	Den-Ten	Mar-Cor	Mar-Car	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Mar-Cor	Nhi-Cor	Mar-Cor	Mar-Cor	Mai-Cor	Mar-Cor	H.bojarken.	H bolarkan	H bojaritan	H bojarkan,	N.syr, P.pol.	N.syr. P.pol.	N.syrP.pol.	N syr. P.pol.
ľ	C7)	Ν.	[] [] [] []		Pachy.	Cylindia.	( <u>;</u> ) <u>, (</u>	ľ	ľ	ľ	Cylindro,	7	( <u>5) 14</u>	× ×	Cylindro?	1	Cylindro.	Cylindro.	Cylindro.	Cylindro.	Cylindro,	N. (C7)	[2] Y	~	Cylindro.	N. (C7)	ľ	~	(0) <sup>1</sup>	ľ	'	M. (C7)	×.	₩. (C.)	Cylindro,	Cylindia.	Cylindro.	Cyfindio,	Cylindro.	Cylindro.	Y. (C.)		ľ	ľ	Pachy.	Arcto,			~
×	ļ		ļ						-																		×			×	×													~	·   ×	×			
,	1.30	50	.1.45	0.92	023	98	0.03	,	,	,	98	5.79		0.27	020	0.9	0.27	-0.61	0.21	1.8	0.75	80.0	-027	034	5	0.14	,	50	0.41		,	0.15	0.61	0.30	077	1,28	0.87	1.6	0.90	1.24	045	040				0			0.17
	307	1.61	2.58	1.08	1.8	304	3.01	ļ,	l,	Ì,	3.15	2.95	1.80	3.22	3 89	3.79	2.25	4.02	3,98	3,15	2.64	354	2,41	2.75	2.62	1.89		3.87	2.45		,	2.68	2.81	2.62	2,49	211	2.54	2.13	ы 8	214	2 39	084	<u>; </u> _			5			0.85
[	303920.71	304808 82	305617,17	302982.20	294496.21	301665.93	308311.10		ļ		299092.63	304389.32	300250.58	289301.89	307832.38	30113241	305518.97	301249.11	304408.51	305940,18	307649.75	304284.66	29 000962	302041,86	301025.20	302582.10		305670.99	303006.97			301222.40	312783.14	304178,11	311144,15	305334.55	304953,78	297708.71	3058336.68	295361.82	304765,15	305/02.30	304399,14	304497.04	299072.38	302835.23	303273.98	303936 87	303257.50
	980.57	1035,45	1148 09	1250.00	÷ –	1042.31	878.31	,	,		-	8008	857.54	822.01	990.36	899 G2	1050.20	848.50	848.45	1017.85	í		1098.14	1113.05	991.92	1118.73	<u> </u>	788.34	1000 61	  ,	ļ	1004.53	917,86	1004.00	1028.29	1220,43	809.76	880 64	1141.53	1040 00	1172,46	784,73	10,00	641.30	1178.17	770.86	1	1	749.06
	825.05	1300.59	1098.33	1340 02	850,71	1120.04	748.04	ļ,	<u> </u> ,	,	1418.85	1413 92	896.73	8	5885,15	848.41	1370.07	887.24	800 85	908.28	1015.29	942.85	1573.01	1369.88	912.03	1100.74		942,08	1187.33	ļ.	  ,	1063 03	909,76	1334.86	1128,71	1481.37	884.47	1180.51	1574,45	1349.09	1860 88	381.70		200	1157.29	422.48	534.20	405.84	417.25
	31.10	15 46	22	40.12	1. 8	43.77	18 38	,	ļ,		33 IS	37.38	15,16	202	15 S	1272	3	17,05	33.68	23	22.78	16.70	19.61	35.36	43 87	45.29	.	15.70	57.57	],		643	35.47	55 <b>0</b> 0	38 1 J	43.97	30 S7	33.75	29.25	36.70	ង ទ	992			26	8	8	8	8
ļ	280	7.90	5.64	17.24	1.2	044	9.79	,		<u> </u>	1.18	ខ្លួន	7.03	8.98	15.85	4,46	4.70	80	4.75	8	1.2	88.77	21,92	382	13 68	31.07	<u> </u> ,	1.35	44,61	  ,	ļ,	25,18	0.00	0.33	11,74	32.67	0.25	4.76	0.87	0.75	11.77	ay	204	820	85	88	8.75	8.46	8.77
	2.64	23,78	2	278	21.11	23	2	,			19 [2]	23	28	24.24	20	21 19	23	21.68	24,77	29,16	25.28	278.639	24,44	24.14	29.62	20	<u> ,</u>	23	3	<u> ,</u>	ļ,	23	23	77,72	29.57	77.53	20.02	23.87	22 23	22.09	28.96	18.40	2 A BI		8	18.77	100	18.38	19.10
Ŀ	17.25	26.75	23.16	22.85	22.76	12.11	8.22	ļ,		ļ,	14.70	1321	14.39	រី 8	91.00	19.00	128	11.78	13.80	94 Q	19.17	31.97	10.71	1388	74,85	20 38	,	9.57	12.17	,	ļ,	21.47	8	30.78	62,13	27.93	1251	22,689	11.24	12.86	22,45						8	8	8
ļ,	0.93	0.85	1.2	0.94	96.0	1.66	1.01			,	1.94	2 09	1.83	1.06	1.4	1,54	1.17	122	1.18	1.18	1.73	1.80	1.77	1.17	1,49	3.24			2.56	,	,	1.78	1.34	1,39	2.29	1.41	1.11	1.19	2.05	1.20	30 81			0.81		1.18	10	0.99	<u>.</u>
ļ	8	3,78	253	3.26	227	2.71	2.13	,		.	38	27	2.12	219	1.88	1.71	3.33		2.68	2.26	2.2	1.7	3.04	277	283	301	,	2.10	2.63	,		2,95	2.35	2,70	1.93	1.64	1.40	1.52	2.03	1.86	5	199		29		3 3	38	ы 8	3 8
ŀ	421	4.97	3.29	7.48	299	368 89 C	8.28	<u>,</u>	 ,	<u>,</u>	8.14	43.38	944	8.74	11.25	8	3.10	558	9.91	3.97	5.40	22.90	13.92	12,43	849	0		355	14.26	<u>,</u> 	<u>,</u>	13.78	2.58	2.78	8 8	15.25	3.22	5.8	2.83	2.67	11.39					48	2.63	5.92	6.03
ŀ			 					, 	.  -	<u>.</u> 						l İ.										  .	, 			<u> ,</u> 	<u>,</u>		<u> </u>																
ŀ			3.21 10		1		1	,	<b>,</b>	, 	223 10	-	238				i	T.	1	1	38	T	38	Т	T	i	1	338	23	, 	, 	221 8	ì	ī		ί.		2,75 0	1		382 9								8
ļ.	802.78	65.97	0000	823.49	1249	818 65	02.63	ļ.	ļ.	<u>,</u>	1018.24	990 12	02.77	857.58	872.97	1042.48	816,73	88.83	811.59	927,08	833.30	63,79	826 82	8	797,69	810.23	Ι,	877,50	898 50	<u> ,</u>	ļ,	802.88	864,78	861,33	941,06	1058.86	8896 SJ	845.95	861.13	80.80	82.76				13/2 83	120211		1311.05	1306.90
ŀ	1.80	2	1.07	1.83	1	1	1.87	ļ.	<u> </u> ,	<u> </u>	100		1.92		Т	T	1.82	1.8	1 R	19	1.98	T	i	Т	28	1		1.02	217	<u> ,</u>	<u> ,</u>	1.8	1	T - T		1.8	T	Ī	1	1.18	2,18		3 A 7 0	ī	ī		1	T	
ŀ	24.14	8	8	13.52	15 20	21.34	21.33	<u> ,</u>	ļ,	<u> ,</u>	18 88	29.66	20		17	21.15	21.39	22	24,18	24.32	18.12	21.93	25.81	10.48	27,19	21,40	<u> </u> ,	18.46	23.14	<u> ,</u>	<u> </u> ,	16.83	17.47	24.78	31.01	29.40	78,77	31.81	24,17	17.58	39,14						3 3	8	22.33
	<b>×</b>					×		L		ļ						-		ļ		<u> </u> *	×		<u> </u>									<u> </u>	ļ	Ļ				×	<u> </u>	×	Ļ	ļŀ	·	ļ	ļ	ļ	<u> </u>	ļ	$\square$
	-		ļ		ļ	×		Ļ			ļ	ļ			ļ	×		Ļ		×	-			ļ								ļ			Ļ	<u> </u>		×		×	_	·	·	<u> </u>	-	╞	+		$\square$
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<u>س</u> ا		Cor-Oen	2										7.19	R	4.82	8			_		İ	Ì	
<u></u>	1	CorOen	ž			2000		896.09		8	22		8	248	3.13	6	7 882.07		10.00	×	×	×	
		Cot-Den	(-) 'N		880		_			130			1.42	8	5.50	2		202					
		Cor-Den			0.14	_				2.56	24.73	21.67	0.79	8	4.27	1.31		15 2.10					
	E.M. Ort.	CorDen	<u>لا (ن)</u>	×	8	2001 2047						39.18	38	2,2	8.45	B.C.				*	×	×	
T	T	Cor-Den	<u>۲. (C.)</u>	┦		_					20 22 10		9	2.45	5.43	1.57			11 02 8				
Ī	.i	Cor-Den	Pach.				<u> </u>		080 24.60	31.16		1	1.42	3 2	5.87	22	0 1014.54	200	1923	ĺ		ļ	
SK3, 558 (2) E	J	CarDen	Pachy.	<u> </u> 		_	_		969 00 11,16			10.61	1.15	28 7	2.78	7	1010 67		F		ĺ	Ì	
<u>ש</u>	E-M. Orf.	Cor-Den	N. (C.)		9 9 9	3 05 3002	303202.25 67	675.38 71	715 02 10.18	25.60	8 28	20	880	2,46	5 65	306	5 000 S4	2.16	6 19.30				
<u>a</u>	Ī		ž	×			_		697,92 24.49	G 902	8	0.00	1.16	2.67	3.35	1.28		3 2.14	4 17,56	M	×	×	
<u>ש</u>	E-M. Orf.	Cor-Den	Cylindro.		20	3.30 2974	297462.02 1012.59		747.70 14.16	0.00	00 23.87	1.78	3.06	3.6	5.52	3.14	617,31	2.11	1 17.78				
E	E-M. Ort.	Cor-Den	M (C.)		0.83	3 01 301Z	301227,51 784	784.06 74	749.17 17.17	11.30	30 23 60	Ro	96.0	268	2.06	254		32 2.14	20.67				
SK3, 6, 15 B		Cor-Den	Cylindro?										18	282	4.83	1.51				×	×	×	
SK3, 6, 15 C	E-M. Orf.	Cor-Den	~			3.96 3040							107.10	260	270	300		8			H	×	
SK3, 6, 15 C	E-M, Ord,	Cor-Den	,			3120	312072.83 781	797,68	729.31 0.00	26.63	83 52 68	80	<b>98</b> .68	800	4.32	3.16	B 701.60	20.012	7 49.24				
	E-M, Ori,	Cor-Den	Cylindio,		0.42	4,14 30200	302004.00 781		670.81 13.40	000	24.01		0.96	2.16	2,41	3.60	0 628.30	_					
SK3; 6.40 A	E-M. Ort.	Cor-Den	Cylindro.		0.68	2.87 2990	296014.35 826	828.10 92	924.01 16.65	35 1,62	22 23 63	0.78	800	2.96	3.10	0.61	1 812.19	19 2.15	23.94				
SK3; 6.40 B	E-M. OH.	Cor-Den	Pactry.		1.30	1.74 30200	302051,50 867	867.76 83	830.96 12.41	13.66	56 24 65	80	1.29	2.46	3.48	8	82,038	208	8 18,18				;
ш	E-M, Ort	Cor-Den	~			3.53 2997		924.31 78	782.34 15.81	000	24.93	0.20	0.81	305	4.05	1.74		2 09	17.20				
ш	E.M. Oct.	Cor-Den	Pachy.		0.83	2.31 3015	301522.23 84		985.52 14.11	0000	<u>00</u> 25,13	0.18	080	3.06	1,96	4.94		(7 2.12		×		×	
<u></u>	E.M. Ort.	Corden	Pachy?		0.81	2.50 3011	301190.19 980	083.51 871	879.66 14.53	2000	24.43	8	1.7	3.24	2.52	5.10		37 2.14	16.53				1
Ì	E-M. Ort.	Cor-Den	, ,			3.61 31040		969.36 111	1113.47 17.73	7.32	32 27.38	4.96	1.87	3.13	6.87	0.30	917,37	37 2.05	5 23.32				
	E.L. Cell.	Koo-Lam	Cylindro.		0.27	2.74 2949	294915.34 860	B00.55 B51	958.25 7.SS	X 18.21			1.52	2.22	10,32	3.40			32.48				
SK4; 0,20 B		Koo-Lam	Pachy.		-0.74	1.92 3007	300744.05 1064.12	1427,63	1.63 22.31	0.00	00 25.31		1.85	2.67	4,43	3.46	879.95	5 2.10	0 24.36				
	EL Cal.	Konlam	Pachy		C 120		304012.76 890					2.21	1,81	2.26	14,68	252		77 2.10	27,61				
	1	Koelem	Cylindro?							X 111.37	37 24.76	4.10	20	22	25.15	2,73	9.42	12 2.31	24.14	M	×		Ola.
SK4 0.65 B	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	Koo-Lam	Cylindro.			3.20		. 1	919.00 9.00		2		R.	8	88	336	5 1050.27	20	100			ĺ	
	Ţ	Kon-Lam	دی ۲	╡		2.40 2854		858.46 122	1224.09 20.43		202	8	8-	2.17	18.84	311	1 803.47	1.91	1 29.66				
1	T	Ī	Cylindia.	┤		_			_				1.47	8	18.54	217		57 1.81	29.75			Ì	
Ī	1		Cylindia.	~		_	1	-			_		8	213	12.85	8					ĺ	İ	
	T	Koelan	Cylindro.		ļ		<u> </u>						8	8	8	581	1					İ	
5K4.1.60 C	T			+				T		Ĩ	_			8	2.2						Ť	Ť	
		T		1	1		1				1	1			3 7						İ	T	
SKA 3.20 F				<u> </u>	× ₽ ₽	780 107	205214,48 14/3,34		1136 M 230		8		8		202	8	2 1009 7	202	89	×	×	×	Decalc
SK4, 6.80 A E	t		Cylindro?		0 18	3.01 2005	200873.17 945	949.27 1510	1510.24 13.94	17.94	34 59	03	8	   P   R	11.67	12	897.46	1.87	39.02	×	,	_	
			Cylindro.				<u> </u>		•				1.65		22	12	<u> </u>		<u> </u>	Ī		İ	
SK4: 6.80 C E	E-L, Can,	Koe-Lam	Beternn,		000			3.41 1175.47					1.15	3.00	6.62	4,13			1			İ	
SX4 6.90 A E	E.L. Call.	Koe-Lem	Belemn,		0.52	2.91 29615	296156.99 012	912.22 89:	692.71 40.88	80 000	23.26		1.06	2.50	5.31	4	1 584.06	90 1,75					
		Koe-Lam	(B) - N		0.06	3.70 2660	20022.73 120.27	87 1783 49	3.49 41.31	31 15.12	23.48	8	2.00	3.70	10.20	0.76		1,76	5 20.02				
		Koe-Lam	,	×	. '	7	1	,	,		•			'									
SK4; 11.50 E	E.L. Call.	Koe-Lam		×	'	4	'	'	•	,	•	'	,	•	•	, ,							
<u></u>	ī	BayCom	 الا (ن)		82.0	1282 12.0		1.59 1344.60	1.80 45.20	01,01 05	10 22.75	8	1.96	3.41	800	1.55	917,19	9 1.75	5 19.78				
	1	Bay-Cym	2		10	- 1	_			4.60	29.68		1.7	4 41	9.34	306	800.31	1.76	36.44				
	-1	Brom B	<u>د</u>	╡			_						28	8	344	4.34	-	1.65	32.00	×	×	*	
SKS 1.00 B	1	By Com	Cylindia		8	1.56 2867		1	905.09 35.63	80			2	3.42	2.14	3.49		1.86	20.38				
<u> </u>	I	ByCm	- 			1.18	300743 89 792	1					1.5	5 8 7	3.75	265		79.1	13.66	Ì		İ	
		ByCom				_	-1	1			- 1		2	4,15	10.57	3.16	Į	1.84	10.59				
SK5 2.45 A E	E. Kimm,	Bay-Cym	Cylindro7		072	0.40 289323.49		<b>PS1.57</b>						1		-							
					ł		I	I	11.008			3	-	8	3.15	1,63	867.29	2.13	13.54	×	×	~	

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							295481.21	875.65	1153.89	44,11	0.00	24,26	0.00	1.60	2.82	6.05		0.38	910.63	1.75	27.04				
384 SK5 2.95	E, Kimm.		<u>v.</u>		-1.68	1.50	296877.62	910.04	865.06	41.89	34.38	23.51	0.00	1.60	2.99	5.01		4.16	908.34	3.09	19.82				
385 SK5 3.10	E. Kimm.	Bay-Cym	<u>/</u>		-0.64	2.12			781.36	43.36	22.98	23.36	0.00	1.86	1,90	10.90		1.41	1016.40	1.73	21.37				
386 SK5; 3.40	E. Kimm,	Bay-Cym	Cylindro.	I	<u>-1.13</u>		297965.29	733.76	/01.30					<u> </u>											
~ SKS 3.90	E, Kimm,	Bay-Cym	<u> </u>	<u> </u>		1.39	296457.60	768.95	958.69	46 28	259.78	22.34	0.00	2.46	2.22	83 06		1.56	875.31	1.69	24.62	x	×	×	
387 SK5, 4.00	E, Kimm.	Bay-Cym	<u>.</u>		0.30	2.17	293690.26	689.59	659.52	38.70	51,46	22.51	0.00	3.14	1.67	25.19		4.02	928.29	1.64	24.08				
388 SK5, 4.15 A	E, Kimm.	Bay-Cym	Cytindro.	_ <u>*</u>	-0.58		295585.79	839 52	670 37	11.37	36 02	21.98	0.00	3.78	1.86	15.32		0.84	894.31	1,73	20 62			<u> </u>	
389 SK5; 4,15 B	E, Kimm,	Bay-Cym	Pachy.			2.28	292132.40	918.22	973 65	21.38	105.87	23.84	0.00	1,40	2.45	48.01		3.21	868.84	1.69	28 82	<u>C</u>			
390 SK5; 4.35	<u>E. Kimm.</u>	Bay-Cym	<u>w.(c.)</u>	_ <u>*</u>	_0.53	1.38	298239.72	811.58	760.79	40.53	17.36	23.59	0.00	1.29	2.03	11.07		4.02	1017.95	1,75	20,74				
391 SK5, 4.60	E.Kimm.	Bay-Cym	<u>IV.</u>		-0.47 -0.62	<u>2.73</u> 2.32	257616.70	747.48	791.75	23 01	41.33	22.70	0.00	2.03	1.66	11.16		2.18	972.84	2.21	27.96				
392 SK5, 4.70	E. Kimm.	Bay-Cym	Pachy?	X	-0.62	2.37	294059.26	703.70	778.84	8.02	68.59	21.34	0.00	1,41	2.05	32.34		2.17	865.62	1.60	19.28				
393 SK5 5.25	E.Kamm.	Вау-Сут	Cylindro.	2	-1.70	3.57	295126.28	759.81	795.27	12.87	56.16	23.21	0.00	2.56	1.61	17.18		4.44	1112.55	1.61	20.41				
354 SK5; 5.70 A	E <u>. Kimm.</u>	Bay-Cym	Cylindro.	<b>*</b>	0.09	3.31	294232.38	749.65	580 95	12.21	0.00	21.66	0.00	1.23	2.03	1.68		2.46	968.39	1.62	28.76			<u> </u>	
385 SK5; 5.70 8	E, Kimm,	Bay-Cym	Pachy.		0.45	1.87	295395.49	1015.37	778 69	14.12	168 67	22.09	7.50	2.89	2.43	82.06		4.41	1038 97	1.67	18,14	<u> </u>			
396 SK5; 5.90 A	<u>E. Kimm.</u>	Bay-Cym	Pachy?		0.22	1.63	296760.32	768.19	849.06	18.60	107.44	23.91	0.00	1.76	2.05	49.13		1.26	927.50	1.74	22.10				· · · · · · · · · · · · · · · · · · ·
397 SK5; 5.90 B	E <u>. Kimm.</u>	Bay-Cym	V		-1.48	2.32	294698.02	794.97	848.86	13 36	0.00	24.22	0.00	1.50	2.36	2.62	<u> </u>	1.69	975.58	1.68	28.60			·	
388 SK5, 6.25 A	E, Kimm,	Bay-Cym	Cylindro.		-0.19	2.05	291091.86	748.56	767.45	18.07	77.73	22.80	6.89	2.56	2.51	35.31		1.48	899.36	1.67	21,47				
399 SKS; 6.25 B	<u>E. Kimm.</u>	Bay-Cym	<u>Iv. (C)</u>		-0.19	2.94	286334.51	724,43	626.70	14.69	4,12	22.87	9.81	1.38	2.07	8.65		2.79	917.13	1.68	19.40	×	×	_×_	
400 SKS; 7.20 A	E, Kimm. E. Kimm.	Bay-Cym	Pactry?		-0.23	1.93	295868.39	990.85	1023 68	14.78	52.64	22.90	8 64	1.00	3.24	31.22		0.84	927,58	1.74	19.17				
401 SK5; 7.20 B		Bay-Cym			-1,23	3 06	287623 03	740.74	971.84	19.63	97,63	22.28	7,10	2.29	1,85	44.57		3 29	922.94	2.09	27,72				
402 SK5; 7.20 C	E. Kimm.	Bay-Cym	Cylindro,		0.62	0.80	294211.56	1130.34	1115.63	19.98	23.52	21.89	5.69	1.23	5.57	18.96		2.48	928.32	1.65	17.27	X	×	×	
403 SK5; 7.40 A	E. Kimm.	Bay-Cym	Pachy.		-1.39	2.76	298998.42	725.63	800.85	8.35	30.65	22.55	8.47	1.69	2,10	6.31		2.47	949.20	1,67	25.48			1	
404 SK5; 7.40 B	E. Kimm.	Bay-Cym	Cylindro,		-1.23	2.89	292421,36	694,33	727.44	14.33	72.69	22.68	0.82	1.95	1,69	36.56		2.96	965.57	1,72	28 69			i	
406 SK5: 7,70 A	E. Kimm,	Bay-Cym	Cylindro.		-0.49	2.11	296265.92	1205.48	1015.54	21.64	0.00	23 61	11,71	1,46	3.60	1,20		4.25	1075.19	1.67	15.57				
409 SK5; 8,10 A 407 SK5; 8,10 B	E. Kimm.	Bay-Cym	Pachy.	<u> </u>	0.09	2.55	289268.55	768.16	681.54	14,42	28.13	21.03	0.00	1.56	1.74	16.79	-	2.26	965.67	1.84	28.68				
	E. Kimm.	Bay-Cym	Pachy.		-1,15	298	292781.28	661.08	670 94	12.92	185.34	23.07	0.00	2,72	1.80	34,39	-	2.12	942.23	1.70	20 00				
408 SK5; 8,10 C	E, Kimm,	Bay-Cym	Cylindro,		-1.38	2.45	296404.09	686 62	740.22	14.50	147.27	21,90	0.00	2.30	1.67	53.76		1.83	971.75	1.64	25.42				
409 SK6, -0.30 A	E.Kimm.	Cym	M? (C.)		0.09	1.29	296053.74	1027.59	1373.19	15.11	0.00	21.82	0.00	1.10	3.57	4.54		2.64	948.81	1.65	21.00		×	×	
410 SK6 0.00 A	( <u>E. Kimm.</u>	<u>Cym</u>	Cudindan		-1.53	1.69	292040.20	779.00	1095 61	18 07	158.68	22.58	0.00	2.60	2.28	44.51		481	931.32	1.66	35.28			1	
411 SK6 0 00 B	E. Kimm,	Cym	Cylindro.		-0.81	2.32	288508.98	751,15	538.69	0.00	0.00	22.15	5.69	2.61	1.30	5.95		2.18	971,41	2.03	29.41	-			
412 SK6 0.50 A	E. Kimm. E. Kimm.	Суп	Cylindro.		-0.97	2.49	296118.05	769.82	834.43	18.06	402,41	23.12	13.62	3.57	2.05	206.93		1.12	921,98	1,74	27.65	x	×	<u> </u>	
413 SK0 1.50 A	E. Kimm.		Cylindro.	<u> </u>	-1,12	2.24	294902.37	922.20	1429 86	10.76	158.95	25.51	0.00	2.80	2.63	36.99		2.98	982.50	1.82	33.47			<u> </u>	
414 SK6; 1.50 B	E. Kann.	Cym	Cyanau.				20-002.01	022.20		10.70												i	<u> </u>		
~ SK8; 1.90 415 SK8; 2.30	E, Kimm.	Cym	<del>[</del>	<b> </b>	0.04	1.69	295780.59	905 06	1117.33	28.44	131.01	23.93	0.00	3.43	2.67	71.81		1.88	929.01	1.74	19.25	i—			
416 SK6 2.40 A	E, Kimm,	Cym			0.31	1.77	295521.95	847.35	1090 85	15.46	173.63	22.90	0.00	1.68	2.75	91.74		2.21	888.99	1.62	20.15			1	
417 SK6: 2.40 B	E. Kimm,	Cym	1 <u>.</u>	- <u>-</u> -	-0.83	1.21	289482.99	1047.46	1737.15	54.24	2134.34	65.58	2.50	2.95	2.93	173.52		2.95	928.75	2.67	14.50			I	Borings
418 SK8; 2.50	E, Kimm,	<u>Cym</u>	1 <u></u>	f	-1.48	3.63	294089.46	951.25	860.56	18 89	0.00	21.14	7,71	1.90	1.78	2.03		1.78	1072.87	1.58	36.47	×	x	x	
418 SK8; 2.60 A	E. Kimm.	<u>Cym</u>	Cylindro?		0.44	1.88	292826.42	844.14	894,94	14.16	86.57	21.67	0.00	1,37	2.84	45.14	tt	1.95	912.14	1.59	23.24	<b></b>		1	
420 SK6: 2.60 B	E. Kimm.	<u>Cym</u>	N. (C7)		-0.35	1.77	289240.47	805.39	910.48	_17,28	143 09	22.70	0.00	2.09	2.38	61,93	-	1.01	983.99	1.75	18.11				
421 SK6 4.05	E, Kimm,		Cylindro.	1	-0.53	1.95	300128 02	937.82	899.21	13 00	53 07	22.68	0.00	2.58	2.81	28.53	i	2.74	1019.19	1.68	17.22				
~ SK6: 4.50	E. Kimm,	<u>Cym</u>			<u></u>		300120 02		000.21							<u>-</u>					-	<u> </u>	l	1	
	E. Kimm.	Cym	Pachy?	1	-1.09	1.63	287405.72	1004.99	1287.58	17.86	374.10	23 50	0.00	4 63	2.01	59 84		2.56	1029.75	2.01	17,45	×	×	×	Decate.
422 SK8; 5 30 423 SK8; 5.55	E. Kimm.		Cylindro.	·}	-1.09	0.39	287849.61	933.68	1218 80	14.12	151.55	21.92	0.00	1.91	2.36	78.13	<u>├</u> ──┼─	2.49	986.91	1.58	18.69	+			
~ SK6: 5.60	E, Kimm.	<u></u>	15 m 00.	1		0.35											t-	-				1		1	
424 SK6 5.90 A	E, Kimm.		<u>k.</u>	I	-1.74	0.84	304637.33	1029 81	1370 95	22.24	665.63	28 69	17.71	3.91	2.93	284.22	l——l-	5.90	954.68	1.58	23,10	1	1	<u> </u>	Decale,
424 SK6 5.90 A	E. Kimm.	Cym Cym	Cylindro.	1	0.09	0.69		962.69	1183.55	9.40	723.76	23.49	7.66		2.33	305.05	1	0.00	1041,48	1.64	_21.96	1			
			SYNAMIO.	1													<u> </u>					<u> </u>		<u> </u>	
~ SK6, 6.40	E. Kimm.		Cylindro.	× ×	0.45	1.48	293036.35	1118.16	1338.40	14.31	11.86	22.01	0.00	3 82	2.77	4.25	<u>†</u> }-	0.75	986.70	1.61	16.88	<u> </u>	1	<b> </b>	
427 SK6 6.90	E. Kimm.	<u></u>	Cylindro,	·	-1.41	2.68	296328 06	838 61	715.19	8.02	92.10	23.44	0.00	384	1.65	40.30	-	2.36	1132.00	1.71	28.91				<b> </b>
427 SK6 890	E. Kimm,	Com ICom	Cylindro.	†	-1.18	1.47		775.59	897,81	10.73	68.93	23.66	0.00	3.14	1,67	41,71	1t-	3.70	1023.25	1.68	45.12	1	r	r —	
	E. Kimm.			1	-0.67	1.31		878.08	841.25	12.95	321	23.20	0.00		2.35	9.24	<b> </b>  −	4 06	994.77	1.73	18.24		<b></b>	1	Borings
429 SK6 7.20 AI	<u>jc. Kmm.</u>		Cylindro.		1 -0.0/	1.31	400120.11	010.00	0~1.23	1 16.03	141	لاله وره	1,000					~ ~ ~ ~							

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19.29	30.37	256	21.55	27.88	'	24,43	22	28	8	24.02	19.78	88	18.34	ľ	10.34	82	1	21.67	8	8	88	2	833		8	8	19.65	10.56	21.94	17.44	ลิ	21.49	2 2	8	19.45	19.74	17.63	20.77	28.55	16.74	22.97	20	243	7	8		84
1.08	1.75	201	1.67	1.7.1	1	1.74	1.81	1.83	1.80	R -	5	8	2.13	ľ	1.83	18	2	2	1.75	3	8.1		8	1.92	1.02	312	25	2,41	2.61	2.55	28	8			2.78	284	253	2.60	250	2.94	2.67	2.47	2,58	1	0000		38
997,50	977.44	853.78	1000 23	1072.52		1042.23	8,8	BBB 13	1147.90	682.21	<b>BK5.26</b>	021.51	824.92	ľ	1130.40	940.60	977.54	<b>81.25</b>	12.108	908.36	807.71	911.24	802.01	1231.01	<b>865 83</b>	831.70	878.18	869.23	1031.08	1087,05	1166.63	1002.09	1075.74 1077.85	60 60 G	1078.16	1199.06	1013.11	1022.72	1001.00	1008.89	1029.13	1107,96	1019.49	ĺ	BAA 47	Į	851,99
3.12	4.42	151	8	4.11	7	28	8	1.64	5	1.16	R.	8	8	ľ	1.40	800	1.7	8	211	9	2	016	010		36	8	60	262	82.0	60	1.51	8	2 8	89	5	600	2	2.60	20	236	1.36	<u>6</u>	20	1	1 81		2
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30.37	71.14	21.31	17.62	68.21		34.41	8	4	6.28	21.34	13.25	88	34.48	ľ	1,85	0.46	20.02	30.10	24.31	30.02	28.12	6.52	62.81	97.24	31.60	37.65	21.29	30.10	54.50	4.09	4 05	11.87	20.27	900	3.6	12.70	7,34	3.40	17.06	17.34	6.54	7.02	48.87	"	4.78		4.18
2.45	1.97					2.05	3.16	27					212	ľ	2.32		2.15		1.8					<b>_</b>			1.74	2		2,09			2.3				1.52	1.89	1.47	1.57	1.35	11.1	230		2.35	Į	
2.65	2.56	2.75	2.10	2.37		3,19	28	4.34	58	1.04	3.06	8	1.50		1.48	1.54	3	8	8	243	1.5		2.09	4 62	1.68	1.74	1.46	601	1.78	1.68	2.05	1.8	2.38	2.38	1.58	2.48	1.65	1.51	1.84	1.81	1.54	1.61	3.15	ĺ	0.69		80
000	000					80		80							80											-	ļ		33.64	17.67			8				88	24.30	14 86		10 07	-1	8.29		7.05		
34.44	23.42	21.58	-			22.22	ļ	20.35	22.23						2002	2365	202			258		!		8					20.85	19.77			8 9	1	1		21.00	83	19.68		19.35	3 20.14	19,23	1	19.22	I	
10.03	144.59	10.54	1.8	124.48		47.78	172.87	189.64	14,43	12.98	21.34	7.05	99.70		000	000	51.07	2902	43.35	8	1002	8	152.83	284.12	74.59	<b>99</b> ,46	7057	80.83	180.47	15.00	9.42	8		109.18	11.64	30.02	14 06	9.08	48.79	22.77	4.98	8.46	50.87		12.41		10 80
21.75		8.8	1			18.96		34.65	ł			<u> </u>			7 80	14.82	7.55	Ľ			1	I	8.64	88		Į	L 1			ļ				7.36			7,06	3.45	2.60		3.20		12,10		280	l	
902.34	868.60	1763.19	1386.94	780.05		864,10	1742.68	1437,60	1365 04	25 696	760.58	904 68	740.13	'	037,92	694.65	905.13	988.9M	678.45	702.37	87.278	867.27	807.11	4219.81	850.16	112360	1232.21	692.58	1152.79	1224.42	1050.89	888	1061.00 1074.65	782.65	669 26	827.35	771.88	883.44	863 62	1120.79	889.04	828.66	1326.66	Ί	1450.06		640.37
894.32	847.00	1252.09	1070.18	876.10	1	827.28	1125.06	1058.75	1130.22	828.38	79.97	910.56	781.84		1005.73	775.83	814.34		714.57	708.16	865.74	828.7	10.34	27.080.7	815,46	12.829	1001.01	900.00	1005.49	987.72	1014.00	837.27	1189.16 88 7	76.17	837.66	908 86	820 66	660.43	758.44	656.33	801.84	840.90	1013.51	'	1048.87		10 929 929
296390.26	205634 92	<u> </u>	·			294529 00		284788.06		· · · ·	287866.13	300406,16	284Z34.00	'	287141.36	277644.83	18 60 1282	587.14	282069.27	284174.41	267647,60	280853.56	281546.34		-	306347,84		303098.24		311608.70		_	307339.51	313165.45	305453.68	311610.82	8.88	309050.68	318431.22	315118.06	307823.22				296018.37		
1.19 29	2.01 28	0.01	<u> </u>		•	28	1.10 27	1.75 28	0.12 29	1	1.87 235		_		2.15 28	1.20 27	1,27 28					1.75			!			1.60 300	1.44 314	2.05 311				-			2.95 310	2.10 30	1,70 316		1.35		1.73 315		3.05	Į	8
80	R Q					8		80			8				0.06	0.41	-1,00			230		8		100				0.13	20	20					198 19			89		0.0	2		8		8	ļ	
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Cylindro.	 	Cytinatro.	Cylinato.	Cytinatio.		<u>к (с)</u>	<u>ار (ن) ا</u>	Cylindro.	Pachy.						Pachy.	Pachy.	Cylindro.	Cylindro.					Pactry.	Pachy.	N. (C.)	v. (c,)	Cylindro?	N. (C7)	Cylindro.	Cylindro?					Pactry	Cylindro?	Pachy.	Cylindro?	N. (C)	-	<u>۲. (C.)</u>		N. (C?)		v. (c.)		
0	<u>×</u>	ú	<u>10</u>	6		<u> </u>	<u> </u>	<u> </u>			<u>v</u>		<u>۲</u>	, ,				t		۲. ۲	<u> </u>	ېر ۲									<u> </u>		T	Ī			ĺ							Ť	ž		
E O	E Si		Ι.		Ē	<u>چ</u>	5	E S		Ī.						Reg-Bay							Γ.	Ι.	i			1		Rep-Bay	i	T	Rep-Bay	i			Reg-Bay	Rep Bay	Reg-Bay		Rep-Bay	Rep-Bay	ī	i	3		ð.
E. Khin.	E. Kbun.	E. Kimm.	E. Kimm,	E. Kimm.	E. Kimm.	E King	E. Kinn.	ά King t	Ort -Kim	EQ-FC	Ord - ICm	Ort Kin	Ort Kim	Ort,-IQm,	Ort,-Kim,	Ort,-Kim,	Ort, Kin.	Ort, KIM,	Ort, IQM	Ort. Kim	ON, KI	Ort, IQM	Oxf. Km.	Ort, Kim,	0-1-Km,	Ort Km.	Ort, Km.	Ort-Kim,	Ort-Km,	E. YO	EX FO	E F		EN PO	Ort. KIM.	Con KG	NA NA NA	OXI-Ka	Ort. NM	<u>B</u>	EY KO	е У Ю	Of Kin	<u><u></u></u>	ы Э		δ
430 SK6, 7,20 AB	431 SK6 7.20 B	432 SKB 7.40	433 SKG 7.50 A		- SK6, 7,70	436 SK8, 7,80 A	436 SK6, 7,80 B	437 SK8, 7,80	438 SK7; 0.70	439 SK7, 1,10	440 SK7, 1.20 A	441 SK7 1.20 B			443 SK7; 3 00	444 SK7, 5,70 A	446 SK7; 5,70 B			448 SK7: 10 BO	448 SK7, 11, 10	460 SK7 11,90	461 SK7, 12.10(1)	462 SK7; 12.10 (2)	463 SK7, 14 80 A	464 SK7, 14 50 B	466 SK7, 15.40 A	468 SK7: 15.40 B	487 SK7; 15,40 C	468 SK7; 16 50 A			441 SK7 17.35 442 SK7 17.60 A	463 SK7, 17,80 B	484 SK7: 17.80	46.6 SK7, 18.40	466 SK7: 19 90	487 SK7, 20 25	468 SK7: 20.70		470 SK7, 20.00 A	471 SK7, 20.90 B	472 SK7, 27, 30		473 SKB, 14.80		474 SK8 18.50

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			SK4	2 SK4							SK2	_	<u> </u>		ė –	IN SKID	B SK10	a skio		e skia	SK10		J SK10	2 SKIO			B SK10		7 SK10	B SK10	SICO.	A SK9	SKO	ŝ			3 SKB, 4,90	Sig	SKA	7 SKG	SKQ.	SKG	SKB	SXG	Z SKG	1 SKG	SX8	ŝ	E SKO
SKS; 2.45 H	SKS: 2.10 ii	SK4; 8.90 AB	SK4; 6.80 All	SK4; 2.50 li	SK3; 7.65 0	SK3, 7,35	SK3, 5,80 li	SK3; 3,50 li	SK3; 1,20 II	SK2, 4,45 H	SK2; 2,15 ii	SK2, 0,45 ii	SK1; 52.50 il	SK1; 5.90 AI	SK1; 4,50 BJ	SK10, 21,90	SK10, 15.70	SK10, 15,30	X10, 14.30 B	K10; 14,30 A	K10, 13,40	SK10; 12.70	SK10; 12:20 A	K10, 8 20	SK10; 4,60	SK10; 4.00 B	SK10; 4:00 A	K10,090	SK10, 0.40 B	1040A	SK9, 13.40	SK9, 13.10	SK9, 1275	SIG 12 60	SK9: 12:50		SK9, 4,90 B	SK9, 4.90 A	SK8, 39,40	SK8: 38.20	SK8, 35 80 B	SK8, 35 80 A	SK8; 34,70	SK(8; 33 70	5KG: 3335	SK8: 31.80	SK8; 27,40 B	SKB; 27,40 A	SK8: 27.20 B
E. Kimm.	E. Kimm	E-L, Call,	E4. C3	E-L. Call.	E-M, Orf,	E-M, Ord	E-M. Oxt	E-M. Ort.	E-M. OM	M. OH	M, 04,	M.OT.	<u>п</u> 9	<u>1.</u> 2	E, 01	g	2	1. OM	g	<b>r</b> 94	1.01	<u>,</u>	Г <u>о</u>	F or	- or	-0 <u>-</u> 0	8	2	2	2	MH, Ort.	M-L, Ord,	₩. 91	£			ξ <u>γ</u> 2 9	H Q	E, Ord,	E S	E.OX	E, OX	E. 0x1	E. 01.		E, OM,	E. 02		E. 04
<b>昭</b> (6) 10 10 10 10 10 10 10 10 10 10	Bayom	Koo-Lam	Koe-Lam	Kon-Lam	Cor-Den	Cor-Den	Cor-Den	Cor-Den	Cor-Den	Den-Ten	Den-Ten	Den-Ten	Mar-Cor	Mar-Cor	MarCox	Ser-Rag	Ser-Rag	Ser-Reg	Ser-Reg	Ser-Rep	Ser-Reg	Ser-Reg	Ser-Reg	Ser-Rog	Ser-Reg	Ser-Rog	Ser-Reg	Ser-Reg	Ser-Reg	Ser-Reg	Ten-Glo	Ten-Gio	Ten-Gb					Ten-Glo	Ş	ę	8	8	Cor	Q	6	ğ	£	٤	ð
Cylindro?	K. (C.)	Betenn,	Cylindro?	Pachy	Pach	Pachy	Cylindro	~	14. (C7)	Cylindro.	Cylindro.	<b>1</b> 20 1		Cylindro.	Cylindro.	Cymaro?	<u>,</u>	ऱ	, F	5	Cylindro7	Pac Tr		Pachy.	(Ld) (M)	- [[1]	(E3) 51	<u>ج</u>	7	[]) <u>-</u>	×	Pachy.	Cylindro			ſ	Cylindro7	, ,	ľ	ऱ	- (5.3) '시 -	F	(Fd) .A	Ņ	_ (F4)	V. (C7)	7	7	<u>ج</u> [0]
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080	ь	083	8	04	082	085	0.01	8	1.09	5	5	68	52	1.2	0 62	-0.13	5	-0,12	0.13	000	-0.71	045	520	0.75	070	0.23	180	ა 8	02	0.68	ა 8	1.20	027	5	5		649	5	Ì,	0 18	80	0,17	99	000	022	6	0.02	080	8
0.26		2.91	2.97	2.63	241	2.47	3.24	2.55	272	32	280	128	1.26	1.80	2.70	213	1.96	2.04	1.20	1.72	2 20	2.83	1.69		1.53	1.83	0.69	80	0.44	0.73	0,48	1.5	1.2	1 49	191		00	300		261	3.30	363	2.63	78.0	322	1.7	290	2.30	333
303584 80	307748 X	289196.25	301695.91	314391.73	303326.23	306889.78	305055.45	308018.65	312306.77	3053958.97	310080,38	289126.20	308282.00	310179.64	303687.71	300582.32	311236.98	321580 86	317880 29	305101.71	309538 65	300084 86	311072.00	313525.24	309524.35	312282.52	313882.61	310250.51	308952.77	308278.87		3068277.34	315720.68	OL LOUTIN	3187704 89		308497,11	1		312741.48	300924.81	310086.88	313094 85	313312.03	315368.08		1	_	311217.89
i i		995.S1	1065.55	1059.41	1	898.14	i	-	1023.98	878.89	1.	7	ī	900,19								1	_	1	ī	i T	963.71	<u> </u>	1	1				-		T	818 68	1	ĺ,	1024.76	1	ĺ			<u> </u>	. 1	900.56	T	15.539
1000 80	2198	1028.26	1642.08	80008	9277.66	1185 59	2 008	998.23	867,01	1037.04	1620.62	1211.31	948 43	1747.69	1885.50	950,18	1242.70	1041.81	2085,73	1049.35	740.28	817.40	1300 02	1042.98	1260 23	1098.26	1088.64	1170.73	942.05	8968	1023 27	1061.23	980 92		R54 40	,   ,	824,44	817.33		1183 04	770 55	963 696	855 93	1148.25	874.20	1349.43	777,19	914.12	845.55
8.10	-	7,63	8.22	9.13	1.8	00	8.80	-0. 85	7.8	10.71	377	2.67	10.77	13	1.01	2.65	38.34	13.12	18.70	8.22	0.38	3.44	4.73	23.90	2.13	23.70	8.16	1.81	11.21	-0.28	5 05	811	22				508	8	,	6.30	0.71	7,35	11,49	13.58	4.66	12.24	0.00	378	31.31
4 68	1813	7.38	82,44	640	8,45	5.01	843	10.33	62.9	17.23	16.28	30.95	10.59	9.92	23.07	10 81	18,41	85.77	183 87	200.13	5.20	5 09	151.80	69,40	351.10	52.51	34.31	78.23	55,41	68 67	14.78	27.74	8	200	14.07		36,46	29,99		45.94	33.72	242	S 39	137.69	38	38.43	25.08	88.65	148 44
18 29	19 79	8	21.10	10.02	19.27	18,51	18,97	19.08	18.70	19.63	19.83	17.21	19,46	19.37	19.89	19.78	19,70	20 02	21.13	21.22	19.48	19 09	19.30	20.99	21,15	19,58	18.02	20.77	19.78	19.97	19 65	21.53	19.44		10 40	<u>.</u>	20,18	18.27	.	19 68	19.42	19.72	17,63	19 65	19.70	19.62	20.12	10 43	19.62
8	B	8	8	80	8	8	080	8	8	000	08	0,17	28	0.00	5.0	1.17	8	8	2.85	0.15	0.45	0.40	80	2.77	270	1.09	22	6.52	278	<b>65 E</b>	1.8	8	082	,	5	; ,	38	28		535	4,42	5.79	0.31	16.01	10.65	20.72	8	4.6	5 19
0 82	1 24	0.91	1.39	1.47	0.79	0,76	0.77	0.08	0.58	1.83	2.37	112	19 69	0.84	2.22	1.34	2.04	7.07	2.06	3,44	1,29	1.18	1.78	1.8	1,64	3.36	1.69	1.55	1,49	1.52	1.27	1.26	1.2				5.51	1.02		0.59	0.81	0.70	066	1.2	058	8	8	0.84	500
2.27	3	<u>ال</u> .1	1.38	0.87	1.94	1.74	2,10	220	1.78	1.52	2.32	1.2	0.51	1.36	2.62	1.04	1.84			22.I					1,67	1	11					2.64		Т		T		0,41	ļ	2.38	Í	Ī	ĪĪ				0		
1.96	3	19.6	20 87	4.33	2.24	2.00	5.94	277	3.36	4.34	9,42	17.18	3.97	5.61	661	5,48	8.54	22.87	52.10	62.37	2.94	3.39	43.99	44.96	30.60	27.82	27,88	38 68	29.21	30.09	5.53	10,19	50 OI		2 2 2	;  ; ,	14.04	8.60		14 82	12.16	9.97	18,45	54.38	9.68	15.8	9.45	9.91	2111
4.28	5	1.10	334	3 88	210	258	1.7	90	1.7	0.00	272	38	211	0.60	305	4.21	80	2,22	3.32	2.20	0.76	2.03	304	4 08	2.37	1.96	3.04	0.77	1.88	1.14	1.82	1,45	ຄື			j,	213	5.43	ĺ,	214	1.39	068	1.84	325	202	274	4.41		-
852.45	B	683 65	984.59	1091.72	855.37	971.35	874,42	808.26	<b>813.4</b> 2	894 23	1041.17	871,27	8098.28	680,56	877.65	977,87	1100.67	1077.01	963 96	945.85	50.01	842.66	868.30	1014.52	958,76	894.93	1009.53	955 82	998.12	948.36	1067,50	1000 OI	80	34.3	1080 51		883.07	1082.42	ļ,	802.55	824.62	891.25	871.90	805.90	878,15	632.30	870.32	850.93	AFA 74
2.30	2	2.98	2.43	239	2.39	2.35	2	2.37	241	2,42	2.38	2.78	234	2.40	2.33	24	2,49	2.50	2.52	2.39	2,40	2.70	2,46	2,51	2,49	2.52	2.45	2,46	2.44	2,42	2,42	200	2			;   ,	2,42	2.72	,	2.53	2.44	2,44	2.92	2.51	2 57	2,51	2	2.46	344
13.14		11.87	13 03	30.62	18,78	21.09	16.06	24.37	21.8	22.13	19.42	21.15	24.74	32.58	26.26	29.56	21.30	24 63	23) 03	26.06	24,11	22.30	19.87	14.91	22,13	24.66	20.52	25 80	21,42	24,15	15.33	19.68	8	3 2 4	3 2 2	3	23	28.64	,	20 30	24,12	22.26	21,49	19.80	19,48	17.78	18.77	30 13	3
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627 SK5	628 SKS	629 SK5	630 SKS	631 SKG		533 SKI				<u>537 SIC</u>		639 SK1					3		_						661 FS1	662 FS1	663 FS1	664 FS1	666 FS1	660 739			668 FS2	669 FS2												121 121 24	

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IJS1:58	131:0	151:7	JS1: 8	131; 9	670 JS2 1	680 JS2 21	JS2 20	JS2; 3	682 JS2: 4	JS2 6	192.6	686 JS2, 71	668 JS2; 7 #

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## APPENDIX 3 DATA TABLES : ORGANICS

			<u> </u>				T	oc				Rock-Eva			
No.	Sample No.	Age	Am. Zone	Туре	SEM	1	2	3	mean	тос [%]	MINC [%]	HI [mg HC/g TOC]	OI [mg CO2/g TOC]	Tmax [°C]	d13C
1	KH1-4; -1.10	ValHaut.	D.bidH.boy.	Ch	x										-23.47
2	KH1-4; -0.80 A	ValHaut.	D.bidH.boy.	?								_			-23.92
3	KH1-4; -0.60 B	ValHaut.	D.bidH.boy.	Ch-Co											-23.35
4	KH1-4; -0.60	ValHaut.	D.bidH.boy.	?							_				-22.83
6	KH1-4; -0.40	ValHaut.	D.bidH.boy.	Ch-Co											-25.16
6	KH1-4; -0.30	ValHaut.	D.bidH.boy.	?											-24.21
7	KH1-4; 0.05	ValHaut.	D.bidH.boy.	<u>Ch-Co</u>											-23.06
8	KH1-4; 0.90	ValHaut.	D.bidH.boy.	Co											-24.90
9	KH1-4; 1.30	ValHaut.	D.bidH.boy.	Ch-Co											-22.71
10	KH1-4; 1.70 A	ValHaut.	D.bidH.boy.	<u>co</u>											-22.91
11	<u>KH1-4; 1.70 B</u>	ValHaut.	D.bidH.boy.	Ch	<u> </u>										-22.75
12	KH1-4; 2.00	ValHaut.	D.bidH.boy.	<u>Co</u>							_				-22.00
13	KH1-4; 2.20	ValHaut.	D.bidH.boy.	<u>Ch-Co</u>											-23.24
14	KH1-4; 2.35	ValHaut.	D.bidH.boy.	?											-22.99
16	<u>KH1-4; 2.75</u>	ValHaut,	D.bidH.boy.	Ch (w)											-22.82
16	<u>KH1-4; 2.80</u>	ValHaut.	D.bidH.boy.	Ch-Co						_					-23.81
17	KH1-4; 3.25 A	ValHaut.	D.bidH.boy.	Ch-Co											-23.85
18	KH1-4; 3.25 B	ValHaut,	D.bidH.boy.	Ch-Co						-					-22.73
19	KH1-4; 3.30	ValHaut.	D.bidH.boy.	Ch											-22.85
20	KH1-4; 3.40	ValHaut.	D.bidH.boy.	Ch-Co											-23.58
21	KH1-4; 3.60 A	ValHaut.	D.bidH.boy.	Ch											-22.83
22	KH1-4; 3.60 B	ValHaut.	D.bidH.boy.	Ch											-24.23
_23	KH1-4; 3.75	ValHaut.	D.bidH.boy.	Ch (w)	x										-23.13
24	KH1-4; 3.90	ValHaut.	D.bidH.boy.	S				[							-23.27
26	KH1-4; 4.00 A	ValHaut.	D.bidH.boy.	Ch-Co											-23.32
26	KH1-4; 4.00 B	ValHaut.	D.bidH.boy.	Ch (w)											-23.95
27	KH1-4; 4.10	ValHaut.	D.bidH.boy.	Ch-Co				<u> </u>							-22.38
28	KH1-4; 4.20	ValHaut.	D.bidH.boy.	Ch (w)				]							-22.70
29	<u>KH1-4;</u> 4.40 A	ValHaut.	D.bidH.boy.												-23.85
	KH1-4; 4.40 B	ValHaut.	D.bidH.boy.	Ch-Co					<u> </u>	l — l					-21.36
31	KH1-4; 4.50	ValHaut.	D.bidH.boy.	Col	x			[						i	-22.16
32	<u>KH1-4;</u> 4.80	ValHaut.	D.bidH.boy.	60											-23.38

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33 K	(H1-4; 5.10 A	ValHaut.	D.bidH.boy.	Ch-Co									-24.0
<u>34 K</u>	(H1-4; 5.10 B	ValHaut.	D.bidH.boy.	Ch-Co									-24.5
35 K	(H1-4; 5.20	ValHaut.	D.bidH.boy.	Ch						_			-25.0
		ValHaut.	D.bldH.boy.	?									-24.5
<u>37 K</u>	(H1-4; 5.40	ValHaut.	D.bidH.boy.	Co									-23.7
38 K	(H1-4; 6.00 A	ValHaut.	D.bidH.boy.	Ch-Co	<u>x</u>								-24.6
39 KI	(H1-4; 6.00 B	ValHaut.	D.bldH.boy.	<u>60</u>									-24.4
<u>40 K</u>	(H1-4; 6.30 A	ValHaut.	D.bidH.boy.	<u>Co</u>						 			-25.5
<u>41 K</u>	(H1-4; 6.30 B	ValHaut.	D.bidH.boy.	?			-						-24.0
42 KI	(H1-4; 6.30 C	ValHaut.	D.bidH.boy.	Ch-Co									-25.1
43 KI	(H1-4 <u>; 7.00</u>	ValHaut.	D.bidH.boy.	Col									-25.0
44 KI	(H1-4; 8.45	ValHaut.	D.bidH.boy.	<u>Ch-Co</u>									-24.3
		ValHaut.	D.bidH.boy.	Ch-Co									-24.3
		ValHaut.	D.bidH.boy.	Ch									-25.1
47 KI	H1-4; 8.90 B	ValHaut.	D.bldH.boy.	Ch-Co									-24.1
48 KI	H1-4; 9.30	ValHaut.	D.bidH.boy.	Ch	x								-23,9
49 KI	H1-4; 9.40	ValHaut.	D.bidH.boy.	Ch									-23.9
<u>60 KI</u>	H1-4; 9.80	ValHaut.	D.bldH.boy.	Ch-Co					_				-24.3
61 KI	<u>H1-4; 11.40</u>	ValHaut.	D.bidH.boy.	Co									-24.2
52 KI	H1-4; 11.60 A	ValHaut.	D.bidH.boy.	Co									-24.1
63 KI	H1-4; 11.60 B	ValHaut.	D.bidH.boy.	Ch-Co									-24.2
64 KI	H1-4; 11.80	ValHaut.	D.bidH.boy.	Co						 ·			-21.2
66 KI	H1-4; 12.10	ValHaut.	D.bidH.boy.	Col	_								-22.8
66 KI	H1-4; 12.60	ValHaut.	D.bidH.boy.	Co!									-21.9
<u>67 KI</u>	H1-4; 13.00	ValHaut.	D.bidH.boy.	Co						 			-25.0
<u>58 KI</u>	H1-4; 13.20	ValHaut,	D.bldH.boy.	Ch-Co	x							I	-22.9
69 KI	H1-4; 13.60	ValHaut.	D.bidH.boy.	Ch-Co									-24.6
60 KI	H1-4; 14.50	ValHaut.	D.bldH.boy.	Ch-Co									-25.0
61 KI	H1-4; 15.20	ValHaut.	D.bidH.boy.	Coll						 			-23.2
62 KI	H1-4; 15.40 A	ValHaut.	D.bidH.boy.	Co									-23.5
63 KI	H1-4; 15.40 B	ValHaut.	D.bidH.boy.	Co									-23.2
64 KI	H1-4; 16.00	ValHaut.	D.bidH.boy.	Ch									-24.3
65 KI	H1-4; 17.60	ValHaut,	D.bidH.boy.	Coll						 			-23.3
<u>66 KI</u>	H1-4; 17.80	ValHaut.	D.bidH.boy.	Co									-23.3
_67 KI	H1-4; 18.20	ValHaut.	D.bidH.boy.	Ch-Co									-23.3
	H1-4; 18.50	ValHaut.	D.bldH.boy.	Col						 	·		-24.2

_											
69	KH1-4; 19.70	ValHaut.	D.bidH.boy.	Co!!			 				-23.90
70	KH1-4; 19.80	ValHaut.	D.bidH.boy.	Co!	_ <u>x</u>	 				 	-22.50
71	KH1-4; 21.00	ValHaut.	D.bldH.boy.	?					 		-25.13
72	KH1-4; 21.40	ValHaut.	D.bidH.boy.	?							-25.39
73	KH1-4; 21.60 A	ValHaut.	D.bidH.boy.	Co		 	 		 	 	-22.75
74	KH1-4; 21.60 B	ValHaut.	D.bldH.boy.	<u>Co</u>	_	 	 		 		-23.57
76	KH1-4; 22.60	ValHaut.	D.bidH.boy.	?							-25.56
76	KH1-4; 23.80	ValHaut.	D.bidH.boy.	<u>Co</u>		 			 		-24.68
77	KH1-4; 24.30	ValHaut.	D.bidH.boy.	<u>co</u>		 	 			 	-23.59
78	KH1-4; 25.80	ValHaut.	D.bidH.boy.	?							-23.91
79	KH1-4; 26.80	ValHaut.	D.bldH.boy.	C₀		 					-24.85
80	KH1-4; 26.90	ValHaut.	D.bidH.boy.	<u>Co</u>		 	 				-24.91
81	KH1-4; 27.30	ValHaut.	D.bldH.boy.	Ch-Co							-23.77
82	KH1-4; 27.90 A	ValHaut.	D.bidH.boy.	?							-24.99
83	KH1-4; 27.90 B	ValHaut.	D.bidH.boy.	Ch-Co	<u>x</u>	 	 		 	 	-23,19
84	KH1-4; 28.15	ValHaut.	D.bidH.boy.	Co			 				-23.92
85	KH1-4; 28.70	ValHaut.	D.bidH.boy.	Ch-Co							-23.33
86	KH1-4; 30.00	ValHaut.	D.bidH.boy.	Co			 				-23.02
87	KH1-4; 30.70	ValHaut.	D.bidH.boy.	Ch-Co							-23.81
88	KH1-4; 31.90	ValHaut.	D.bidH.boy.	Co							-23.63
89	<u>KH1-4; 32.10</u>	ValHaut.	D.bidH.boy.	?		 					<b>-25</b> .70
90	KH1-4; 32.30	ValHaut.	D.bidH.boy.	?							-23.43
01	KH1-4; 35.70	ValHaut.	D.bidH.boy.	<u>Co</u>				_			-23.91
92	KH1-4; 41.30	ValHaut.	D.bidH.boy.	S							-23.15
93	KH1-4; 41.90	ValHaut.	D.bidH.boy.	Co					 		-23.97
94	KH1-4; 42.00	Val,-Haut.	D.bidH.boy.	Co							·23.55
96	KH1-4; 42.30	ValHaut.	D.bidH.boy.	Co							-24.03
96	KH1-4; 43.10	ValHaut.	D.bidH.boy.	Ch				_			-23.00
97	KH1-4; 43.50		D.bidH.boy.								-24.27
98	KH1-4; 47.10 A		D.bidH.boy.		x		[				-23.25
99	KH1-4; 47.10 B		D.bidH.boy.								-23.76
	KH1-4; 49.90		D.bidH.boy.							 	-23.54
101	KH1-4; 52.70		D.bidH.boy.								-22.62
102	KH1-4; 54.00		D.bidH.boy.								-23.39
103	KH1-4; 59.30		D.bidH.boy.							 	-24.67
104	KH1-4; 61.40	ValHaut.	D.bidH.boy.	Ch (w)							-23.99

						<u> </u>		·							
105	KH1-4; 61.60	ValHaut.	D.bidH.boy.	<u>Co</u>											-23.12
106	KH1-4; 62.10	ValHaut.	D.bidH.boy.	<u>Co</u>											-24.68
107	KH1-4; 64.00	ValHaut.	D.bidH.boy.	?										·	-24.39
108	KH1-4b; -8.00	L. Val.	D.bidichot.	?											-23.24
109	KH1-4b; -8.60	L. Val.	D.bidichot.	?				<u> </u>							-25.23
110	<u>KH1-4b; -8.80 A</u>	L. Val.	D.bidichot.	?				<del>_</del>						·	-25.34
111	KH1-4b; -8.80 B	L. Val.	D.bidichot.	?											-23.31
112	KH1-4b; -9.00	<u>L. Val.</u>	D.bidichot.	Ch	<u>×</u>										-22.76
113	KH1-4b; -13.15	L. Val.	D.bidichot.	?										-	-22.55
114	KH1-4b; -15.50	<u>Ļ</u> . Val.	D.bidichot.	?											-23.85
115	KH1-4b; -16.60	L. Val.	D.bidichot.	<u>60</u>										┝_───╄	-23.17
116	KH1-4b; -20.00	L. Val	D.bidichot.	Ch										-	-23.96
117	KH1-4b; -20.05	L. Val.	D.bidichot.	Ch										<b>↓</b> .	<u>•23.15</u>
118	KH5; Loose A	E. Val.	N.klimov.	Ch (w)											24.34
119	KH5; Loose B	E. Val.	N.klimov.	Ch										-	na
120	KH5; Loose C	E. Val.	N.klimov.	Ch (w sil)	x				<u> </u>			<u> </u>		└───┼	<u>-24.80</u>
121	KH10-11; Loose A	E. Val.	P.stuben.	Ch-Co											-25 <u>.45</u>
122	KH10-11; Loose B	E. Val.	P.stuben.	Ch-Co			l			<u> </u>				.	-26,08
123	KH10-11; Loose C	E. Val.	P.stuben.	Ch					ļ					_	-24,78
124	KH13; 1.30	E. Val.	N.klimov.	Ch											-24.45
125	KH13; 1.50	E. Val.	N.klimov.	Ch								<b> </b>			-26 <u>.62</u>
126	KH13; 1.70	E. Val.	N.klimov.	Ch										<u>  </u>	-25.30
127	KH13; 2.05	E. Val.	N.klimov.	Co								<u> </u>			-25.28
128	KH13; 2.40	E. Val.	N.klimov.	Ch								<u> </u>	<u> </u>	<u> </u>	-24.30
129	KH13; 2.60	E. Val.	N.klimov.	Ch								]	<u> </u>		-24.87
130	KH13; 3.20	E. Val.	N.klimov.	Ch											-26.22
	KH13; 3.30	E. Val.	N.klimov.	Ch (w sil)							<b>_</b>	L	<b></b>		-24.39
132	KH13; 3.90	E. Val.	N.klimov.	Ch-Co										<u>  </u>	-26.42
	KH13; 4.45 A	E. Val.	N.klimov.	Ch-Co											-24,72
	KH13; 4.45 B	E. Val.	N.klimov.	Ch-Co	x										-24.33
	KH13; 4.45 C	E. Val.	N.klimov.	Ch (w sil)											-25.06
·	KH13; 5.25 A	E. Val.	N.klimov.	Ch											-24.33
	KH13; 5.25 B	E. Val.	N.klimov.	Ch											ņa
	KH13; 5.40	E. Val.	N, klimov.	Ch-Co								<u> </u>	<u> </u>	<u> </u>	-27.20
	KH13; 5.50	E. Val.	N.klimov.	C0											na
	KH13; 5.60	E. Val.	N.klimov.	Co											-24.31

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141	KH13; 6.10	E. Vai.	N.klimov.	Ch-Co				 						-24.50
142	KH13; 6.30	<u>E. Val.</u>	N.klimov.	Ch-Co				 						-24.40
143	KH13; 7.90	<u>E. Val.</u>	N.klimov.	<u>60</u>			,	 						-25.25
144	KH13; 8.20	E. Val.	N.klimov.	Co				 						<u>na</u>
145	KH13; 8.90 A	E. Val.	N.klimov	<u>Ch (w)</u>	<u>×</u>			 					ł	-23.86
148	KH13; 8.90 B	<u>E. Val.</u>	N.klimov.	<u>Ch (w)</u>		. <u> </u>		 						-24.00
147	KH13; 11.00	E. Val	N.klimov.	<u>co</u>				 						na
148	KH13; 15.60 A	E. Val.	N.klimov.	<u>co</u>				 						-24.65
149	KH13; 15.60 B	E. Val.	N.klimov.	<u></u>				 						-24.74
160	KH13; 18.30	E. Val.	N.klimov.	Ch-Co				 					l	na
161	KH16; -0.25	E. Ryaz.	H.kocS.an.	Ch (w sil)	X			 						-24.03
162	KH16; 0.90	<u>E. Ryaz.</u>	H.kocS.an.	Ch-Co				 						
163	KH16; 1.00 A	E. Ryaz.	H.kocS.an.	Ch-Co				 						-25.08
164		E. Ryaz.	H.kocS.an.	Ch-Co				 					I	24.78
156	KH16; 1.10	E. Ryaz.	H.kocS.an.	Ch-Co				 <u> </u>	]		·			-26.98
166		E. Ryaz.	H.kocS.an.	Ch-Co		_		 	<b></b>	<u> </u>				<u>-24.53</u>
167		E. Ryaz.	H,kocS.an.	Ch-Co	x					l				-23.81
168		E. Ryaz.	H.kocS.an.	Co				 						-24.33
169		E. Ryaz.	H.kocS.an.	Co			<u> </u>	 	<u> </u>		<b></b>	<u> </u>		<u>-23,77</u>
160		E. Ryaz.	H.kocS.an.	?					L		1	L		-25,43
161		E. Ryaz.	H.kocS.an.	?				 . <u> </u>	ļ	<b></b>				-25.46
162	KH16; 3.80	E. Ryaz.	H.kocS.an.	60			<u> </u>	 			ļ			-24.95
163	KH17a; 0.25 B. Lst		B.meses.	Ch (w sil)	x									<u>-26,20</u>
164	KH17c; 2.25 A	L.Ryaz.	B.meses.	Ch-Co				 				l		<u>-24.71</u>
165	KH17c; 2.25 B	L.Ryaz.	B.meses.	Ch-Co				 ]				<u> </u>		-24.43
	KH17c; 2.25 C	L.Ryaz.	B.meses.	Ch (w sil)										-26.72
_	KH17c; 2.50	L.Ryaz.	B.meses.	S		I						L		-24.88
	KH17c; 2.90	L.Ryaz.	B.meses.	S										-23.74
	KH18; 0.60	E. Val.	P.stuben.	Ch-Co	x									-25.19
	KH18; 1.75	E. Val.	P.stuben.	?										-24.98
	KH18; 1.80	E. Val.	P.stuben.	?							<u> </u>	I		-25.30
	KH18; 2.30	E. Val.	P.stuben.	60										-24.90
	KH18; 2.80	E. Val.	P.stuben.	Ch-Co								L		-25 <u>.</u> 12
	KH18; 5.45	E. Val.	P.stuben.	?						<u> </u>	<u> </u>			-24.38
	KH18; 5.85	E. Val.	P.stuben.	?								ļ		-23.20
	KH18; 6.30 A	E. Val.	P.stuben.	Ch										-23.3 <u>1</u>

177	KH18; 6.30 B	E. Val.	P.stuben.	<b>Co</b>		<u> </u>	I		<u> </u>				I	I	-23.70
	KH18; 6.30 C	E. Val.	P.stuben.	Ch	×	ł				i					-24.13
	KH18; 6.60	E. Vai.	P.stuben.	2	<u> </u>								ł		-25.20
	KH18; 8.40	E. Val.	P.stuben.	Ch											-24.32
	KH18; 8.55	E. Val.	P.stuben.	Ch-Co											-23.78
	KH18; 8.65 A	E. Val.	P.stuben.	Ch		·						I_			-24.11
	KH18; 8.65 B	E. Val.	P.stuben.	2											-24.98
	KH18; 10.00	E. Val.	P.stuben.	2									P		-24.55
·	·1.		· /			]							r		
185	SK1; -1.00	E. Oxf.	Mar-Cor	M.W.D.		1.07	0.88	1.05	1.00	1.41	0.91	95	62	426	-22.29
	SK1; 1.20	E. Oxf.	Mar-Cor	M.W.D.		3.20	2.99	2.77	2.99						-21.67
187	SK1; 2.80	E. Oxf.	Mar-Cor	M.W.D.		1.67	1.77	1.05	1.50						-22.50
188	SK1; 3.70	E. Oxf.	Mar-Cor	M.W.D.		1.32	1.31	1.38	1.34						-22.35
189	SK1; 4.00	E. Oxf.	Mar-Cor	M.W.D.		1.10	1.89	1.25	1.41						-22.30
190	SK1; 4.50	E. Oxf.	Mar-Cor	M.W.D.		0.00	0.94	0.92	0.93						-22.04
191	SK1; 5.90	E. Oxf.	Mar-Cor	M.W.D.								ĭ_			-21.58
192	SK1; 6.60	E. Oxf.	Mar-Cor	M.W.D.		3.84	3.75	3.70	3.76	1.30	0.50	52	51	421	-21.29
193	SK1;14.20	E. Oxf.	Mar-Cor	M.W.D.		0.43	0.30	0.42	0.38						-22.82
194	SK1; 15.80	E. Oxf.	Mar-Cor	M.W.D.											-22.36
195	SK1; 18.20	E. Oxf.	Mar-Cor	M.W.D.		0.26	0.15	0.37	0.26						-22.59
196	SK1; 21.50	E. Oxf.	Mar-Cor	M.W.D.											-22.70
197	<u>SK1; 22.10</u>	E. Oxf.	Mar-Cor	M.W.D.											-22.69
198	SK1; 24.30	E. Oxf.	Mar-Cor	M.W.D.		0.59	0.62	0.59	0,60						-22.65
189	SK1; 26.10	E. Oxf.	Mar-Cor	M.W.D.								,			-22,32
200	SK1; 28.60	E. Oxf.	Mar-Cor	M.W.D.											-22.59
201	SK1; 30.60	E, Oxf.	Mar-Cor	M.W.D.		0.36	0.37	0.46	0.40	0.66	1.76	81	104	424	-23.43
202	SK1; 33.20	E. Oxf.	Mar-Cor	M.W.D.						1.45	4.19	41	55	425	-22.31
203	SK1; 35.50	E. Oxf.	Mar-Cor	M.W.D.		0.59	0.56	0.46	0.54						-22.81
204	SK1; 37.40	E. Oxf.	Mar-Cor	M.W.D.											-22.09
205	SK1; 38.70	E. Oxf.	Mar-Cor	M.W.D.		0.58	0.89	0.81	0.76						-22.37
206	SK1; 41.40	E. Oxf.	Mar-Cor	<u>M.W.D.</u>								[			-22.55
207	SK1; 41.50	E. Oxf.	Mar-Cor	<u>M.W.D.</u>						3.38	1.60	43	36	433	-21.73
	SK1; 43.00	E. Oxf.	Mar-Cor	M.W.D.		1.07	1.15	0.92	1.05						-22.34
209	SK1; 44.60	E. Oxf.	Mar-Cor	M.W.D.		I							]		-22.11
210	SK1; 46.60	E. Oxf.	Mar-Cor	<u>M.W.D.</u>		I									-22.73
211	SK1; 47.10	E. Oxf.	Mar-Cor	M.W.D.									·		<u>-22.64</u>

		E 0.4	hu 0			0.04	0.00	0.00		<u> </u>				
	SK1; 50.00	E. Oxf.	Mar-Cor	M.W.D.	0.63	0.61	0.80	0.68						-22,80
	SK1; 52.30	E. Oxf.	Mar-Cor	M.W.D.	-									<u>-22.31</u>
	SK1; 52.50	E. Oxf.	Mar-Cor	M.W.D.	-									-22.29
	SK1; 55.10	E. Oxf.	Mar-Cor	M.W.D.	1.10	0.81	0.81	0.91						-22.55
	SK1; 58.90	E. Oxf.	Mar-Cor	M.W.D.	— ——									-22.81
	SK1; 60.20	E. Oxf.	Mar-Cor	M.W.D.										-22.25
	SK1; 61.60	E. Oxf.	Mar-Cor	M.W.D.	0.45	0.55	0.70	<u>0.57</u>	1.16	1 <u>.49</u>	53	73	423	-22.78
	SK1; 66.30	E. Oxf.	Mar-Cor	M.W.D.	<u> </u>						<u> </u>			22.55
	SK1; 66.50	E. Oxf.	Mar-Cor	M.W.D.										
	SK1; 66.70	E. Oxf.	Mar-Cor	M.W.D.	3.58	1.71	3.59	2.96	9.22	0.93	40	21	428	-21.55
	SK2; 0.00	M. Oxf.	Den-Ten	M.W.D.	2.09	2.07	2.06	2.07	2.60	0.67	28	32	426	-21.56
	SK2; 0.25	M. Oxf.	Den-Ten	<u>M.W.D.</u>	<b>-</b>			·						21.64
	SK2; 0.50	M. Oxf.	Den-Ten	M.W.D.										-22.18
	<u>SK2; 0.75</u>	M. Oxf.	Den-Ten	M.W.D.	7.59	7.13	7.07	7.26						-21.91
	SK2; 1.00	M. Oxf.	Den-Ten	M.W.D.										-22.13
	SK2; 1.05	M. Oxf.	Den-Ten	M.W.D.										-22.04
	SK2; 1.25	M. Oxf.	Den-Ten	M.W.D.					3.20	0.94	45	56	427	-21.83
229	SK2; 1.50	M. Oxf.	Den-Ten	M.W.D.									<u> </u>	-22.01
230	SK2; 1.75	M. Oxf.	Den-Ten	M.W.D.	_									-22.47
-	SK2; 2.00	M, Oxf,	Den-Ten	M.W.D.	0,19	0.38	0.32	0.30						-23,71
	SK2; 2.15	M. Oxf.	Den-Ten	M.W.D.					3.43	2.21	60	23	429	-23.74
233	SK2; 2.25	M. Oxf.	Den-Ten	M.W.D.										-23.66
234	SK2; 2.50	M. Oxf.	Den-Ten	M.W.D.					1.00	1.52	89	79	424	-23.63
235	SK2; 2.80	M. Oxf.	Den-Ten	M.W.D.					0.66	2.23	57	113	423	-23.39
236	SK2; 3.25	M. Oxf.	Den-Ten	M.W.D.										-22.24
237	SK2; 3.30	M. Oxf.	Den-Ten	<u>M.W.D</u> .										~
238	SK2; 3.50	M. Oxf.	Den-Ten	M.W.D.					1.99	1.68	66	36	427	-21,82
239	SK2; 3.70	M. Oxf.	Den-Ten	M.W.D.	2.65	2.41	2.63	2.56	_					-21.84
240	SK2; 3.90	M. Oxf.	Den-Ten	M.W.D.								-		-21.96
241	SK2; 4.15	M. Oxf.	Den-Ten	M.W.D.										-21.67
242	SK2; 4.40	M. Oxf.	Den-Ten	M.W.D.										-22.48
243	SK2; 4.55	M. Oxf.	Den-Ten	M.W.D.	1.26	1.09	1.13	1.16						~
244	SK2; 4.80	M. Oxf.	Den-Ten	M.W.D.										-22.47
246	SK2; 5.05	M. Oxf.	Den-Ten	M.W.D.					3.41	1.93	53	28	430	-22.28
248	SK3; 0.10	E-M. Oxf.	Cor-Den	M.W.D.	1.50	1.56	1.47	1.51				··		-22.21
	SK3; 0.25	E-M. Oxf.	Cor-Den	M.W.D.										-21.79

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	SK3; 0.70	E-M. Oxf.	Cor-Den	M.W.D.	I									~
_	SK3; 0.85	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 				2.79	1.25	37	39	<u> </u>	22.06
	SK3; 1.20	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 					ł-				-21.57
	SK3; 1.50	E-M. Oxf.	Cor-Den	M.W.D.	 4.50	5.31	4.76	4.86						-21.80
·	SK3; 2.00	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 l									<u>-21.79</u>
	SK3; 2.20	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 					-	l			-22.23
	SK3; 3.00	E-M. Oxf.	Cor-Den	M.W.D.	 4.63	4.60	4.66	4.63						-21.89
	<u>SK3; 3.50</u>	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 									-21.88
	SK3; 5.20	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 				3.36	1.10	23	37	425	
	SK3; 5.55	E-M. Oxf.	Cor-Den	M.W.D.	 									-22.06
	SK3; 5.65	E-M. Oxf.	Cor-Den	M.W.D.	 2.10	2.44	2.05	2.20						~
269	SK3; 5.80	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 									-21.86
260	SK3; 5.90	E-M. Oxf.	Cor-Den	M.W.D.										~
261	SK3; 6.15	E-M. Oxf.	Cor-Den	M.W.D.	6.24	6.23	6.30	6.26						-21.68
262	SK3; 6.40	E-M. Oxf.	Cor-Den	<u>M.W.D.</u>	 									-22.08
263	SK3; 7.35	E-M. Oxf.	Cor-Den	M.W.D.										-22.26
264	SK3; 7.55	E-M. Oxf.	Cor-Den	M.W.D.										-22.26
285	SK3; 7.90	E-M. Oxf.	Cor-Den	M.W.D.	1.41	1.86	1.28	1.52	1.98	1.42	82	43	426	-22.50
266	SK4; 0.20	E-L. Call.	Koe-Lam	M.W.D.	0.71	0.66	0.72	0.70	0.78	0.14	92	105	422	-24.90
267	SK4; 0.45	E-L. Call.	Koe-Lam	M.W.D.										-25.19
268	SK4; 1.05	E-L. Call.	Koe-Lam	M.W.D.					2.04	0.40	223	57	418	-26.28
269	SK4; 1.55	E-L. Call.	Koe-Lam	M.W.D.										-25.34
270	SK4; 1.80	E-L. Call.	Koe-Lam	M.W.D.	ľ				1.02	0.33	114	72	420	-24.96
271	SK4; 2.50	E-L. Call.	Koe-Lam	M.W.D.										-25.18
272	SK4; 3.20	E-L. Call.	Koe-Lam	M.W.D.						i	i			-25.10
273	SK4; 3.70	E-L. Call.	Koe-Lam	M.W.D.							ľ			-24.81
274	SK4; 6.80	E-L. Call.	Koe-Lam	M.W.D.	1.01	1.08		1.05						-23.05
	SK4; 6.90	E-L. Call.	Koe-Lam	M.W.D.					0.50	1.87	49	317	421	-23.67
	SK4; 8.95	E-L. Call.	Koe-Lam	M.W.D.						<u> </u>				-23.04
	SK4; 10.50	E-L. Call,	Koe-Lam	M.W.D.					1.88	1.27	44	97	426	-22.52
	SK4; 11.50	E-L. Call.	Koe-Lam	M.W.D.	0.36	0.33	0.45	0.38						-22.92
	SK5; -1.10	E. Kimm.	Bay-Cym	M.W.D.	 2.89	2.85	2.88	2.87			ł			-25.12
_	SK5; -0.60	E. Kimm.	Bay-Cym	M.W.D.	 								——	-24.46
	SK5; 1.90	E. Kimm.	Bay-Cym	M.W.D.										-24,40
	SK5; 2.10	E. Kimm.	Bay-Cym	M.W.D.	 				I					-24.39
	SK5; 2.45	E. Kimm.	Bay-Cym	M.W.D.	 1.93	2.38	2.12	2.14	i	l	l:			-24.27

					— T	r							T	Ī	-24.40
-		E. Kimm.	Bay-Cym	M.W.D.						1.68	0.48	111	73	428	-24.81
		<u>E. Kimm.</u>	Bay-Cym	<u>M.W.D.</u>						<u> </u>	0.40			- 420	-24.01
		<u>E. Kimm.</u>	Bay-Cym	<u>M.W.D.</u>	ŀ	1.98	1.99	2.08	2.02	l			ł·		-24.74
		E. Kimm.	Bay-Cym	M.W.D.				ł					ł		-24.07
·		E. Kimm.	Bay-Cym	<u>M.W.D.</u>	ŀ						ŀ	·	ŀ		-24,07
		<u>E. Kimm.</u>	Bay-Cym	<u>M.W.D.</u>	ŀ	7.99	8.06	9.03	<u> </u>				43	419	-23.84
		E. Kimm.	Bay-Cym	M.W.D.	ł					3.54	0.29		43	419	-23.04
·		E. Kimm.	Bay-Cym	<u>M.W.D.</u>	ŀ						ŀ				-24.05
		E. Kimm.	Bay-Cym	M.W.D.	ŀ	3.11	3.19	3,19	3.16		ł		ŀ		-23.97
		E, Kimm.	Bay-Cym	M.W.D.	ł										
		E. Kimm.	Bay-Cym	M.W.D.		2.18	2.14	2.14	2.15						-23.91
295	SK5; 7.20	E. Kimm.	Bay-Cym	<u>M.W.D.</u>											-24.22
	SK5; 7.40	<u>E. Kimm.</u>	Bay-Cym	<u>M.W.D.</u>		4.99	4.65	5.54	5.06						~
297	SK5; 7.70	E. Kimm.	Bay-Cym	M.W.D.											-24.67
298	SK5; 8.10	E. Kimm.	Bay-Cym	<u>M.W.D.</u>					·	<u>3.19</u>	0.40	<u> </u>	47	420	-24.71
299	SK5; 8.95	E. Kimm.	Bay-Cym	M.W.D.		1.66	1.79	1.85	1.77						-24.00
300	SK6; -0.30	E. Kimm.	Cym	<u>M.W.D.</u>		1.39	1.34	1.37	1.37						-23.94
301	SK6; 0.00	E. Kimm,	Cym	<u>M.W.D.</u>											-24.07
302	SK6; 0.50	E. Kimm.	Cym	<u>M.W.D.</u>											-24.07
303	SK6; 1.50	E. Kimm.	Cym	M.W.D.						1.28	0.20	31	70	421	-23.54
304	SK6; 1.90	E. Kimm.	Cym	<u>M.W.D.</u>											-23.90
305	SK6; 2.30	E. Kimm.	Cym	M.W.D.											-23.89
308	SK6; 2.40	E. Kimm.	Cym	M.W.D.		1.95	1.86	1.60	1.80						~
307	SK6; 2.50	E. Kimm.	Cym	M.W.D.	_										-23.75
308	SK6; 2.60	E. Kimm.	Cym	M.W.D.											23.85
309	SK6; 4.05	E. Kimm.	Cym	M.W.D.		3.57	3.29	3.33	3.40						-2 <u>4.5</u> 7
	SK6; 4.50	E. Kimm.	Cym	M.W.D.					_						-24.47
	SK6; 5.30	E. Kimm.	Cym	M.W.D.		-			-						-24.81
	SK6; 5.55	E. Kimm.	Cym	M.W.D.											-25.28
	SK6; 5.80	E. Kimm.	Cym	M.W.D.						2.76	0.26	165	45	4 <u>16</u>	-25.30
	SK6; 5.90	E. Kimm.	Cym	M.W.D.		3.27	3.26	3.18	3.24						-25.06
	SK6; 6.40	E. Kimm.	Cym	M.W.D.											-24.93
	SK6; 6.55	E. Kimm.	Cym	M.W.D.											-24.99
	SK6; 6.90	E. Kimm.	Cym	M.W.D.		3.58	3.77	3.75	3.70						-24.88
	SK6; 7.00	E. Kimm.	Cym	M.W.D.											-24.95
	SK6; 7.20	E. Kimm.	Cym	M.W.D.						2.18	0.31	82	56	415	-24.72

			. <u>.</u>			<u> </u>		<u> </u>				T	T		-24.79
		E. Kimm.	Cym	M.W.D.				<u> </u>						ł	-25.29
	SK6; 7.50	E. Kimm.	Cym	<u>M.W.D.</u>				ŀ							
	SK6; 7,70	E. Kimm.	Cym	M.W.D.	<b> </b> -		ł	·		2.89	0.19	147	43	418	-25.36
		E. Kimm.	Cym	<u>M.W.D.</u>										ł	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
	SK6; 7.90	E. Kimm.	<u>Cym</u>	<u>M.W.D.</u>		2.27		2.90	2.59						-25.27
326	<u>SK7; 1.20</u>	OxfKim.	Reg-Bay	<u>M.W.D.</u>		2.64	2.53	2.75	2.64		l			ŀ	-23.34
	SK7; 1.40	OxfKim.	Reg-Bay	M.W.D.										ł	-23.69
327	SK7; (2.80)	OxfKim.	Reg-Bay	<u>M.W.D.</u>											-24.36
328	<u>SK7; 3.00</u>	OxfKim.	Reg-Bay	<u>M.W.D.</u>						3.70	0.55	68	42	425	-23.22
329	SK7; 5.70	OxfKim.	Reg-Bay	M.W.D.											-24.28
330	SK7; 6.80	OxfKim.	Reg-Bay	M.W.D.		1.44	1.50	1,43	1.46						-24.54
331	SK7; 9.30	OxfKim.	Reg-Bay	<u>M.W.D.</u>											
332	SK7; 10.80	OxfKim.	Reg-Bay	<u>M.W.D.</u>						1.08	0.28	<u>63</u>	75	421	-24.40
333	SK7; 11,10	OxfKim.	Reg-Bay	M.W.D.											-25.06
334	SK7; 12.10	OxfKim	Reg-Bay	M.W.D.											-24.86
335	SK7; 12.20	OxfKim.	Reg-Bay	M.W.D.						1.09	0.40	62	83	423	-25.06
	SK7; 14.80	OxfKim.	Reg-Bay	M.W.D.		3.04	3.17	3.11	3.11						-24.56
	SK7; 15.40	OxfKim.	Reg-Bay	M.W.D.											<u>-24.50</u>
	SK7; 16.90	OxfKim.	Reg-Bay	M.W.D.	r										-25.29
	SK7; 17.35	OxfKim.	Reg-Bay	M.W.D.	r				_	4.56	1.05	396	40	420	26.07
_	SK7; 17.70	OxfKim.	Reg-Bay	M.W.D.	_	1.63	1.58	1.85	1.69						~
	SK7; 17.80	OxfKim.	Reg-Bay	M.W.D.											-24.69
	SK7; 17.90	OxfKim.	Reg-Bay	M.W.D.						2.56	0.22	68	47	417	-24.45
_	SK7; 18.40	OxfKim.	Reg-Bay	M.W.D.							_				-25.40
	SK7; 19.90	OxfKim.	Reg-Bay	M.W.D.		4.79	4.93	4.85	4.86						-24.08
	SK7; 20.25	OxfKim.	Reg-Bay	M.W.D.		î									-24.14
	SK7; 20.75	OxfKim.	Reg-Bay	M.W.D.						2.19	0.18	52	48	421	-24.27
	SK7; 20.90	OxfKim.	Reg-Bay	M.W.D.			······					_			-24.21
	SK7; 27.30	OxfKim.	Reg-Bay	M.W.D.								·			-25.03
	SK7; 27.95	OxfKim.	Reg-Bay	M.W.D.		2.38	2.45	2.41	2.41						-24.73
	SK8; 14.80	E. Oxf.	Cor	M.W.D.		0.11	0.23	0.19	0.18	0.90	2.15	61	158	424	-22.62
	SK8; 18.50	E. Oxf.	Cor	M.W.D.										i	-22.24
	SK8; 25.75	E. Oxf.	Cor	M.W.D.		3.35	3.30	·	3.33	3.77	1.06	35	35	425	-21.51
	SK8; 26.70	E. Oxf.	Cor	M.W.D.											-21.57
	SK8; 27.20	E. Oxf.	Cor	M.W.D.											-21.66
	SK8; 27.40	E. Oxf.	Cor	M.W.D.	ł			·							-21.71

356	SK8; 31.80	E. Oxf.	Cor	M.W.D.	1.77	1.61	1.30	1.56	·					-21.86
	SK8; 33.35	E. Oxf.	Cor	M.W.D.					5.44	1.68	44	28	427	-21.26
	SK8; 33.70	E. Oxf.	Cor	M.W.D.				I						-21.66
·	SK8; 34.70	E. Oxf.	Cor	M.W.D.				[						-21.46
_	SK8; 35.80	E. Oxf.	Cor	M.W.D.	_		î							-21.50
·	SK8; 36.20	E. Oxf.	Cor	M.W.D.	_			··		t			· ·	-21.56
	SK8; 39.40	E. Oxf.	Cor	M.W.D.	3.64	3.94	3.67	3.75		i				-21.95
	SK9; -2.00	M-L. Oxf.	Ten-Glo	M.W.D.	2.24	2.79	2.23	2.42	5.23	1.72	64	28	424	-21.98
	SK9; -1.70	M-L. Oxf.	Ten-Glo	M.W.D.				î						-22.59
385	SK9; -0.30	M-L. Oxf.	Ten-Glo	M.W.D.					1.04	3.28	59	94	424	-22.91
366	SK9; 0.40	M-L. Oxf.	Ten-Glo	M.W.D.										-22.30
367	SK9; 0.60	M-L, Oxf.	Ten-Glo	M.W.D.										-
368	SK9; 0.90	M-L. Oxf.	Ten-Glo	M.W.D.					3.31	1.73	61	34	428	-22.19
369	SK9; 1.00	M-L. Oxf.	Ten-Glo	M.W.D.										~
370	SK9; 1.20	M-L. Oxf.	Ten-Glo	M.W.D.	3.77	3.87	3.86	3.83						-22.29
371	SK9; 1.50	M-L. Oxf.	Ten-Glo	M.W.D.										-22.59
372	SK9; 2.00	M-L. Oxf.	Ten-Glo	M.W.D.										-21.77
373	SK9; 2.40	M-L. Oxf.	Ten-Glo	M,W.D.										-21.76
374	SK9; 2.70	M-L. Oxf.	Ten-Glo	M.W.D.						]				-21.70
376	SK9; 2.90	M-L. Oxf.	Ten-Glo	M.W.D.										-22.05
376	SK9; 3.40	M-L. Oxf.	Ten-Glo	M.W.D.	4.95	5.76	5.27	5.33						-22.10
377	SK9; 3.70	M-L. Oxf.	Ten-Glo	M.W.D.										-22.25
378	SK9; 3.90	M-L. Oxf,	Ten-Glo	M.W.D.				_						-22.25
379	SK9; 4.20	M-L. Oxf.	Ten-Glo	M.W.D.	2.61	2.53	2.53	2.56						-22.50
380	SK9; 4.70	M-L. Oxf.	Ten-Glo	M.W.D.					5.90	0.99	30	24	433	-21.69
381	SK9; 4.90	M-L. Oxf.	Ten-Glo	M.W.D.										~
382	SK9; 5.25	M-L. Oxf.	Ten-Glo	M.W.D.					1.81	2.56	45	49	426	-22.58
383	SK9; 5.65	M-L. Oxf.	Ten-Glo	M.W.D.										-22.53
384	SK9; 6.05	M-L. Oxf.	Ten-Glo	M.W.D.	2.05	2.15	2.01	2.07					_	-22.81
385	SK9; 6.70	M-L. Oxf.	Ten-Gio	M.W.D.	_									-22.75
386	SK9; 7.30	M-L. Oxf.	Ten-Gio	M.W.D.										-23.24
387	SK9; 7.55	M-L. Oxf.	Ten-Glo	M.W.D.										-23.11
388	SK9; 7.80	M-L. Oxf.	Ten-Glo	M.W.D.										~
389	SK9; 7.95	M-L. Oxf.	Ten-Glo	M.W.D.				]						-22.69
390	SK9; 8.55	M-L. Oxf.	Ten-Glo	M.W.D.	-1.08	-1.18	-1.50	-1.25	1.14	5.31	73	69	427	-23.27
391	SK9; 10.80	M-L. Oxf.	Ten-Glo	M.W.D.					4.43	0.19	29	28	422	-22.35

392	SK9; 12.50	M-L. Oxf.	Ten-Glo	M.W.D.											-23.19
393	SK9; 12.60	M-L. Oxf.	Ten-Glo	M.W.D.											~
394	SK9; 12.75	M-L. Oxf.	Ten-Glo	M.W.D.		3.84	3.83	4.13	3.93						~
395	SK9; 13.10	M-L. Oxf.	Ten-Glo	M.W.D.										_	-23.79
396	SK9; 13.40	M-L. Oxf.	Ten-Glo	M.W.D.	_	1.66	1.65	1.65	1.65	1.96	0.16	250	_26	419	-24.26
397	SK10; 0.40	L. Oxf.	Ser-Reg	M.W.D.		1.59	1.58	1.59	1.59	1.78	0.19	123	26	427	-24.49
398	SK10; 0.90	L. Oxf.	Ser-Reg	M.W.D.											-24.43
399	SK10; 3.40	L. Oxf.	Ser-Reg	M.W.D.									_		-23.97
400	SK10; 4.60	L. Oxf.	Ser-Reg	M.W.D.						2.22	0.28	58	33	425	-23,15
401	SK10; 8.20	L. Oxf.	Ser-Reg	M.W.D.											-23.83
402	SK10; 12.20	L. Oxf.	Ser-Reg	M.W.D.		2.43	2.41	2.46	2.43						-24.34
403	SK10; 12.70	L. Oxf.	Ser-Reg	M.W.D.											~
404	SK10; 13.40	L. Oxf.	Ser-Reg	M.W.D.						1.63	0.24	91	30	425	-24.13
405	SK10; 14.30	L. Oxf.	Ser-Reg	M.W.D.		1.14	1.10	1.13	1.12		-				-24.28
406	SK10; 15.30	L. Oxf.	Ser-Reg	M.W.D.											~
407	SK10; 15.70	L. Oxf.	Ser-Reg	M.W.D.											-24.68
408	SK10; 21.90	L. Oxf.	Ser-Reg	M.W.D.		1.23	1,21	1.34	1.26	1.35	0.27	123	_44	427	-25.18