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Catagenic ankerite replacing biogenic calcite in the Marhøgda Bed (Jurassic), Sassenfjorden, Spitsbergen

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ABSTRACT: The Marhøgda Bed occurring at base of the Adventdalen Group in Sassenfjorden, Spitsbergen contains common ankerite–replaced belemnite skeletons. Petrographic, major element geochemical, and stable carbon and oxygen isotopic data indicate that the ankerite originated in a catagenic environment associated with thermal degradation of kerogen and hydrocarbon generation in the sequence. It formed at maximum temperature of 150°C under burial of approx. 2 000 m, most probably during Paleogene filling and subsidence of the Central Spitsbergen Basin. Dissolution of biogenic calcite and precipitation of ankerite reflect extensive heat flow through the Adventdalen Group sequence related to the Cretaceous and Paleogene magmatic and orogenic activity in Svalbard.

Key words: Arctic, Spitsbergen, Jurassic, Marhøgda Bed, ankerite, palaeotemperatures, burial diagenesis, hydrocarbon generation.

Introduction

Organic-rich, fine-grained facies of the Sassendalen, Kapp Toscana and Adventdalen groups (Triassic–Early Cretaceous) in Spitsbergen, Svalbard (Fig. 1) contain carbonate concretions, bands and cementstone horizons originated in subsurface diagenetic environment (Harland 1997 and references therein). The nature of these deposits suggests their preferential formation at shallow depths under conditions of intense microbiological degradation of sedimentary organic matter. It is, however, likely that some of the carbonates originated in deep burial environment under increased temperature and pressure. These carbonates might potentially provide important information on conditions and processes related to thermal degradation of kerogen and hydrocarbon generation in organic-rich intervals of the Mesozoic sedimentary sequence in Svalbard.

Fig. 1. Sketch map of the Svalbard archipelago showing studied locations of the Marhøgda Bed at the southern margin of Sassenfjorden in Spitsbergen.

The base of the Adventdalen Group in central Spitsbergen (Fig. 2) is marked by a sideritic cementstone horizon, which is classified into the Marhøgda Bed in local lithostratigraphic scheme (Bäckstrom and Nagy 1985, Mørk *et al*. 1999). The cementstone originated in shallow suboxic diagenetic environment dominated by microbial reduction of ferric iron, though deeper processes led to additional formation of ankerite at burial temperatures of approx. 70–90° C in an environment overwhelmed by thermal decarboxylation processes (Krajewski *et al*. 2001).

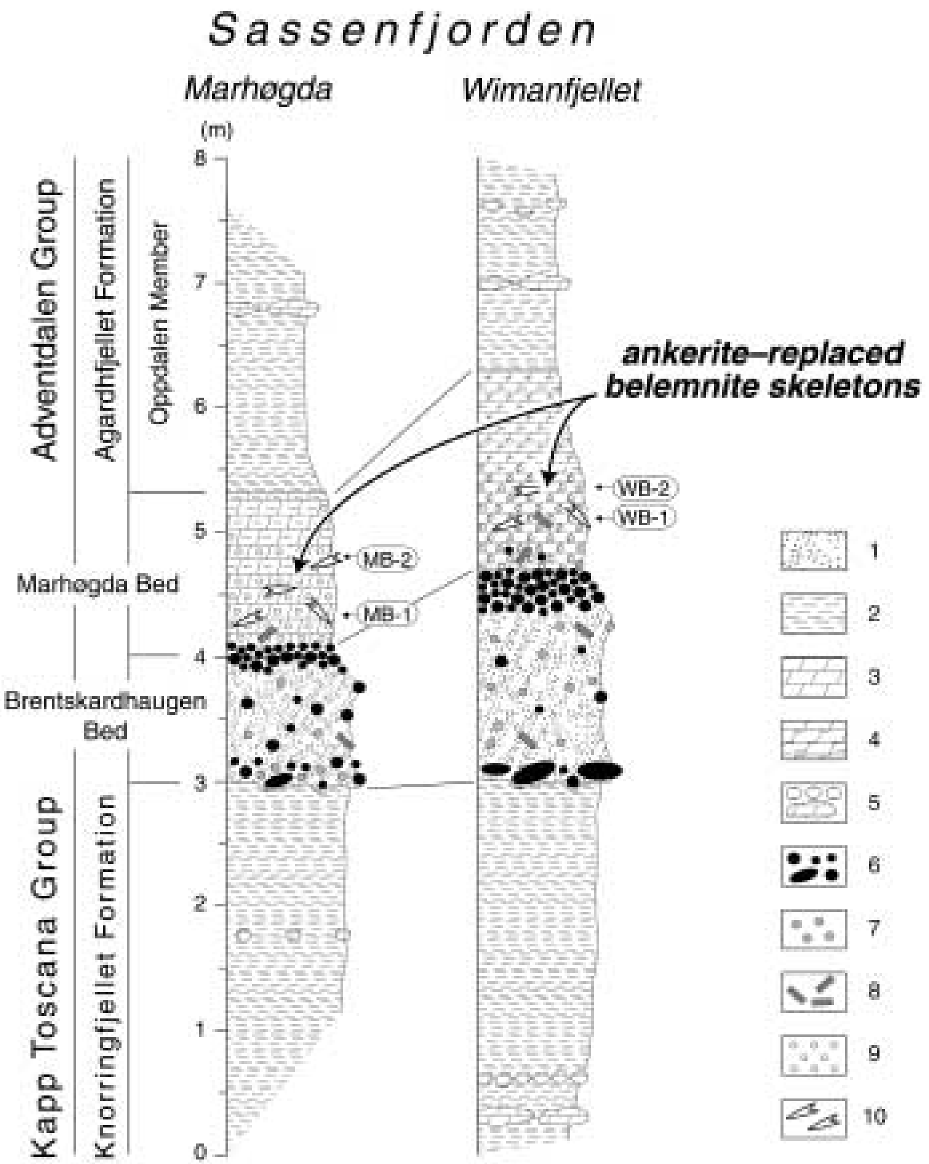

Fig. 2. Sections of the Marhøgda Bed at Marhøgda and Wimanfjellet (southern margin of Sassenfjorden) in Spitsbergen. MB-1, MB-2, WB-1, and WB-2 are ankerite–replaced belemnite samples analyzed for the carbon and oxygen isotopic composition. 1 – medium- to coarse-grained sandstone and conglomerate; 2 – shale, mudstone and siltstone; 3 – carbonate cementstone bands; 4 – clay-rich carbonate cementstone bands; 5 – concretionary carbonate cementstone; 6 – phosphate nodules and pebbles; 7 – quartz and chert pebbles; 8 – wood fragments (commonly phosphatized); 9 – ankerite– and kaolinite–replaced pellets, ooids and grains; 10 – ankerite–replaced belemnite skeletons.

This paper documents the presence of ankerite replacing biogenic low–Mg calcite in the Marhøgda Bed that formed at high burial temperatures, most probably during a maximum subsidence of the Central Spitsbergen Basin in Paleogene. Petrographic, major element geochemical, and stable carbon and oxygen isotopic data are presented to support its catagenic origin associated with hydrocarbon generation in the sequence.

Materials and methods

The present study is based on the Marhøgda and Wimanfjellet sections of the Marhøgda Bed at the southern margin of Sassenfjorden in central Spitsbergen (Fig. 2). Detailed description of the sequence can be found in papers by Bäckstrom and Nagy (1985), Kopik and Wierzbowski (1988), Krajewski (1989), Dypvik *et al.* (1991a, b) and Krajewski *et al.* (2001).

Catagenic ankerite in the Marhøgda Bed has been revealed to form replacement structures in belemnite skeletons that commonly occur at base of the Agardhfjellet Formation. 12 ankerite–replaced belemnite samples were analyzed in detail using standard petrographic methods, including transmitted light microscopy (TLM), back-scattered electron imaging (BSE) and energy-dispersive X-ray spectroscopy (EDS). Quantitative EDS analyses of ankerite were obtained using a JEOL JSM-840A equipped with a LINK ANALYTICAL spectrometer AN 1000/85S. Operating conditions were a 15 kV acceleration voltage, 1 to 5 μm beam diameter, and 100-s counting time. Detection limits of the analyzed elements (Ca, Mg, Fe, and Mn) were better than 0.1 wt%. EDS data were recalculated as cation mole fractions to facilitate comparisons among samples.

Mineral composition of four belemnite samples (MB-1, MB-2, WB-1, and WB-2) was analyzed by means of X-ray diffraction. The detailed location of these samples is shown in Fig. 2. Crushed samples were hand picked under binocular microscope to provide material without contamination by the rock matrix. Samples were ground to < 63 μm fraction using an agate mortar and pestle. Powder diffraction patterns were recorded on a SIGMA 2070 diffractometer using a curved position sensitive detector in the range 2–120° 2θ with Co$K\alpha$ radiation and 20 h analysis time. DIFFRACTIONEL software v. 03/93 was used to process the obtained data.

The same samples and size fraction were analyzed for the carbon and oxygen isotopic composition of ankerite. CO_2 for isotopic analyses was produced from samples by reaction with anhydrous phosphoric acid (d = 1.90 g cm^{-3}) at 25°C for 20h. Isotopic $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios were determined using a FINNIGAN MAT DELTA^{PLUS} spectrometer working in dual inlet mode with universal triple collector. The δ values were calculated relative to isotopic ratios of the international standard NBS 19. Oxygen isotope fractionation factor $\alpha = 1.01098$ was used for isotopic calculation (Becker and Clayton 1976). The results are expressed as $\delta^{13}C$ and $\delta^{18}O$ notations with respect to VPDB (Vienna Peedee Belemnite). Analytical reproducibility in laboratory was better than ± 0.05‰ and ± 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

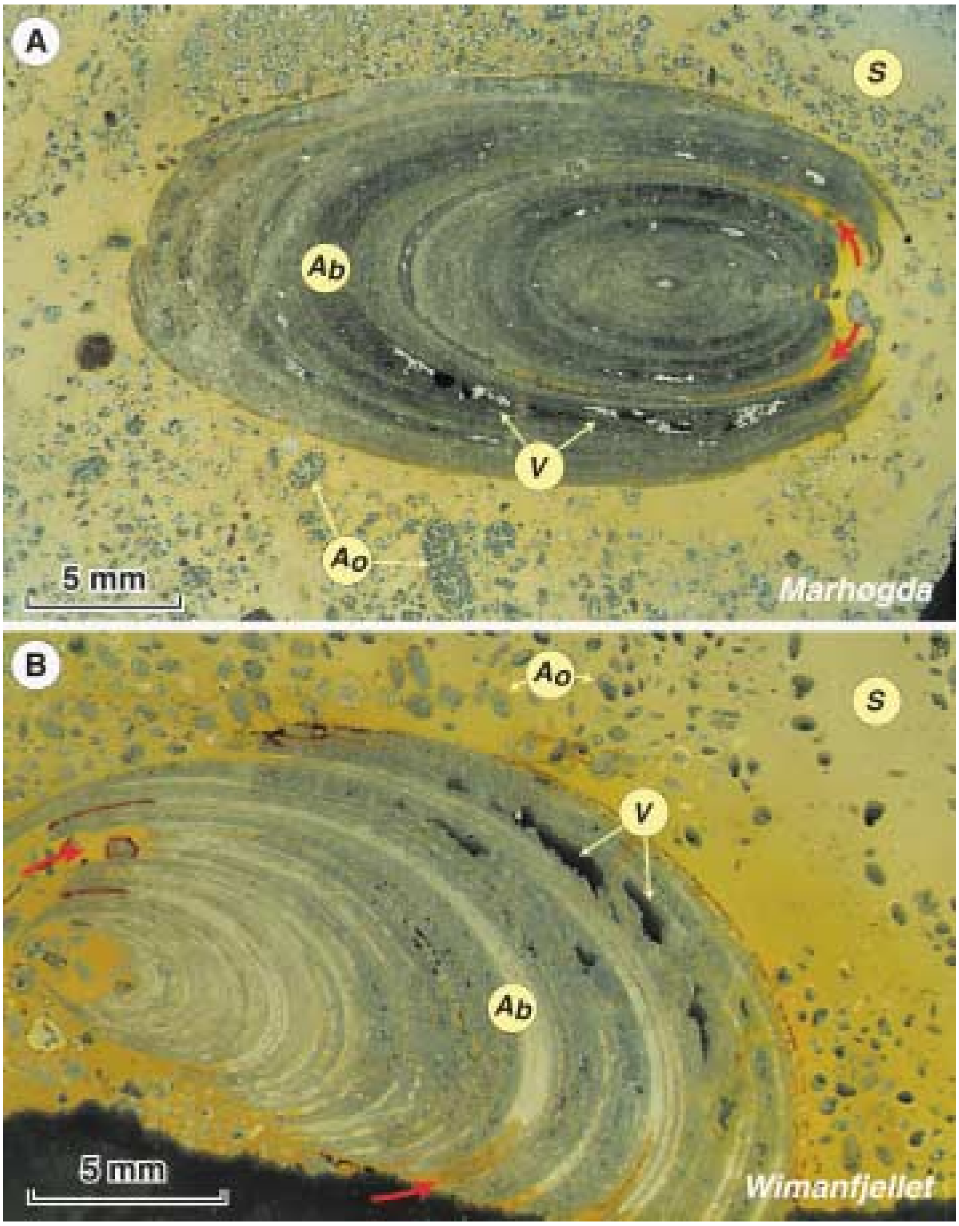

Fig. 3. Ankerite–replaced belemnite skeletons in the Marhøgda Bed at Marhøgda (**A**) and Wimanfjellet (**B**). Belemnite rostra occur in early diagenetic microsparitic siderite matrix (*S*) that contains common ankerite– and kaolinite–replaced ooids and grains (A_o). They show early diagenetic dissolution microstructures filled by siderite (red arrows), and are replaced by zoned ankerite (A_b) that reflects stages of biogenic calcite dissolution and carbonate precipitation during burial. Voids (*V*) occurring in incompletely replaced rostra contain bitumen inclusions. **A**, **B** – thin section photographs.

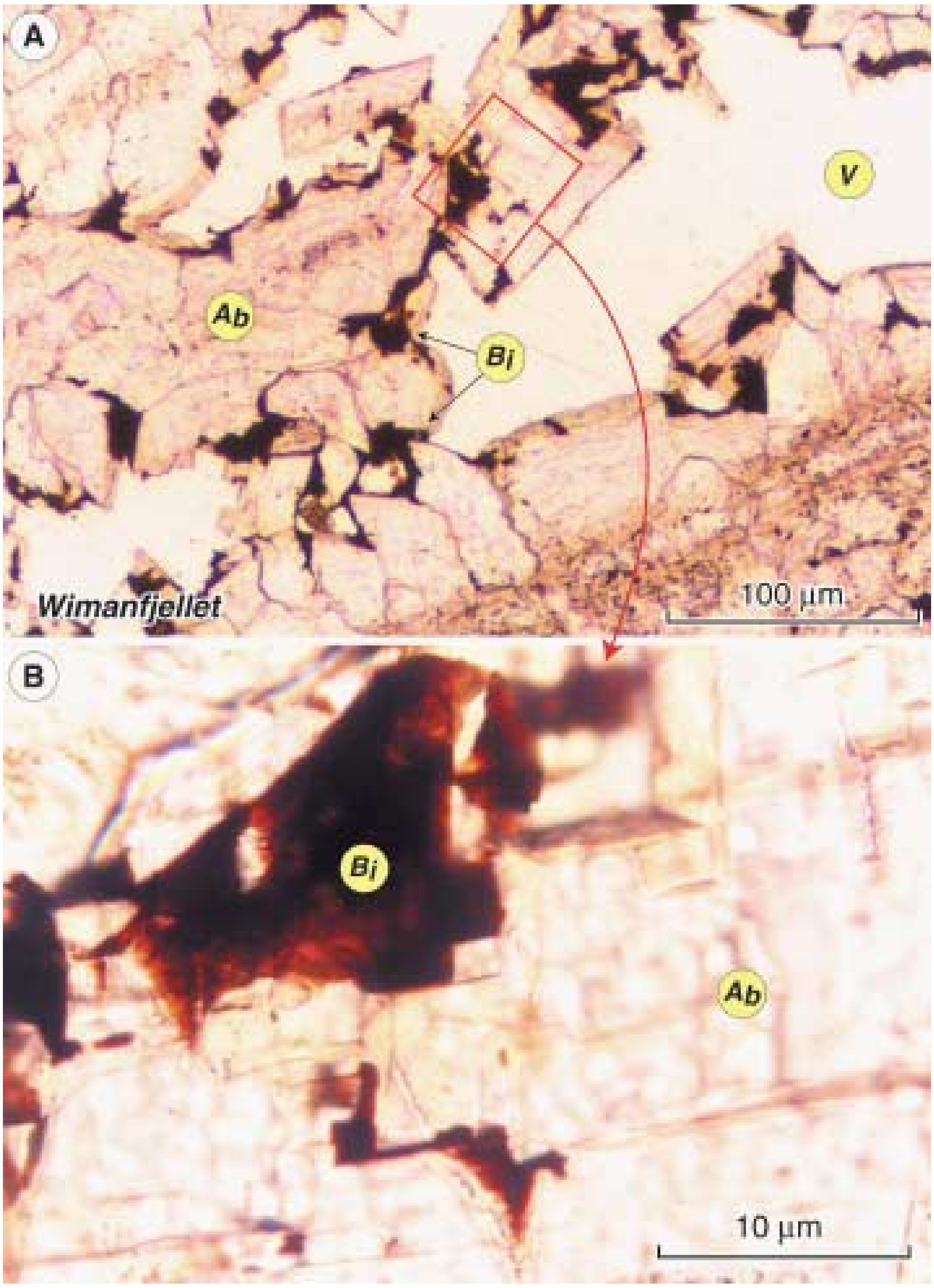

Fig. 4. **A**. Bitumen inclusions (B_i) in ankeritic fabric (A_b) replacing belemnite skeleton at Wimanfjellet. The inclusions tend to concentrate in later generation of ankeritic fabric, which leaves common voids (V) in incompletely cemented structure. **B**. Bitumen inclusions (B_i) locked within ankerite crystal (A_b) suggest that the crystal growth occurred during generation and migration of hydrocarbons in the sequence. **A**, **B** – TLM photomicrographs, normal light.

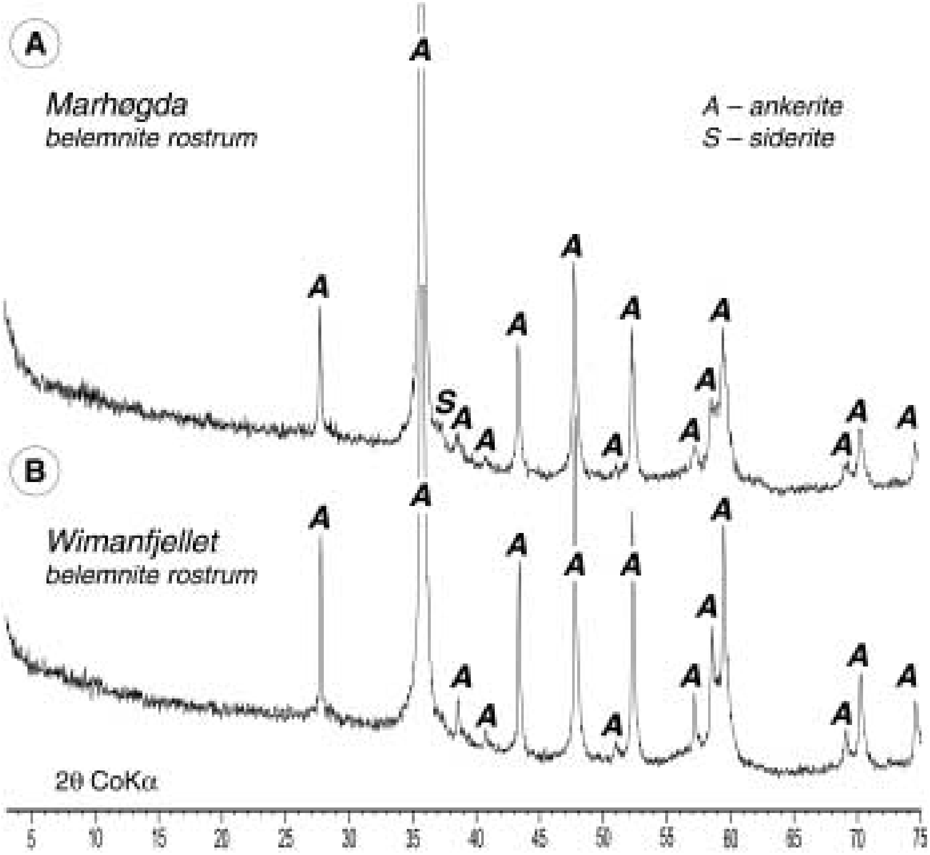

Fig. 5. Mineral composition of replaced belemnite rostra in the Marhøgda Bed at the southern margin of Sassenfjorden. X-ray diffraction patterns of samples MB-1 in the Marhøgda section (**A**) and WB-1 in the Wimanfjellet section (**B**).

Results

Petrography

Belemnite skeletons in the Marhøgda Bed at Sassenfjorden are preserved mostly as whole or fragmented parts of rostra, though proostracum skeletal parts have also been encountered. All these remnants show fairly well preserved anatomic shapes when examined under moderate magnifications. However, their mineralogy is invariably ankeritic, documenting a post–depositional replacement process that affected the original biogenic calcite. The replacement structures observed in thin sections show complex and somewhat variable internal organization, suggesting that the process was multi–stage and associated with changing intensity of calcite dissolution and ankerite precipitation (Fig. 3). Incipient dissolution structures in belemnite rostra formed during very early stages of diagenesis, and

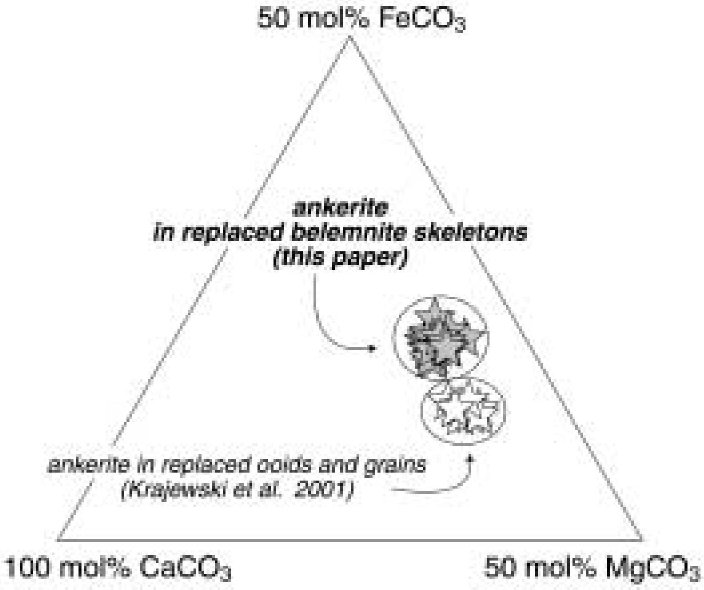

Fig. 6. Ternary diagram illustrating chemical composition of ankerite replacing belemnite skeletons versus ankerite replacing ooids and grains in the Marhøgda Bed at the southern margin of Sassenfjorden. Relative mol percentages of $FeCO_3$, $CaCO_3$, and $MgCO_3$ recalculated for $MnCO_3 = 0\%$. Data from Table 1 and Krajewski *et al.* (2001)

were then cemented by microsparitic siderite making matrix of the Marhøgda Bed. Bulk of the replacement structures formed after induration of the sideritic cementstone. They are composed of concentric ankeritic zones originated as a result of mineral precipitation in a sequence of concentric dissolution voids that roughly imprint the original skeleton structure. Ankerite precipitated from the void margins inside forming rings of blocky to acicular cement composed of well-defined subhedral and anhedral crystals. The replacement structures show voids in incompletely cemented ankeritic rings (Fig. 4). The voids contain in places dark brown bitumen inclusions up to 50 μm in size. Small bitumen inclusions (1–10 μm) are also incorporated in compact ankeritic fabric where they occur between individual crystals and within the crystals themselves.

Major element geochemistry

Ankerite replacing belemnite skeletons in the Marhøgda Bed at Sassenfjorden is a Fe-rich (16–24 mol% $FeCO_3$), Mg-depleted (21–23 mol% $MgCO_3$) variety of ankerite (Table 1). Its mean composition in the Marhøgda and Wimanfjellet sections is $Ca_{1.14}Mg_{0.45}Fe_{0.39}Mn_{0.02}(CO_3)_2$. This composition is different from the one noted in ankerite replacing ooids and grains in the matrix of the Marhøgda Bed, which is noticeably depleted in iron and enriched in magnesium (Fig. 6). The content of calcium and manganese in the two ankerite types is, however, similar (Fig. 7).

Table 1

Chemical composition of ankerite replacing belemnite skeletons in the Marhøgda Bed at the southern margin of Sassenfjorden.

Location	Analysis	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$
		mol %			
Marhøgda	1	57.84	22.12	19.86	0.18
	2	57.90	23.26	18.50	0.34
	3	57.59	23.46	18.62	0.33
	4	57.82	22.31	19.87	–
	5	57.32	22.50	19.93	0.25
	6	57.49	21.36	20.98	0.17
	7	55.35	21.03	23.62	–
	8	57.95	21.96	19.92	0.17
	9	54.63	23.27	21.73	0.37
	10	58.29	22.18	19.33	0.19
Wimanfjellet	11	58.45	22.65	18.68	0.22
	12	58.90	22.55	18.34	0.22
	13	59.29	22.43	18.24	0.04
	14	58.39	22.68	18.92	0.01
	15	54.84	26.15	18.90	0.11
	16	57.92	22.90	19.18	–
	17	58.21	22.22	19.49	0.08
	18	58.30	21.68	20.02	–
	19	57.98	22.28	19.65	0.08
	20	57.99	22.81	19.16	0.04

Table 2

Isotopic composition of carbon and oxygen in ankerite replacing belemnite skeletons in the Marhøgda Bed at the southern margin of Sassenfjorden

Location	Sample	$\delta^{13}C$	$\delta^{18}O$
		(‰ VPDB)	
Marhøgda	MB-1	–10.20	–15.51
	MB-2	–10.66	–14.90
Wimanfjellet	WB-1	–10.46	–15.57
	WB-2	–10.97	–15.71

Carbon and oxygen isotopes

The $\delta^{13}C$ and $\delta^{18}O$ values for ankerite replacing belemnite skeletons fall in narrow ranges between –11.0 and –10.2 ‰, and between –15.7 and –14.9 ‰ VPDB,

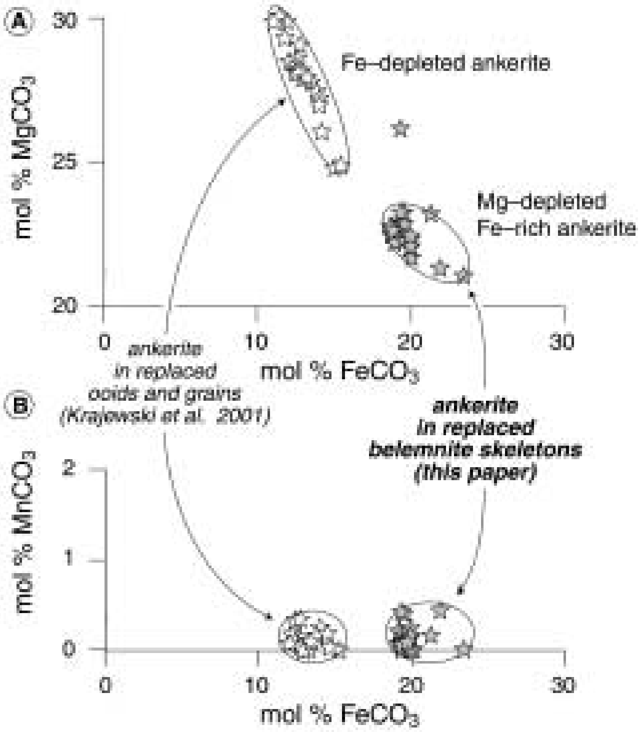

Fig. 7. **A**. Mol% $FeCO_3$ versus mol% $MgCO_3$ content in ankerite replacing belemnite skeletons. **B**. Mol% $FeCO_3$ versus mol% $MnCO_3$ content in ankerite replacing belemnite skeletons. Marhøgda Bed at the southern margin of Sassenfjorden. Data from Table 1 and Krajewski *et al*. (2001).

respectively (Table 2). These values are clearly more negative compared with the ones obtained from ankerite replacing ooids and grains in the Marhøgda Bed matrix (Krajewski *et al*. 2001). Particularly well–pronounced is the difference in oxygen isotopic composition, amounting to approx. 7 ‰ (Fig. 8).

Discussion

Petrographic development of ankerite replacing belemnite skeletons in the Marhøgda Bed suggests its origin in deep burial environment under conditions of increased temperature and thermal decomposition of kerogen. Internal complexity of the replacement structures implies their formation during prolonged period of time as a result of stages of biogenic calcite dissolution and ankerite precipitation in mouldic pores. Bitumen inclusions in these structures are observed to concentrate in voids that remained open after ankerite cementation, though they also occur in later generations of ankerite crystals. This suggests that the major stage of ankerite precipitation slightly preceded the major stage of saturation of pore fluids with

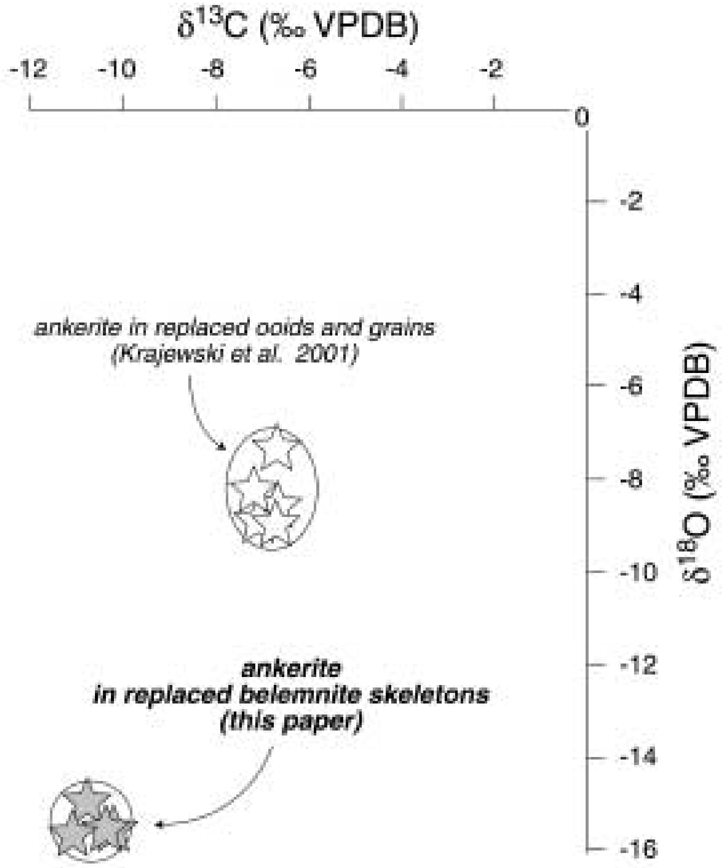

Fig. 8. Diagram illustrating isotopic composition of carbon and oxygen in ankerite replacing belemnite skeletons versus ankerite replacing ooids and grains in the Marhøgda Bed at the southern margin of Sassenfjorden. Data from Table 2 and Krajewski *et al*. (2001)

hydrocarbons and their migration in the sequence. Development of this ankerite post–dated the one in replaced ooids and grains in the matrix of the Marhøgda Bed, the latter formed under conditions of intense generation of organic acids to pore fluids and their thermal decarboxylation (Krajewski *et al*. 2001). These data suggest that ankerite replacing belemnite skeletons precipitated in an early catagenic environment that evolved towards oil window in the lower part of the Adventdalen Group. Chemical composition of the ankerite points to accelerated liberation of ferrous iron and a decrease in magnesium availability in this environment, compared with the one overwhelmed by thermal decarboxylation processes. Also more negative $\delta^{13}C$ values suggest increased contribution of biogenic carbon to the carbonate pool in deeper burial environment.

Burial origin of ankerite replacing belemnite skeletons allows to interpret the oxygen isotope values in terms of temperature controls of its formation (Krajewski

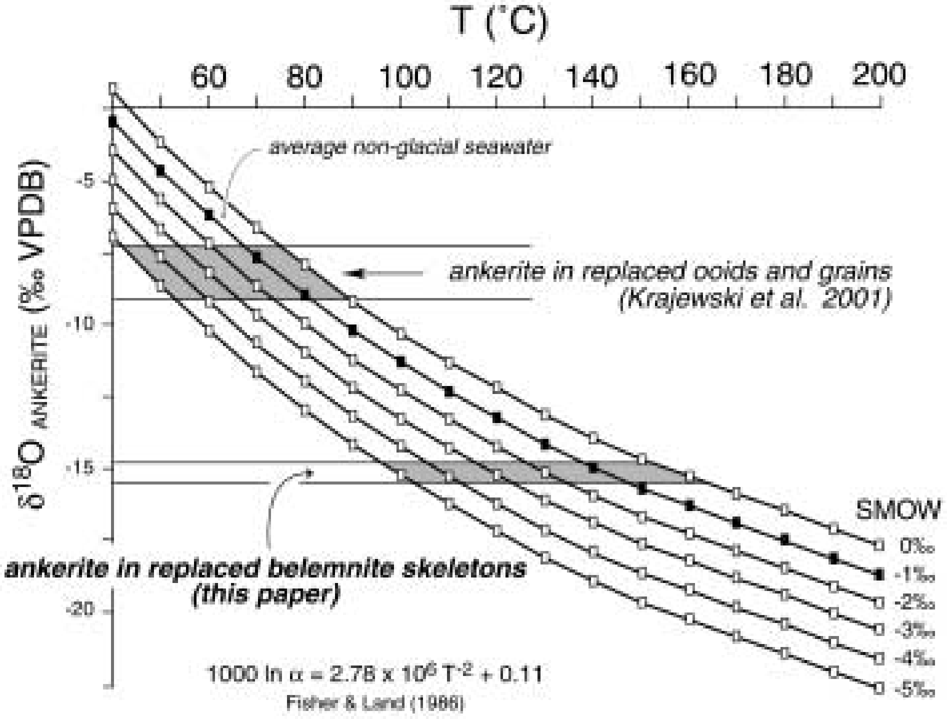

Fig. 9. Range of δ^{18}O values (‰ VPDB) of ankerite replacing belemnite skeletons versus ankerite replacing ooids and grains in the Marhøgda Bed at the southern margin of Sassenfjorden against precipitation temperature T (˚C) of inorganic ankerite, with the calculated isotopic composition of diagenetic fluids from which they may have formed, assuming isotopic equilibrium. The water lines were calculated using the fractionation equation of Fisher and Land (1986). Data from Table 2 and Krajewski *et al.* (2001)

et al. 2001 for discussion). Precipitation temperatures calculated using the equation of Fisher and Land (1986) and a range of compositions of pore water fall between 90 and 160˚C, i.e. between values noticeably higher than the ones calculated for iron–depleted ankerite replacing ooids and grains in the Marhøgda Bed matrix (Fig. 9). For isotopic composition of pore water with assumed average value of non–glacial seawater (–1 ‰ SMOW), the calculated temperature range is between 140 and 150˚C. This range is above that one typical for peak organic acid generation and decarboxylation in organic–rich sedimentary sequences (Hendry *et al.* 2000 and references therein). It is within the temperature range at which thermal generation of hydrocarbons from kerogen occur in burial environments (Tissot and Welte 1984). This agrees with measured vitrinite reflectance R_o = 0.6–0.8% in the basal part of the Adventdalen Group at the southern margin of Sassenfjorden, high bitumen extracts obtained from organic–rich sequences under– and overlying the Marhøgda Bed as well as with short-range hydrocarbon migration revealed therein (Mørk and Bjorøy 1984, Krajewski 1989).

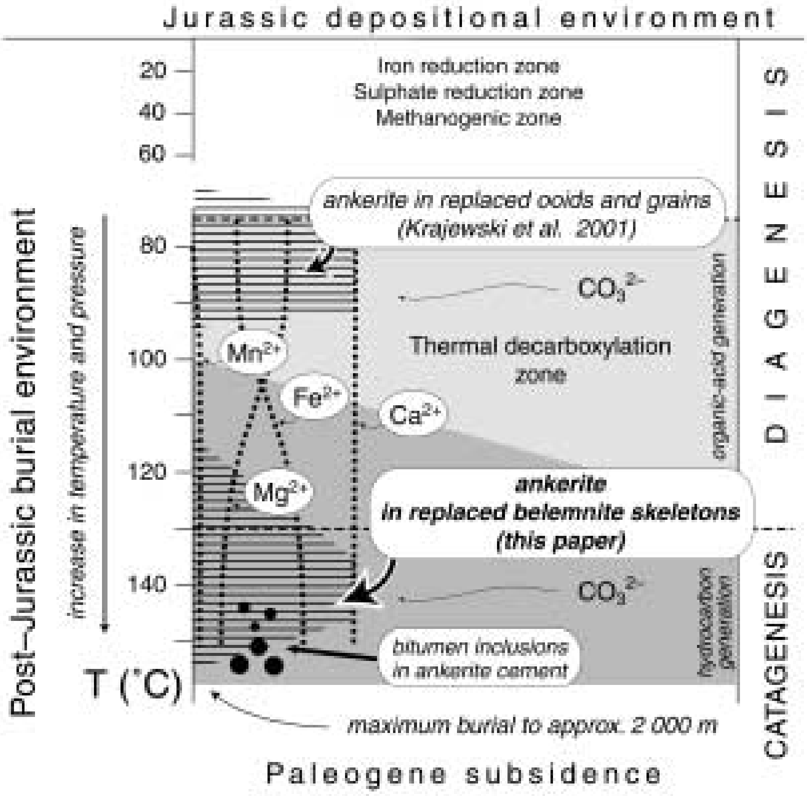

Fig. 10. Allocation of ankerite formation during post-depositional history of the Marhøgda Bed in central Spitsbergen against burial temperatures, relative availability of calcium, magnesium, iron, and manganese cations in pore fluids, and peak generation of organic acids and hydrocarbons in the sequence

The basal part of the Adventdalen Group at the southern margin of Sassenfjorden experienced burial to approximately 2000 m (Major and Nagy 1972) that was reached during late Paleogene filling of a foreland basin in central Spitsbergen (Harland 1997). Maximum precipitation temperature estimated in this paper at approximately 150°C fits exactly the maximum Paleogene burial temperature for central Spitsbergen reported by Harland (1997, p. 398). Thus, if it is assumed that ankerite replacing biogenic calcite in the Marhøgda Bed precipitated at maximum temperatures attained by the sequence under steady burial conditions, geothermal gradient of 70–75°C/km could be suggested for the Central Spitsbergen Basin at the end of Paleogene subsidence (Fig. 10). Such anomalously high geothermal gradient suggests extensive heat flow through the Adventdalen Group sequence during the post–Jurassic history of central Spitsbergen, reflecting magmatic and orogenic activity related to the Cretaceous and Paleogene stages of separation of Svalbard and Greenland (Birkenmajer 1981).

Conclusions

Petrographic, major element geochemical, and stable carbon and oxygen isotopic data indicate that ankerite replacing belemnite skeletons in the Marhøgda Bed at base of the Adventdalen Group in Sassenfjorden, Spitsbergen originated in a catagenic environment associated with thermal degradation of kerogen and hydrocarbon generation in the sequence. It formed at maximum temperature of 150°C under burial of approx. 2000 m, most probably during Paleogene filling and subsidence of the Central Spitsbergen Basin. Dissolution of biogenic calcite and precipitation of ankerite reflect extensive heat flow through the Adventdalen Group sequence related to the Cretaceous and Paleogene magmatic and orogenic activity in Svalbard.

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