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33. STABLE ISOTOPIC COMPOSITION ($\delta^{18}O_{CO_3^{2-}}$, $\delta^{13}C$) OF EARLY EOCENE FISH-APATITE FROM HOLE 913B: AN INDICATOR OF THE EARLY NORWEGIAN-GREENLAND SEA PALEOSALINITY[1]

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ABSTRACT

Fish-apatite (teeth and bone fragments) of early Eocene age from Ocean Drilling Program Hole 913B (Greenland Basin) was analyzed, in the absence of biogenic calcite, for stable isotopic ($\delta^{18}O_{CO_3^{2-}}$, $\delta^{13}C$) composition to determine paleosalinity. Comparisons are made with isotopic results for early Eocene fish-apatite from Deep Sea Drilling Project (DSDP) Hole 550 (northeastern Atlantic) and the Røsnæs Clay Formation (Denmark). These two sites represent fully marine and semimarine conditions, respectively. The $\delta^{18}O_{CO_3^{2-}}$ values of the fish-apatite from Hole 913B are 4.3‰ to 8.1‰ more negative than the fish-apatite values from DSDP Hole 550, and 1.9‰ to 6.1‰ more negative than the values from the Røsnæs Clay Formation. The results indicate reduced salinity in the early Eocene Greenland Basin relative to the open ocean. Using the present salinity/$\delta^{18}O$ relationship in the North Atlantic, the salinity in the Greenland Basin was 22 ppt to 28 ppt. The reduced salinity is in agreement with an isolated early Eocene Greenland Basin, as suggested in earlier geophysical and paleontological studies. It is also likely that other parts of the Norwegian-Greenland Sea, such as the Lofoten Basin, exhibited brackish water conditions.

Because of similar oxygen-isotopic composition of fish-apatite and excellently preserved foraminifer tests in the samples from the Røsnæs Clay Formation as well as DSDP Hole 550, we consider the fish-apatite $\delta^{18}O_{CO_3^{2-}}$ to be a reliable instrument for paleosalinity determination. It is possible that the fish-apatite was exposed to diagenesis and isotopic reequilibration shortly after deposition on the seafloor. This should not, however, reduce the possibility of using $\delta^{18}O_{CO_3^{2-}}$ as an indicator of paleosalinity, because both $\delta^{18}O$ and salinity usually are very similar in the uppermost pore water and the overlying water mass. The fish-apatite $\delta^{13}C$ values may support that early diagenesis has affected the original isotopic signal. The values seem to be related to the organic carbon content of the sediment as the lowest $\delta^{13}C$ values, −4.6‰ to −10.5‰, are found in the fish-apatite from the very dark sediment of Hole 913B, whereas the highest $\delta^{13}C$ values, +0.6‰ to −1.7‰, are found in the pale, oxidized sediment of DSDP Hole 550.

INTRODUCTION

During Ocean Drilling Program (ODP) Leg 151, in the northern Norwegian-Greenland Sea, the shipboard scientific party recovered sediment of early Eocene age in Hole 913B (located in the Greenland Basin; 75°29′N, 6°57′W). The age is supported by silicified *Subbotina triangularis* (ranging from P2 to P8a; Blow, 1979) in Samples 151-913B-44R-3, 58–60 cm, and 45R-1, 11–14 cm (Spiegler, this volume).

The primary objective of this study was to determine the salinity of the early Eocene Norwegian-Greenland Sea in general and the Greenland Basin in particular. It appears, from what we know at present, that the Greenland Basin was relatively isolated from its adjacent basins in the early Eocene. The Greenland Basin started to develop during the earliest phase of the seafloor spreading initiated in C24R (about 56 to 53.5 Ma; Berggren et al., 1995) between Greenland and northern Europe (Talwani and Eldholm, 1977; Eldholm and Thiede, 1980; Eldholm et al., 1987) (Fig. 1). This seafloor spreading created an early Norwegian-Greenland Sea dominated by shallow basins with restricted water interactions and exchange with the open ocean (Eldholm, 1990; Eldholm and Thomas, 1993).

The range of *S. triangularis* and the time of the initiation of the seafloor spreading enable us to restrict the stratigraphic range of the samples of Hole 913B dealt with in this study (Cores 151-913B-43R to 50R) to upper P6 to P8 or NP11 to NP12, which is roughly equivalent to 54 to 51 Ma (Berggren et al., 1995).

The isolation of the early Eocene Greenland Basin, and the humid climate as indicated by the clay mineralogy of Eocene sediments from northern latitudes (Froget et al., 1989; Robert and Chamley, 1991), should have resulted in reduced salinity of the Greenland Basin relative to the open ocean. In the modern North Atlantic there is a strong correlation between salinity and $\delta^{18}O$, reflecting mixing of marine and fresh water (Craig and Gordon, 1965). The paleo-$\delta^{18}O$ of the water in a particular basin can be determined by analyzing the $\delta^{18}O$ of, for example, biogenic minerals, usually calcite, that formed in the water (e.g., Wang et al., 1995; Schmitz et al., 1996). Assuming that the present relationship between salinity and $\delta^{18}O$ has remained similar during time (see later discussion), it is then possible to reconstruct the paleosalinity of the basin, on the condition that we can make a realistic estimate of the water-temperature range.

Calcareous tests are absent in the lower Eocene sediment from Hole 913B, possibly because of dissolution. Therefore, to determine the salinity of the early Eocene Greenland Basin, we used CO_3^{2-} in fish teeth and bone fragments for the isotopic analyses. In apatite, the mineral of teeth and bone, the site of CO_3^{2-} is still not completely agreed upon. Some evidence suggests that CO_3^{2-} can substitute for PO_4^{3-} in the crystal structure (McClellan, 1980). A large part of the CO_3^{2-} found in apatite is also supposed to be adsorbed on the crystal surface (Posner et al., 1984; Newesely, 1989). The carbonate content, up to 6%, differs between skeletal tissues, being higher in bone than in teeth (Carlson, 1990). The $\delta^{18}O_{CO_3^{2-}}$ of teeth from modern, living fish appears to agree well with the salinity of the fish habitat (Schmitz et al., unpubl. data). Fish-apatite may be exposed to diagenetic processes shortly after deposition on the seafloor resulting in isotopic re-

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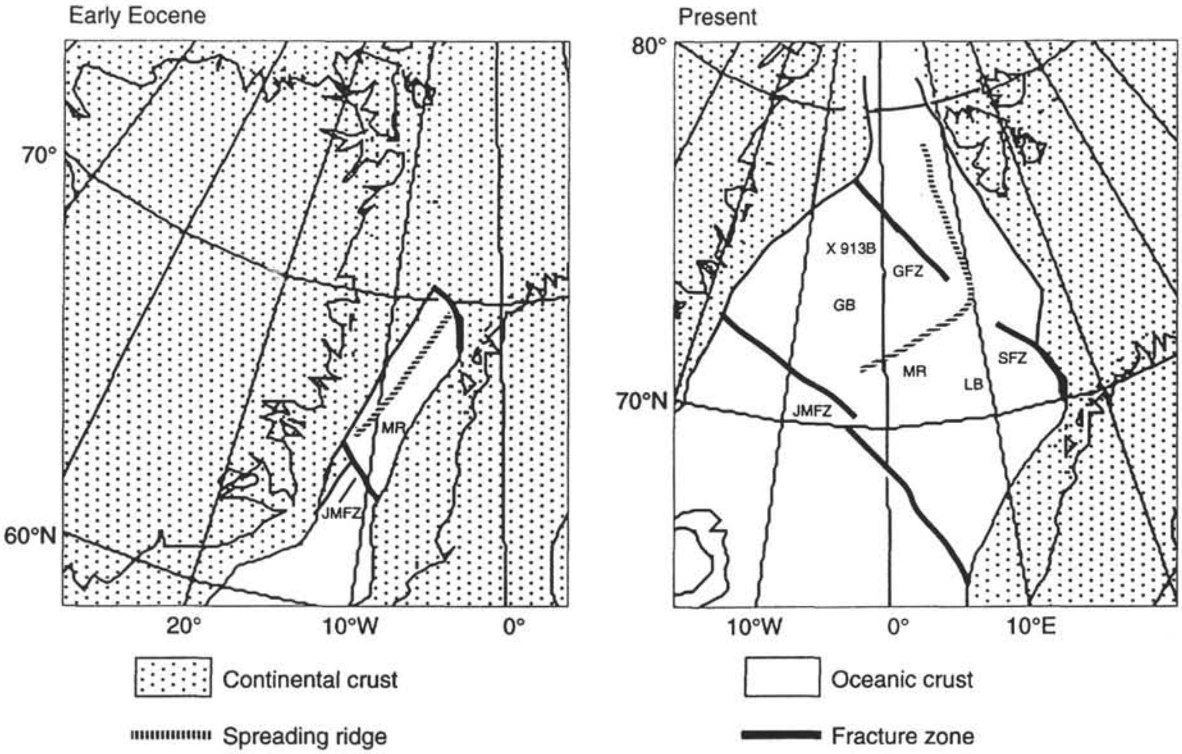

Figure 1. The Norwegian-Greenland Sea in the early Eocene and at present. GB = Greenland Basin; LB = Lofoten Basin; GFZ = Greenland Fracture Zone; SFZ = Senja Fracture Zone; MR = Mohns Ridge; and JMFZ = Jan Mayen Fracture Zone (based mainly on Talwani and Eldholm [1977] and Scotese and Denham [1988]).

equilibration with the pore water. However, pore water in the uppermost sediment usually has the same salinity and $\delta^{18}O$ as the overlying water mass, therefore early diagenesis of the fish-apatite does not invalidate the use of $\delta^{18}O_{CO_3^{2-}}$ as a paleosalinity indicator (Kolodny and Luz, 1991; Schmitz et al., unpubl. data; see later discussion).

In order to test the potential of fish-apatite $\delta^{18}O_{CO_3^{2-}}$ as an indicator of paleosalinity, we also analyzed the isotopic composition of early Eocene fish-apatite from the semimarine Røsnæs Clay Formation in Denmark (Schmitz et al., 1996) and the fully marine Deep Sea Drilling Project (DSDP) Hole 550 in northeastern Atlantic (Charisi and Schmitz, 1996). At these sites, the isotopic composition of fish-apatite and excellently preserved, calcareous foraminifers could be compared. The comparison is legitimate, as Shemesh et al. (1988) showed that carbonate in apatite and coexisting calcite behave very similar isotopically.

THE ISOTOPIC CHEMISTRY OF FISH-APATITE

Instead of using the fish-apatite CO_3^{2-} for isotopic analyses, as in this study, it is possible to analyze $\delta^{18}O$ of the PO_4^{3-} phase in the apatite to determine fish habitat environmental conditions (e.g., Longinelli and Nuti, 1973; Kolodny and Raab, 1988; Kolodny and Luz, 1991; Lécuyer et al., 1993). Kolodny et al. (1983) argued that by using the PO_4^{3-} phase, instead of analyzing calcite or apatite CO_3^{2-}, the problem with post-depositional, isotopic alteration is reduced because of the very slow isotopic exchange between water and PO_4^{3-} during reactions that are not enzyme catalyzed. Shemesh et al. (1988) and Kastner et al. (1990), however, found high correlations between $\delta^{18}O_{PO_4^{3-}}$ and $\delta^{18}O_{CO_3^{2-}}$ in Precambrian to Holocene and Miocene apatites, respectively, although the slope of the line in the correlation plots differed significantly from unity. It was suggested that the results indicated that $\delta^{18}O_{PO_4^{3-}}$ could be affected by diagenesis, contrary to what was previously believed possible, although to a lesser extent than $\delta^{18}O_{CO_3^{2-}}$. Kolodny and Luz (1991) also found a relatively high correlation between $\delta^{18}O_{PO_4^{3-}}$ and $\delta^{18}O_{CO_3^{2-}}$ in a study of Devonian to Holocene fish-apatite. In the post-Mesozoic samples, the difference between $\delta^{18}O_{PO_4^{3-}}$ and $\delta^{18}O_{CO_3^{2-}}$ was close to 9.5‰, which is expected when both phases are in equilibrium with the ambient water. In the older samples, however, the $\delta^{18}O_{CO_3^{2-}}$ values were lower than would be expected if the PO_4^{3-} and the CO_3^{2-} were in isotopic equilibrium. As Shemesh (1990) presented evidence showing that post-depositional changes in the $\delta^{18}O_{PO_4^{3-}}$ and REE patterns of fish-apatite may occur as a result of recrystallization, Kolodny and Luz (1991) proposed that early diagenesis had altered the original isotopic signature of PO_4^{3-} as well as of CO_3^{2-} and that a more extensive re-equilibration had affected the $\delta^{18}O_{CO_3^{2-}}$ of the older samples. During early diagenesis the bone-apatite is transformed into the much better ordered, and more stable, carbonate fluorapatite. Wright et al. (1987), Grandjean et al. (1987), and Grandjean and Albarède (1989) showed that the changes in REE patterns of fish-apatite most likely occur very rapidly after deposition on the seafloor. In that sense, if recrystallization occurs, it will result in an isotopic reequilibration giving a signal that reflects the chemical and physical water properties at the water-sediment interface or in the uppermost sediment. As outlined above, there is no fully convincing evidence that $\delta^{18}O_{PO_4^{3-}}$ is a better paleoenvironmental indicator than is $\delta^{18}O_{CO_3^{2-}}$, at least not for post-Mesozoic samples. Because the analytical procedure is much simpler, we have therefore used $\delta^{18}O_{CO_3^{2-}}$ instead of $\delta^{18}O_{PO_4^{3-}}$. Another advantage of using $\delta^{18}O_{CO_3^{2-}}$ is that it permits evaluation of the fish-apatite results by comparing them with the isotopic composition of excellently preserved foraminifer tests. The results in this study clearly indicate that $\delta^{18}O_{CO_3^{2-}}$ of fossil fish-apatite, such as that found in deep-sea sediments, may give reliable information about aquatic paleoconditions, at least in the case of paleosalinity. The method can be an important instrument alone or in combination with other paleosalinity indicators (e.g., fish-apatite $^{87}Sr/^{86}Sr$; Schmitz et al., 1991).

In earlier studies, the carbon-isotopic composition of fish-apatite has been more or less neglected as an environmental indicator. Kolodny and Luz (1991), for example, presented $\delta^{13}C$ values for their fish-apatite samples, but did not discuss those data. Concerning authigenic varieties of apatite, however, several studies have shown that $\delta^{13}C$ may give information about the redox conditions during apatite formation (e.g., McArthur et al., 1980; Benmore et al., 1983; Kastner et al., 1990).

MATERIALS AND METHODS

Fish teeth and bone fragments, ranging in size from 100 to 500 µm, of different species (not determined) were picked from the lower Eocene interval of Hole 913B, the Røsnæs Clay Formation, and Hole 550 (Tables 1–3). The analyzed samples of the Røsnæs Clay Formation are from the interval of P7 or NP12 (Schmitz et al., 1996), whereas the samples of Hole 550 are from upper P6 to P9 or NP11 to lower NP14 (Charisi and Schmitz, 1996).

To make certain that the fish-apatite was free of secondary calcite, several samples were carefully examined using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Two samples from Hole 913B and two from the Røsnæs Clay Formation were also treated with tri-ammonium citrate according to the method by Silverman et al. (1952). The solubility for calcite in tri-ammonium citrate is 50 times higher than for apatite. It is, however, not possible to avoid some loss of apatite during this procedure for which reason only the largest samples could be treated (800–1300 µg as compared to 200–500 µg for the other samples).

Before the analyses, all teeth and bone fragments were cleaned by ultrasound for 15 min in distilled water, dried at 60°–70°C, and ground into a powder in an agate mortar. All samples were subsequently roasted in vacuum for 30 min at 400°C to eliminate possible organic material. After reaction in 100% phosphoric acid for 10 min at 90°C in a VG Isocarb system, the CO_2-gas was analyzed using a VG Prism Series II mass spectrometer. The analytical method is the same as that used on a routine basis for calcite samples. A similar procedure, reaction for 15 min at 75°C, was used by Koch et al. (1992; 1995) on mammalian apatite. The analyses were performed at the Department of Marine Geology, Göteborg University. All isotopic values are presented normalized relative to the PDB-standard, including Craig correction, using the standard δ notation. There is a possibility that the isotopic fractionation factor between apatite carbonate and CO_2 differs from that between calcite and CO_2 (see McArthur et al., 1980). The difference, however, is assumed to be negligible for the problems dealt with in this study.

The mean value of 73 analyses of the NBS-19 standard ($\delta^{18}O$ = −2.20‰, $\delta^{13}C$ = 1.95‰) was −2.21‰ for $\delta^{18}O$ and 1.93‰ for $\delta^{13}C$, whereas the standard deviation (σ) was ±0.18‰ for $\delta^{18}O$ and ±0.10‰ for $\delta^{13}C$. The precision of each NBS-19 analysis (i.e., 10 successive measurements of the same sample) was better than 0.015‰ for $\delta^{18}O$ and 0.009‰ for $\delta^{13}C$; whereas, for each fish-apatite analysis, it was better than 0.043‰ for $\delta^{18}O$ and 0.040‰ for $\delta^{13}C$.

The $\delta^{18}O$ and $\delta^{13}C$ data for the foraminifers from the Røsnæs Clay Formation and Hole 550 are from Schmitz et al. (1996) and Charisi and Schmitz (1996), respectively. We used planktonic *Subbotina patagonica* and benthic *Cibicidoides ungerianus* from the Røsnæs Clay Formation, and *S. patagonica* and benthic *Oridorsalis umbonatus* and *Nuttalides truempyi* from Hole 550. The isotopic composition of the benthic foraminifers is compensated for vital effects as suggested by Shackleton et al. (1984). The $\delta^{18}O$ values of *C. ungerianus* and *N. truempyi* are corrected by +0.5‰ and +0.35‰, respectively, and the $\delta^{13}C$ of *O. umbonatus* by +1.0‰.

Table 1. Oxygen- and carbon-isotopic composition of fish-apatite from Hole 913B.

Core, section, interval (cm)	Fish-apatite $\delta^{18}O$	Fish-apatite $\delta^{13}C$
151-913B-		
43R-1, 13–16	−7.98	−9.12
43R/44R[a]	−7.28	−10.53
44R[a]	−6.83	−10.06
46R-CC	−6.73	−9.26
47R-1, 108–110	−7.78	−9.25
48R-CC	−8.23	−10.11
49R-3, 118–121	−7.28	−8.00
50R-4, 94–97	−6.70	−4.56

[a]Fish-apatite treated with tri-ammonium citrate.

Table 2. Oxygen- and carbon-isotopic composition of fish-apatite and foraminifers from the Røsnæs Clay Formation.

Meters above the base	Fish-apatite $\delta^{18}O$	Fish-apatite $\delta^{13}C$	*S. patagonica* $\delta^{18}O$	*S. patagonica* $\delta^{13}C$	*C. ungerianus*[a] $\delta^{18}O$	*C. ungerianus*[a] $\delta^{13}C$
14.55[b]	−2.10	−3.79	−2.50	+1.20	−1.21	+0.08
14.45	−2.71	−3.49	−2.96	+1.21	−1.67	+0.39
14.35[b]	−2.82	−4.17	−3.05	+1.33	−1.66	+0.40
14.05	−3.02	−4.64	−3.09	+0.99	−1.73	+0.27
13.45[c]	−3.26	−4.09	−2.81	+0.07	−2.32	−1.27
13.35[c]	−2.54	−3.58	−2.97	−0.27	−2.21	−1.29
11.20	−4.84	−0.65	−2.53	+0.12	−0.92	−0.37
11.00	−2.94	−3.81	−2.61	−0.36	−1.69	−0.17
10.90	−2.64	−0.67	−2.59	−0.29	−1.63	−0.14

[a]Compensated for vital effects, see text.
[b]Fish-apatite: mean of two values.
[c]Fish-apatite treated with tri-ammonium citrate.

RESULTS

The $\delta^{18}O_{CO_3^{2-}}$ values of the fish-apatite from Hole 913B are all very negative, between −6.7‰ and −8.2‰ (Fig. 2, Table 1). This can be compared with $\delta^{18}O_{CO_3^{2-}}$ values of −2.1‰ to −4.8‰ and −0.2‰ to −2.4‰ for the fish-apatite from the semimarine Røsnæs Clay Formation (Table 2) and the fully marine Hole 550 (Table 3), respectively. The fish-apatite $\delta^{18}O_{CO_3^{2-}}$ from the Røsnæs Clay Formation and Hole 550 give similar results as the foraminifer calcite tests from the respective sites (Fig. 2), which supports the use of $\delta^{18}O_{CO_3^{2-}}$ of fossil fish-apatite in reconstructing paleosalinities.

The $\delta^{13}C$ of the fish-apatite shows a trend towards higher values from Hole 913B, through the Røsnæs Clay Formation, to Hole 550 (Fig. 2). Very low $\delta^{13}C$ values, −4.6‰ to −10.5‰, are found in the fish-apatite from Hole 913B (Table 1). In the Røsnæs Clay Formation the fish-apatite $\delta^{13}C$ values range from −0.7‰ to −4.6‰, which is on average 4.5‰ lower than the $\delta^{13}C$ of the foraminifers (Table 2), whereas $\delta^{13}C$ values of the fish-apatite from Hole 550 range from +0.6‰ to −1.7‰, more or less similar to the $\delta^{13}C$ of the foraminifers (Table 3).

Samples treated with tri-ammonium citrate give very similar isotopic results as untreated samples (Fig. 2). Furthermore, no diagenetic crystals or coatings were found during the SEM/EDS-scanning (Pls. 1, 2). This strongly suggests that the analyzed carbonate derives from the apatite and not from any diagenetic calcite.

The mixing of teeth and bone fragments in a few samples analyzed could have some minor influence on the isotope values from these samples, because bone is more porous, and therefore more susceptible for isotopic alteration, than are teeth (Banner and Hanson, 1990; Wang and Cerling, 1994; Schmitz et al., unpubl. data). No significant difference in either $\delta^{18}O_{CO_3^{2-}}$ or $\delta^{13}C$ was found between samples with only teeth and samples with mixed teeth and bone fragments.

Table 3. Oxygen- and carbon-isotopic composition of fish-apatite and foraminifers from DSDP Hole 550.

Core, section, interval (cm)	Fish-apatite $\delta^{18}O$	Fish-apatite $\delta^{13}C$	*S. patagonica* $\delta^{18}O$	*S. patagonica* $\delta^{13}C$	*O. umbonatus*[a] $\delta^{18}O$	*O. umbonatus*[a] $\delta^{13}C$	*N. truempyi*[a] $\delta^{18}O$	*N. truempyi*[a] $\delta^{13}C$
80-550-								
24-[b]	−1.35	−0.09			+0.23	+1.26	0.00	+0.69
24-1, 135–138	−0.17	−0.14						
25-[c]	−1.65	+0.58			−0.34	+1.55	−0.59	+0.69
28/29-[d]	−2.38	−1.75	−0.85	+0.57	−0.30	+0.39	−0.57	−0.16

[a]Compensated for vital effects, see text.
[b]*O. umbonatus*: mean of four values.
[c]*O. umbonatus*: mean of five values, *N. truempyi*: mean of six values.
[d]*S. patagonica*: mean of 15 values, *O. umbonatus*: mean of 17 values, and *N. truempyi*: mean of 16 values.

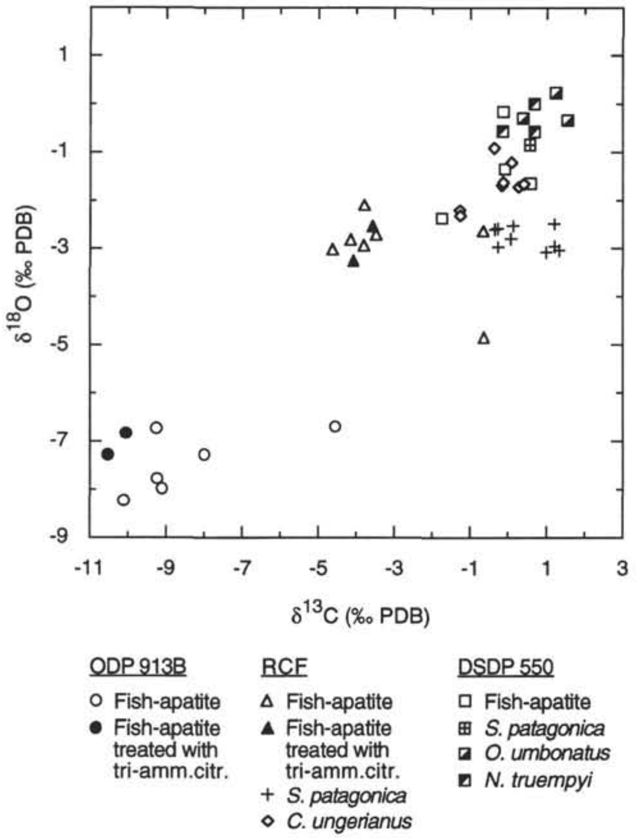

Figure 2. Oxygen- and carbon-isotopic composition (‰PDB) of fish-apatite and foraminifers from Hole 913B, the Røsnæs Clay Formation (RCF), and Hole 550.

DISCUSSION

The oxygen-isotopic signal of the fish-apatite from Hole 913B most likely reflects the isotopic composition of the water in the early Eocene Greenland Basin. There is a possibility that early diagenetic recrystallization and isotopic reequilibration of the fish-apatite have occurred, but as mentioned earlier, this would not reduce the utility of fish-apatite $\delta^{18}O_{CO_3^{2-}}$ as a paleosalinity indicator (Kolodny and Luz, 1991; Schmitz et al., unpubl. data).

During evaporation of seawater, isotopic fractionation leads to a preferential removal of ^{16}O. As a consequence, precipitation and river water have much lower $\delta^{18}O$ values than does seawater. A linear relationship between salinity and $\delta^{18}O$ is established because of the mixing of freshwater and seawater. In modern North Atlantic surface and deep water, a 1-ppt reduction in seawater salinity is equal to a decrease in $\delta^{18}O$ by about 0.6‰ (Craig and Gordon, 1965). The smallest difference between the fish-apatite $\delta^{18}O_{CO_3^{2-}}$ from Hole 550 and Hole 913B is 4.3‰, whereas the largest difference is 8.1‰. The global, latitudinal temperature gradient was very reduced during the early Eocene compared with the present (Boersma et al., 1987; Barron, 1987; Zachos et al., 1994). Ignoring possible minor temperature differences between the northern Norwegian-Greenland Sea and the North Atlantic, the difference in $\delta^{18}O_{CO_3^{2-}}$ indicates that the salinity of the Greenland Basin in the early Eocene was between 22 ppt and 28 ppt, using a salinity of 35 ppt in the Eocene North Atlantic as suggested by the general circulation model results of Barron and Peterson (1991). If we also take into account that the temperature most probably was slightly lower closer to the North Pole, the difference in salinity between the northern North Atlantic and the Greenland Basin may have been even larger, as a 1‰ reduction in $\delta^{18}O_{CO_3^{2-}}$ is equal to an increase in water temperature of about 4.7°C (Erez and Luz, 1983). Eocene sediments from the Arctic Ocean indicate that no perennial ice existed in northern latitudes (Bukry, 1984; Clark, 1988). Consequently, ice-related processes (e.g., Prentice and Matthews, 1988; Strain and Tan, 1993) can not have affected the isotopic composition of the seawater as in modern, high-latitude areas of the oceans.

For the present-day salinity/$\delta^{18}O$ relationship to be valid also for the early Eocene, the $\delta^{18}O$ of meteoric precipitation, a function of condensation temperature and Rayleigh distillation processes (Dansgaard, 1964), would have had to be similar to that of present time. The reduced temperature gradient and atmospheric circulation (Janecek and Rea, 1983; Rea et al., 1985; Hovan and Rea, 1992) not only affected the air temperature, but most likely also the precipitation rate, source area of the vapor, and distance between source area and precipitation area. This probably had influence on the $\delta^{18}O$ of early Eocene precipitation. A possible condition during periods with a more equable global climate is higher $\delta^{18}O$ values at high latitudes (see Railsback et al., 1989; Railsback, 1990). This should have affected the salinity/$\delta^{18}O$ relationship, resulting in higher $\delta^{18}O$ in a water mass with a particular salinity. The salinity of the early Eocene Greenland Basin may therefore have been lower than estimated above. It is presently not possible to determine the $\delta^{18}O$ of the precipitation in the Norwegian-Greenland Sea area in the early Eocene. Some recent studies, however, suggest very similar $\delta^{18}O$ in modern and early Eocene continental precipitation (Dettman and Lohmann, 1993; Seal and Rye, 1993; Koch et al., 1995). This strengthens the possibility of using the present salinity/$\delta^{18}O$ relationship by Craig and Gordon (1965) when estimating early Eocene salinity conditions.

Reduced salinity in the early Eocene is in agreement with the concept of an isolated Greenland Basin, especially as the drainage area/basin area ratio was very large as deduced from paleogeographic reconstructions (Fig. 1). In the south, the Jan Mayen Fracture Zone acted as a deep-water barrier until about C21 (i.e., the early middle Eocene; Eldholm and Thiede, 1980; Berggren and Olsson, 1986; Eldholm, 1990). Further south, the uplifted Greenland-Scotland Ridge prevented deep-water exchange between the North Atlantic and the southern Norwegian-Greenland Sea (Nilsen, 1983). A shallow marine connection was probably established in the early Eocene, as indicated by similar planktonic microfauna and microflora on either side of the Greenland-Scotland Ridge (Berggren and Schnitker, 1983; Hulsbos et al., 1989). Similarities in the Paleocene to early Eocene mollusk and ostracode faunas of Alaska and northwestern Europe indicate that a marine connection existed between the Norwegian-Greenland Sea and the Arctic Ocean, at least during periods of high sea-level stand (Marincovich et al., 1985; 1990). This connection, however, was probably closed during most of the Eocene because of the Spitsbergen Orogeny, which was initiated in the latest Paleocene to earliest Eocene (Steel et al., 1985; Müller and Spielhagen, 1990). In the northeast, the uplift of the western Barents Sea margin had commenced by the late Paleocene (Faleide et al., 1993; Sættem et al., 1994), which further reduced the exchange of water between the Arctic Ocean and Norwegian-Greenland Sea.

The isolation of the Greenland Basin in the early Eocene not only affected the salinity, but probably also supported a strong salinity-stratification, because of limited water exchange with the North Atlantic. The strong stratification would have contributed to a low oxygen concentration in the bottom water and a shallow carbonate compensation depth. This led to temporarily highly corrosive bottom water and very dark, sometimes laminated, sediments with a total organic carbon content of 0.2%–1.2% (modern continental margin ≈1.0%, open ocean environment ≈ 0.35%; Emerson and Hedges, 1988). As a consequence, calcium carbonate was dissolved, and only agglutinated foraminifers are found in the lower Eocene samples from Hole 913B, with the exceptions of silicified specimens of *Subbotina triangularis* in Samples 151-913B-44R-3, 58–60 cm, and 45R-1, 11–14 cm (Shipboard Scientific Party, 1995; Spiegler, this volume). Murray and Alve (1994) showed that dissolution can severely alter the original foraminifer assemblage. In the lower Eocene sediment from ODP Hole 643 (the southeastern Lofoten Basin) agglutinated foraminifers also predominate (Shipboard Scientific Party, 1987; Kaminski et al., 1990), which suggests that the conditions were similar in the Greenland and the Lofoten Basins. The absence of planktonic foraminifers in the lower Eocene samples from Hole 913B, however, may not entirely be a consequence of test dissolution. Hulsbos et al. (1989) concluded, on basis of the fossil assemblage from the shallow DSDP Hole 338 (the outer Vøring Plateau), that the pelagic environment of the Norwegian-Greenland Sea was unfavorable for planktonic foraminifers in the early Eocene.

It is possible that the trend towards higher fish-apatite $\delta^{13}C$ values from the dark gray sediment of Hole 913B, through the brown to greenish gray Røsnæs Clay Formation (Schmitz et al., 1996), to the pale, highly oxidized sediment of Hole 550 (Waples and Cunningham, 1985) indicates that early diagenetic isotopic reequilibration of the fish-apatite has taken place. This is also supported by the relationship between fish-apatite and foraminifer $\delta^{13}C$ from the latter two sites. As long as no methane is produced, as in strongly reducing environments, the decomposition of isotopically light organic matter ($\delta^{13}C \approx -25‰$) leads to lower $\delta^{13}C$ values of dissolved inorganic carbon in the pore water relative to the bottom water (Irwin et al., 1977; McCorkle et al., 1985; McCorkle and Emerson, 1988; Bauer et al., 1995). A higher flux of organic material to the seafloor, as in continental margin environments, results in a higher decomposition rate and a larger difference in $\delta^{13}C$ between the pore water and the bottom water.

In the case of in vivo carbon-isotopic values in the fish-apatite (i.e., that they reflect the composition of the water mass), the $\delta^{13}C$ signal may indicate that the conditions in the early Eocene Greenland Basin were similar to those in the modern Black Sea, in which $\delta^{13}C$ can be as low as −6.3‰ (Fry et al., 1991), or that the salinity as estimated previously actually is too high, a possibility that was emphasized in the discussion about $\delta^{18}O$ in early Eocene precipitation. In nearshore environments there is a correlation, although varying slightly at different localities, between salinity and $\delta^{13}C$ (Mook, 1968; 1971). Using this correlation, the fish-apatite $\delta^{13}C$ values from Hole 913B correspond to a salinity of approximately 10–20 ppt rather than 22–28 ppt. It is not possible, however, to determine the cause of the low fish-apatite $\delta^{13}C$ values before we know more about fish-apatite diagenesis and the original $\delta^{13}C$ signal of modern, living fish.

It is important to state that various processes have potential to alter the $\delta^{18}O$ of pore or bottom water. These processes include volcanic mineral/pore water interactions (Perry et al., 1976; Lawrence and Gieskes, 1981; Lawrence and Taviani, 1988), hydrothermal activity (Bowers and Taylor, 1985; Peter and Shanks, 1992), and oxidation of organic matter by SO_4^{2-} (Sass et al., 1991). None of these processes are likely to have caused the low $\delta^{18}O$ values of Hole 913B in the case of recrystallized fish-apatite. Interactions between volcanic minerals and pore water may reduce the $\delta^{18}O$ of the pore water. To induce the observed low fish-apatite $\delta^{18}O$ values by this process, however, requires that the fish-apatite recrystallized at a depth of several hundred meters below seafloor. As mentioned earlier, recrystallization of bone-apatite towards the much more stable carbonate fluorapatite most likely occurs in the uppermost sediment (Wright et al., 1987; Grandjean et al., 1987; Grandjean and Albarède, 1989; Shemesh, 1990; Kolodny and Luz, 1991). Hydrothermal activity produce fluids with $\delta^{18}O$ values similar or higher than seawater, and for SO_4^{2-} reduction to deplete the pore water in ^{18}O to any larger extent, the content of organic matter in the sediment should be much higher than is observed in Hole 913B.

Provided that the original isotopic signal of the fish-apatite is preserved, the possibility remains that the apatite used for analyses from Hole 913B is derived from fish that lived the major part of their lives close to river mouths, and that the low $\delta^{18}O_{CO_3^{2-}}$ values are not representative of the main Greenland Basin. The proximity of land is obvious and further supported by the high C/N ratio in the sediment (Hedges et al., 1986; Emerson and Hedges, 1988; Shipboard Scientific Party, 1995). It is not very likely, however, that all samples analyzed should derive from fish that lived their entire lives in the vicinity of freshwater outflows.

Post-depositional diagenetic calcite crystals or encrustations may occur in fossil material (Killingley, 1983). These may distort the original isotopic signatures, making paleoenvironmental interpretations impossible. As the Eocene sediment of Hole 913B is free of calcite, and because detailed SEM/EDS-scanning of the fish-apatite did not reveal any diagenetic infillings, secondary calcite in the pores and canals of the fish-apatite is not to be expected. The absence of diagenetic infillings also applies for the foraminifers from the Røsnæs Clay Formation and Hole 550. Rhodochrosite ($MnCO_3$) is found at some levels in Hole 913B. Fish-apatite from sediment samples with rhodochrosite was strictly avoided in this study. The fact that fish-apatite samples treated and untreated with tri-ammonium citrate give the same results, confirm that only apatite carbonate is analyzed.

CONCLUSIONS

The $\delta^{18}O_{CO_3^{2-}}$ of the fish-apatite from Hole 913B indicates that the salinity of the Greenland Basin water was reduced by at least 7–13 ppt relative to the North Atlantic, which is in accord with the proposed isolation of the early Eocene Greenland Basin as suggested by geophysical as well as paleontological data. There are reasons to believe that this brackish water environment was not a local phenomenon and that the main part of the earliest Norwegian-Greenland Sea had reduced salinity as compared with the open ocean.

The method presented in this paper should be useful in reconstructing paleosalinities, especially in Paleogene, high-latitude environments where calcareous fossils seem to be generally absent.

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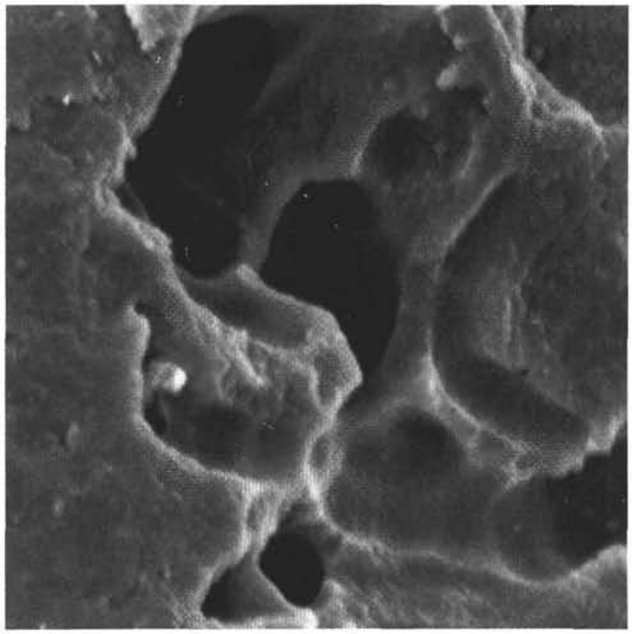
1



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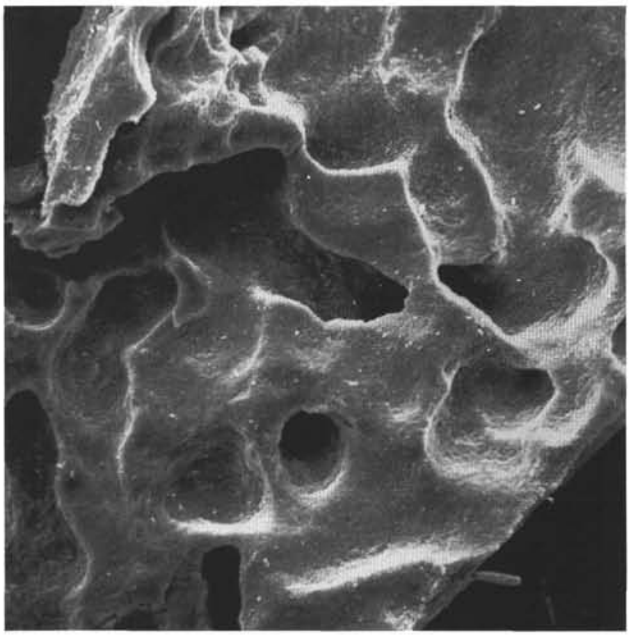

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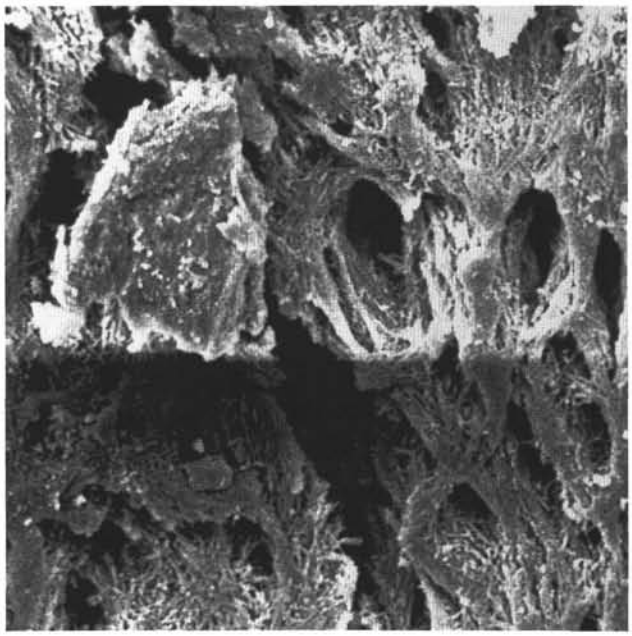

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Plate 1. SEM photographs of fish-apatite. **1.** Sample 151-913B-47R-CC. **2.** Sample 151-913B-49R-3, 54–57 cm. **3.** Sample 151-913B-50R-CC. **4.** The Røsnæs Clay Formation, 11.20 m above the base.

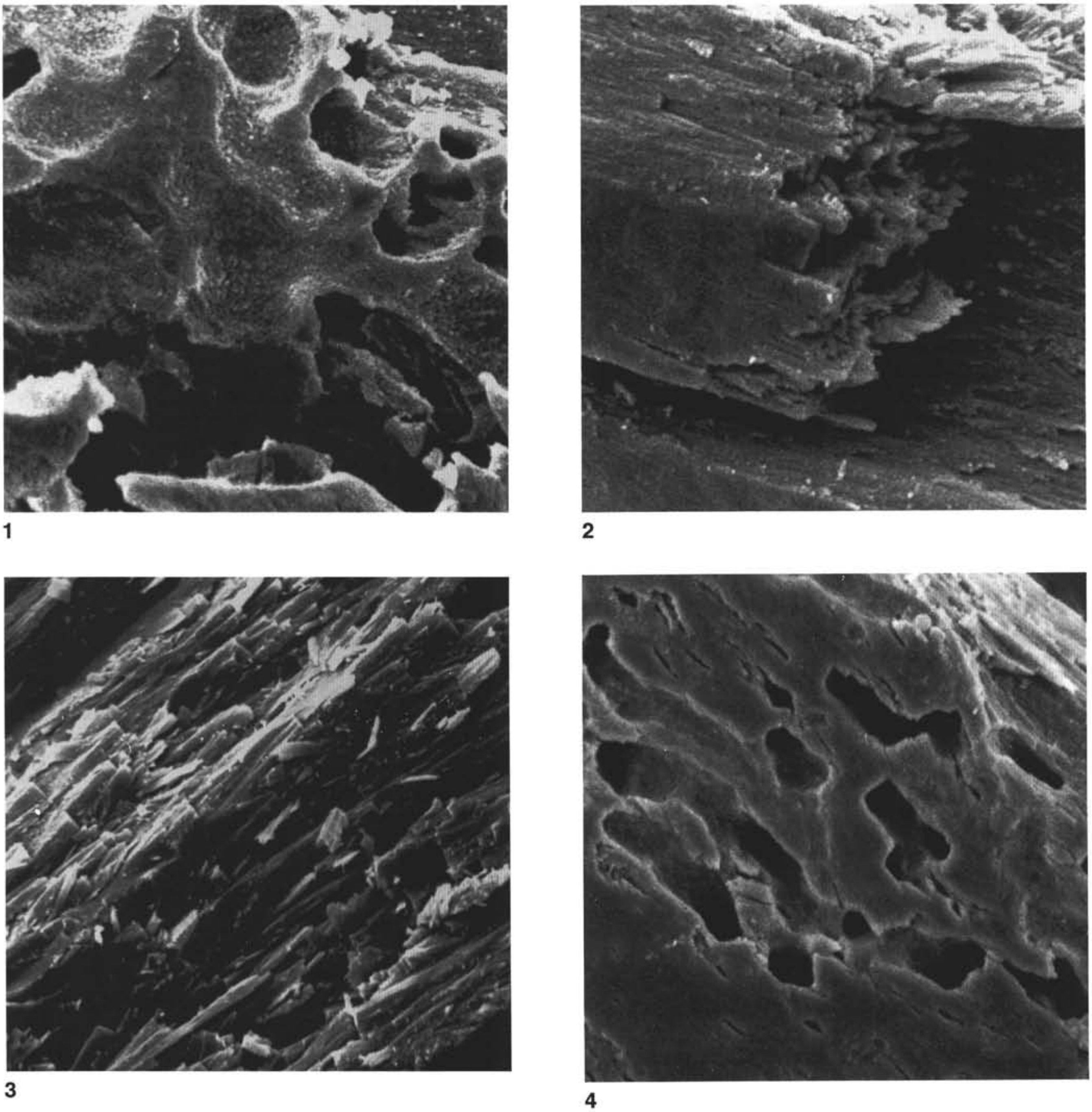

Plate 2. SEM photographs of fish-apatite. **1.** The Røsnæs Clay Formation, 11.20 m above the base. **2, 3.** Sample 80-550-24-1, 31–35 cm. **4.** Sample 80-550-24-3, 38–42 cm.