C. J. Schubert · D. Nürnberg · N. Scheele
F. Pauer · M. Kriews

^{13}C isotope depletion in ikaite crystals: evidence for methane release from the Siberian shelves?

Abstract Ikaite crystals ($CaCO_3 \times 6H_2O$) have been found at 232- to 238-cm sediment depth in *R/V Polarstern* core PS2460-4 from the Laptev Sea continental margin in a water depth of 204 m. δ^{13}C values of this phase average $-36.3 \pm 0.4\%$ PDB ($N = 2$), which is significantly outside the range of normal marine carbonates. The CO_2 involved in the precipitation of the ikaite is most probably derived from methane, which has extremely depleted ^{13}C isotope values. Two possible sources of methane in these sediments are: (1) methanogenesis (decomposition of organic matter under anaerobic conditions); and (2) gas hydrates, which are known to occur in the Siberian shelf regions.

Introduction

Methane (CH_4) is one of the important greenhouse gases (Rasmussen and Khalil 1981) and anthropogenic sources (360×10^{12} g yr^{-1}) currently represent the highest flux of these gases to the troposphere compared with natural sources (150×10^{12} g) (Whiticar 1993; Khalil et al. 1993). Measurements of methane in the atmosphere from the 1960s to 1983 indicate an increasing trend of 1% yr^{-1} (Rasmussen and Khalil 1986; Steele et al. 1987; Blake and Rowland 1988), while more recent measurements show a decreasing rate of accumulation (Steele et al. 1992). Going further back in time, the analysis of gases trapped in ice cores reveals that during the last glacial/interglacial transition, the atmospheric methane concentration nearly doubled from 350 to 650 ppbv (Stauffer et al. 1988; Raynaud et al. 1988; Chappellaz et al. 1990; Raynaud and Chappellaz 1993). In addition to biogenic (methanogenic) sources, a potential source of CH_4 to the atmosphere are the large methane occurrences in Arctic regions both in permafrost soils and beneath the sea floor along the continental margins (Kvenvolden and Grantz 1990; Kvenvolden 1988a). In this paper we document the occurrence of an authigenic mineral phase that probably records an episode of methane release from sediments on continental margins. Suess et al. (1982) investigated the chemistry, mineralogy, stable isotope composition, environment of formation; and mode of precipitation of ikaites found on the Antarctic shelf. The results confirm the properties variously attributed to hypothetical precursors of glendolites. These minerals belong to a group of unusual calcitic pseudomorphs after ikaites, associated with glacial marine deposits of Permian to Recent age (Kemper and Schmitz 1981, and references therein). They are assumed to be important indicators of polar waters at the time of precipitation, and could, therefore, be used as a paleoclimatic tool for glacial conditions (Kemper and Schmitz 1981). Recent glendolites are only found in Arctic regions (e.g., Yenisei Estuary, White Sea, and Taimyr Peninsula) (Kemper and Schmitz 1981, and references therein).

Methods

Core PS2460-4 (78°04.5′N, 133°35.9′E) was taken on the Laptev Sea upper continental slope in a water depth of 204 m during the ARCTIC'93 expedition with the *R/V Polarstern* (Fütterer 1994). Total carbon and organic carbon were determined on ground bulk samples and carbonate-free sediment samples, respectively, by means of a Heraeus CHN analyzer. The carbonate content was calculated as: $CaCO_3 = (TC - TOC) \times 8.33$ where TC is total carbon, and TOC is total organic carbon. Hydrogen indices of samples were determined by the Rock-Eval

C. J. Schubert[1] · (✉) D. Nürnberg · N. Scheele
F. Pauer · M. Kriews
Alfred Wegener Institute for Polar and Marine Research,
Columbusstrasse, 27568 Bremerhaven, Germany

Present address:
[1]Department of Oceanography, University of British Columbia,
6270 University Boulevard, Vancouver V6T 1Z4, Canada

method using cycle 1 where the kerogen yield (S_2) was determined between 300 and 550°C. Stable carbon isotope values of the carbonate-free sediment samples were determined using a Finnigan MAT Delta-S mass spectrometer (Bremen University, precision $\pm 0.1\%_o$). Stable oxygen and carbon isotope values of the ikaite were determined using a Finnigan MAT 251 mass spectrometer with a precision of $\pm 0.1\%_o$. Crystal structure was determined by single crystal X-ray diffractometry using a Siemens STOE-diffractometer with MoK_α radiation ($\lambda = 71.073$ pm). Multielement analyses of sediment samples were determined by X-ray fluorescence (RWTH Aachen, precision of the analyses were $\pm 6\%$). Trace element (Ca, Mg, Fe, Al) contents of the ikaite crystals were measured by atomic absorption spectrometry (AAS Perkin Elmer 4000, precision of the analyses were better than $\pm 5\%$).

Results

The Laptev Sea continental slope is an area with very high sedimentation rates (50–70 cm $10^3\,yr^{-1}$; R. Spielhagen and H. Bauch, personal communication 1996). Steady downslope transport is indicated by the occurrence of bivalves (*Yoldia amygdalea*) in the core, which today live in water depth not exceeding 70 m (E. Rachor, personal communication 1995). The entire core is characterized by homogeneous silty clay. Downcore, increasing amounts of

iron sulfides result in a nearly black sediment sequence. X-radiographs indicate intense bioturbation. The carbonate content is very low ($<3\%$). High organic carbon contents (0.75–1.6%; mean = 1.3%) occur throughout the core (Fig. 1). The low hydrogen indices between 50 and 900 cm (35–70 mg HC g^{-1} C) suggest high input of terrigenous organic matter. In addition, the $\delta^{13}C_{org}$ value of -25.12 to $-25.55\%_o$ vs. PDB between 220-cm and 250-cm core depth also indicates that the organic matter has a mainly terrigenous origin (Fig. 1).

At 232- to 238-cm core depth, nine large (diameter up to 5.5 cm) crystals of calcium carbonate hexahydrate (ikaite = $CaCO_3 \times 6H_2O$) occur within the fine-grained sediment, occupying an area of 8 cm in diameter (Fig. 2). X-ray diffractometry on single crystals derived the mineral structure (a = 8.773 ± 0.009 Å, b = 8.229 ± 0.008 Å, c = 11.008 ± 0.008 Å; $\beta = 110.52 \pm 0.008°$ (crystallographic angle between a and c; cf., Suess et al. 1982). It seems that the crystals grew radially from the centerpoint. X-radiography of sediment slices gives no indication of any changes in sediment structures due to the growth of the crystals. The minerals are not stable at temperatures $>0°C$, but release their crystal water and deteriorate within a few hours. Analyses in duplicate of two dried subsamples of the crystals (30°C) showed that they are more or less homogenous and mainly consist of Ca (458 ± 4 mg/g), with minor contributions from Mg, Fe and Al (Mg = $540 \pm 27\ \mu g\,g^{-1}$, Fe = $43.2 \pm 1.2\ \mu g\,g^{-1}$, and Al = $19.4 \pm 0.2\ \mu g\,g^{-1}$). The total organic carbon content of the dehydrated crystals is 0.15%. Stable carbon and oxygen isotope determinations of the ikaite crystals yielded $\delta^{13}C$ and $\delta^{18}O$ values of $-36.3 \pm 0.4\%_o$ vs. PDB and $1.77 \pm 0.2\%_o$ vs. PDB ($N = 2$), respectively (Fig. 1).

Fig. 1 Carbonate content, hydrogen index (HI), and total organic carbon (TOC) content values of core PS2460-4. Core section where $\delta^{13}C_{org}$ measurements have been performed is marked. Also shown are $\delta^{13}C_{org}$ values of core PS2460-4 and ikaite crystals
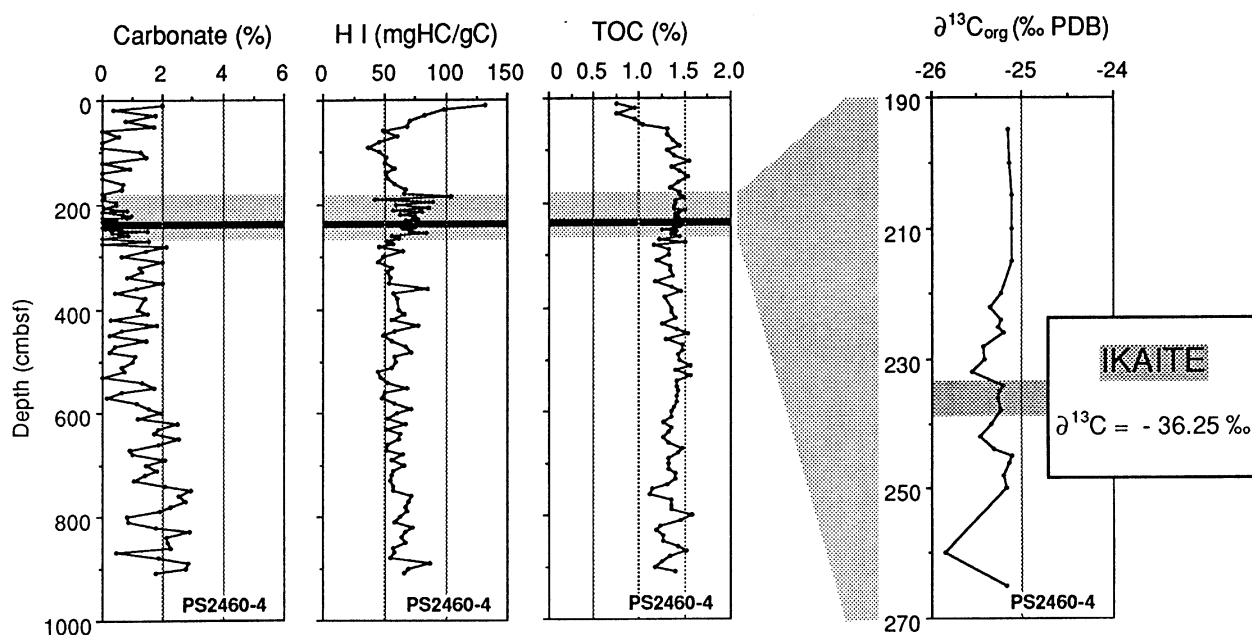
Fig. 2 Photograph of the ikaite crystals (scale = 4 cm) found in core PS2460-4

Discussion

According to Suess et al. (1982), $CaCO_3 \times 6H_2O$ is an authigenic precipitate that forms under subzero temperatures from interstitial solutions of organic-rich sediments undergoing microbial decomposition. Occurrences of ikaite in shoreline sediments of Mono Lake (California) and in sediments from Antarctica have already been described (Bischoff et al. 1993; Suess et al. 1982). The Mono Lake ikaite crystals form during winter months and are transformed to anhydrous $CaCO_3$ or gaylussite during spring time (Bischoff et al. 1993). High pressure (deep water), as described by Suess et al. (1982), seems not to be a prerequisite for ikaite precipitation, as the Mono Lake and the shallow Arctic shelf occurrences (this report) show. Similar crystals have also been found in shallow water (37 m) in the Anabar-Khatanga Valley (Laptev Sea: Dehn et al. 1995). Nevertheless, environments with high accumulation rates of organic-rich sediments in cold waters are evidently the requisite conditions for precipitation of calcium carbonate hexahydrate.

The oxygen isotope composition of the ikaite (1.77‰) reported here is in the normal range of $\delta^{18}O$ values for sedimentary carbonates (cf., Veizer and Hoefs 1976). The extremely ^{13}C-depleted carbon isotope signal, however, lies completely outside the range of $\delta^{13}C$ values of carbonates from the Archaen to Tertiary described by Veizer and Hoefs (1976). However, methane-derived marine carbonates with $\delta^{13}C$ values of $-60‰$ have been described (Hathaway and Degens 1969). Whereas the carbon source for the Antarctic ikaites described by Suess et al. (1982) could have been sedimentary organic matter, this cannot have been the case for the Arctic ikaites described here in view of their extreme ^{13}C depletion. The exceptionally light carbon isotope signal requires an unusual carbon source for this authigenic carbonate phase. Methane and other volatile hydrocarbons are oxidized in the sulfate-reducing zone of modern sediments to CO_2 (Hathaway and Degens 1969; Whiticar and Faber 1986). This oxidation causes an isotopic fractionation (fractionation factor $\alpha_c = 1.002 - 1.014$), leading to enriched $\delta^{13}C$ values of the oxidation product (Whiticar and Faber 1986; Whiticar 1993). The oxidation of isotopically light methane to CO_2 drastically changes the isotopic composition of the dissolved inorganic carbon (DIC) reservoir in the pore water. At a pH value of 8.4 in the pore water of core PS2460-4 (E. Damm, personal communication 1993), the external CO_2 is present exclusively as HCO_3^- (Bjerrum plot; describes the phase of CO_2 at different pH values). Since the carbon isotope fractionation between bicarbonate and carbonate is negligible (Rubinson and Clayton 1969), we suggest a simplified isotope balance equation for ikaite formation:

$$\delta^{13}C_{ikaite} = a \times \delta^{13}C_{(oxidized\ methane)}$$
$$+ (a - 1) \times \delta^{13}C_{(initial\ pore\ water)} \quad (1)$$

in which $\delta^{13}C_{ikaite}$ is $-36.3‰$ PDB; a is the amount of oxidized methane in the pore water; $\delta^{13}C_{(oxidized\ methane)}$ is $-52‰$ to $-73‰$ PDB (see below for explanation); and $\delta^{13}C_{(initial\ pore\ water)}$ is $-1‰$ PDB (Scheele, unpublished data).

Thus, for $\delta^{13}C_{(oxidized\ methane)}$ values of -73 to $-52‰$, roughly 50–70% ($a = 0.50$–0.70) of the inorganic carbon in the pore water originates from methane oxidation (the calculation does not include the isotopic shift of the pore water, which could have been caused by decomposition of organic matter; this would reduce the calculated amount of oxidized methane used for precipitation).

Therefore, oxidation of methane might have more than doubled the concentration of CO_2 in the pore water. The high mobility of methane enables diffusion from a deep-seated source through the sediment column until
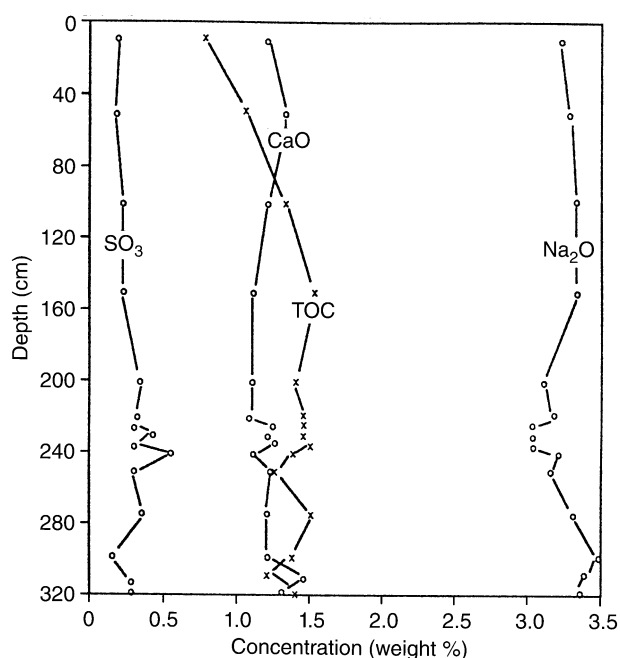
Fig. 3 Concentration profile of SO_3, total organic carbon (TOC), CaO, and Na_2O of sediment samples of core PS2460-4. Small-scale fluctuations in the elemental composition (CaO, Na_2O, SO_3, TOC) of the sediment core cannot explain the dominant occurrence of ikaite in one horizon between 232 and 238 cm core depth

oxidation occurs at a redox barrier. Such an increase in pore water alkalinity by microbial oxidation of methane is considered to be the main reason for the ikaite precipitation (unfortunately, no pore water measurements could be done onboard). Small-scale fluctuations in the elemental composition (CaO, Na_2O, SO_3, TOC) of the sediment core cannot explain the dominant occurrence of ikaite in one horizon between 232 and 238 cm (Fig. 3). The proposed model of ikaite precipitation is in accordance with the results of Bischoff et al. (1993), who explain ikaite precipitation at Mono Lake, California, by the mixing of two different solutions, both with a high HCO_3^- content.

We were not able to determine the source of the methane being oxidized to CO_2, but two processes are likely candidates:

1. The methane may originate from the decomposition of organic matter by methanogenesis due to the absence of other available oxidants (O_2, NO_3^-, SO_4^{2-}). This process is known from high-sedimentation regions accumulating large amounts of organic carbon at sediment intervals where dissolved sulfate concentrations are less than 1.0 mM (Reeburgh and Heggie 1974; Martens and Berner 1977; Reeburgh 1980). Two metabolic pathways are recognized for methanogenesis: (1) acetate fermentation (Buswell and Solo 1948; Stadtmann and Barker 1949) as the major pathway in freshwater sediments; and (2) reduction of carbon dioxide as the dominant pathway in marine

sediments (Oremland and Taylor 1975, 1978; Belaev et al. 1977). Methanogenesis in marine sediments can increase the methane concentration to saturation, leading to bubble formation in shallow water or sediment horizons with free gas occurrence (Schubel 1974; Whiticar 1982). The carbon and hydrogen isotopic composition of biogenic methane has been investigated by several authors (for an overview see Whiticar et al. 1986). The $\delta^{13}C$ values of methane derived from methanogenesis in marine sediments vary from $-52.5‰$ (Schoell 1988) to $-109‰$ (see references in Whiticar et al. 1986). Microbial anaerobic oxidation of the methane produces CO_2, which changes the isotopic composition of the dissolved inorganic carbon (DIC) reservoir in the pore water. Sulfate is generally suggested to be the primary oxidant. The oxidation is associated with a carbon isotope fractionation (fractionation factor $\alpha_c = 1.002 - 1.014$; Whiticar and Faber 1986). Using a typical $\delta^{13}C$ value for biogenically formed methane of $-80‰$ (Whiticar 1993), the $\delta^{13}C$ value of the coexisting CO_2 would be $-73‰$ (using a mean fractionation factor of $\alpha_c = 1.008$). This value has been set in Eq. 1, suggesting that 50% of the CO_2 used for the ikaite precipitation originates from the oxidation of biogenic methane.

2. The methane may be released from gas hydrates (Kvenvolden and McMenamin 1980; Kvenvolden 1981, 1988b; Macleod 1982). Estimates of the amount of methane in gas hydrates in oceanic settings range between 3 and 25×10^{15} m^3 (McIver 1981; Trofimuk et al. 1977). In the offshore Arctic Basin, Kvenvolden and Grantz (in Kvenvolden 1988a) estimated from sediment thickness, porosity, and the amount of gas hydrates a total amount of 10^{15} m^3 of methane.

The Laptev Sea shelf is an area where submarine permafrost occurs on the continental margin (cf., Kassens and Karpiy 1994). Here, gas hydrates occurring at shallow sediment depths could release captured methane to the atmosphere during melting of permafrost (Kvenvolden 1988a, b). The high mobility of methane in the sediment column, as mentioned above, would result in transport to the oxidation front, and this would lead to the incorporation of carbon as CO_2 in the calcium carbonate hexahydrate. Sediment features observed in Parasound echosoundings (records bottom and subbottom reflection pattern down to approximately 100 m, Atlas Electronics, Bremen, Germany) from the Laptev Sea shelf in the uppermost 10 m of the sediment sequence, interpreted to be caused by gas escaped from the depth (F. Niessen, personal communication 1995), strongly support this assumption. The carbon isotope value of $-60‰$ for gas hydrates from Whiticar (1993) is used in this study, which, until direct determinations are available, is probably the best estimate for gas hydrates in permafrost regions. The $\delta^{13}C$ value of the coexisting CO_2 would be $-52‰$ (using a mean fractionation factor of $\alpha_c = 1.008$; Whiticar and Faber 1986). This value has been set in Eq. 1, suggesting that a maximum of 70% of the CO_2 used for the ikaite

precipitation might have originated from the oxidation of methane derived from gas hydrates.

Conclusions

The ^{13}C depletion in ikaite crystals from Laptev Sea sediments may be attributed to the oxidation of methane within the sediments. Two possible processes are involved: (1) oxidation of methane derived from methanogenesis, in which case about 50% of the CO_2 used for the ikaite precipitation originated from this source; and (2) oxidation of methane derived from gas hydrates, in which case about 70% of the CO_2 used for the ikaite precipitation originated from this source. Although the source of the methane could not be identified with certainty, the known occurrence of gas hydrates in permafrost regions and the presence of sediment features in the Laptev Sea that are interpreted to be caused by gas escaping from depth support the possibility of methane release from gas hydrates. Such a process would have a major influence on global climate in view of the large radiative-forcing factor of this gas.

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