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Marine Pore-water Sulfate Profiles Indicate in situ Methane Flux from Underlying Gas Hydrate

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ABSTRACT

Marine pore-water sulfate profiles measured in piston cores are used to estimate methane flux toward the sea floor and to detect anomalous methane gradients within sediments overlying a major gas hydrate deposit at the Carolina Rise and Blake Ridge (U.S. Atlantic continental margin). Here, sulfate gradients are linear, implying that sulfate depletion is driven by methane flux from below, rather than by the flux of sedimentary organic matter from above. Thus, these linear sulfate gradients can be used to quantify and assess in situ methane flux, which is a function of the methane inventory below.

INTRODUCTION

Microbial sulfate depletion, microbial methane production, and gas hydrate formation are interrelated diagenetic processes that occur in deep-sea, continental-margin sediments (Paull et al., 1994). Gas hydrates are crystalline solids composed of water and low-molecular-weight gases (e.g., CH_4) that form under conditions of low temperature, high pressure, and adequate gas concentration (Sloan, 1990). Early diagenesis is strongly controlled by microbially mediated reactions that utilize available oxidants to convert sedimentary organic matter into microbial byproducts (Claypool and Kaplan, 1974) that may ultimately form gas hydrate. Once marine sediment becomes anoxic, sulfate reduction becomes the dominant microbial process that causes interstitial sulfate concentration to decrease with depth below the sediment-water interface (Berner, 1980). When sulfate is essentially depleted, methane production begins (Martens and Berner, 1974), resulting in increasing methane concentration with depth (Claypool and Kaplan, 1974). Using isotopic and compositional data, Brooks et al. (1983), Claypool and Threlkeld (1983), Galimov and Kvenvolden (1983), and Paull et al. (1995) have shown that the methane in gas hydrate of the Carolina Rise and Blake Ridge region is microbial in origin, and does not have a significant thermogenic component.

Detection and Estimation of Gas Hydrate

Currently, the detection of gas hydrate is based on the occurrence of bottom simulating reflectors (BSRs) on seismic sections (Bryan, 1974). Evidence suggests that BSRs correspond to the base of gas hydrate stability below which gaseous methane may occur (Bangs et al., 1993; MacKay et al., 1994). BSRs at the Carolina Rise and Blake Ridge occur at sediment depths of 200–600 m subbottom and outline an areally extensive (~26 000 km^2) gas hydrate field (Dillon and Paull, 1983).

Current global estimates indicate that gas hydrates are the Earth's second-largest organic carbon reservoir (Kvenvolden, 1988), but delimiting hydrate amounts even at particular localities is problematic (Ginsburg and Soloviev, 1995). In addition, the concentration and flux of methane in deep-water, continental-margin sediments are difficult to measure because of degassing during sample recovery. In this paper, we evaluate the potential of using pore-water sulfate profiles as a geochemical sensor to locate underlying gas hydrate deposits and to estimate by proxy the flux of methane from below.

Pore-Water Sulfate Depletion Processes

Typical interstitial sulfate profiles from marine sedimentary environments exhibit curved, convex-up profiles reflecting sulfate consumption ($SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$) by sulfate-reducing microbes (e.g., Berner, 1980; Gieskes, 1981). If steady-state sulfate profiles do not exhibit this typical convex-up curvature, another process must be involved. Microbially mediated, anaerobic methane oxidation ($SO_4^{2-} + CH_4 \rightarrow HS^- + HCO_3^- + H_2O$) is also capable of consuming sulfate, but requires a supply of methane (Reeburgh, 1976; Barnes and Goldberg, 1976). We propose that anaerobic methane oxidation focused at the base of the sulfate reduction zone is the principal sulfate-consuming process at the Carolina Rise and Blake Ridge, indicating that sulfate depletion is driven by methane flux from below.

METHODS

We collected 38 piston cores (mean length ~12 m) from the Carolina Rise and Blake Ridge to assemble a comprehensive, geochemical data set for sediments and their pore waters overlying well-developed methane gas hydrates. Pore waters were squeezed from 6-cm-thick, whole round sections of core sediment. Ammonium and CO_2 were analyzed at sea using the methods of Presley (1971) and Weiss and Craig (1973), respectively. Sulfate was determined onshore by ion chromatography (Gieskes et al., 1991). Total solid-phase sulfide (SO, FeS, FeS_2) was separated using the method of Canfield et al. (1986) and analyzed for $\delta^{34}S$ by Geochron Laboratories.

RESULTS AND DISCUSSION
Observed Geochemical Profiles

At the Carolina Rise and Blake Ridge, most sulfate profiles (27 of 38) are linear (Fig. 1) within ≥95% probability (r test; Young, 1962). In these lithologically similar sediments, linear regressions fit to data for individual cores indicate sulfate gradients of 2.86 to 0.18 millimeter (mM) m^{-1}. Intercepts range from 10 m to extrapolated depths of 155 m and define the depth of no sulfate at the base of the sulfate-reduction zone. Linear gradients in the absence of convex-up curvature suggest that the dominant sulfate-consuming reaction oc-
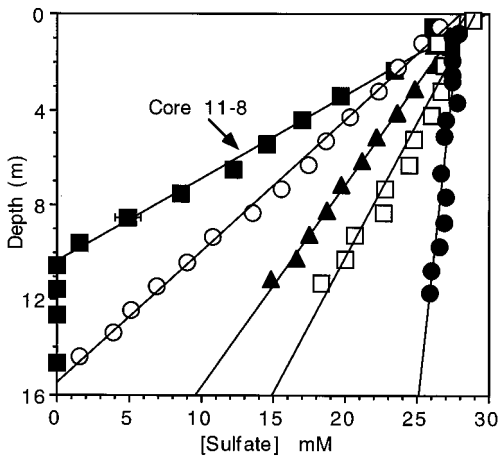
Figure 1. Pore-water sulfate concentrations vs. depth in five piston cores from Carolina Rise and Blake Ridge. Concentration is expressed in millimolar (mM) units; measurement uncertainties are less than symbol size, unless error bars are present. Sulfate concentration gradients show factor of 16 variation, and five illustrated cores represent spectrum of differing sulfate gradients. Data from core 11-8, highlighted with arrow (filled squares), show highest gradient. Cores with lowest sulfate gradients (e.g., core 31-24, filled circles) represent background gradients.

curs at or near the depth of no sulfate, consistent with anaerobic methane oxidation.

Other data are consistent with focused sulfate consumption via aerobic methane oxidation near the depth of no sulfate. (1) CO_2 profiles are generally linear within the sulfate reduction zone, and in core 11-8, the CO_2 profiles change slope markedly near the depth of no sulfate (~10 m; Fig. 2), indicating localized CO_2 production. The linear CO_2 profile above the depth of no sulfate is
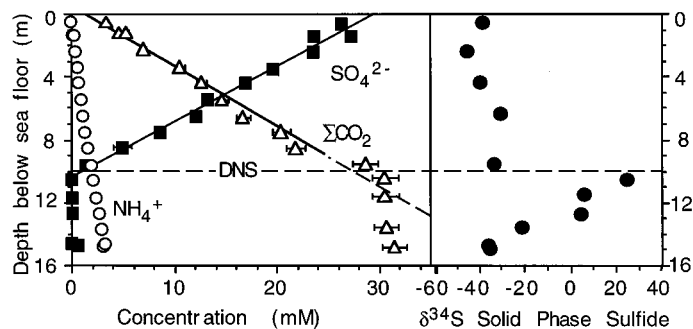

Figure 2. Interstitial SO_4^{2-}, NH_4^+, and CO_2 concentrations and $\delta^{34}S$ of total solid phase sulfide from core 11-8 (lat 31°27.92′N; long 75°8.04′W). Concentration is expressed in millimolar (mM) units; measurement uncertainties are less than symbol size, unless error bars are present. Both sulfate and CO_2 profiles are linear above depth of no sulfate (DNS) at ~10.3 m (correlation coefficients, $r^2 = 0.984$ and 0.980, respectively). However, CO_2 shows marked slope change at ~10 m, suggesting local HCO_3^- production. NH_4^+ profile is linear ($r^2 = 0.995$) in entire core with no slope break at 10 m, suggesting that ammonium produced by sulfate reduction of sedimentary organic matter is low compared to upward flux from deeper source. $\delta^{34}S$ values of total solid phase sulfide are distinctly different above and below DNS. This is consistent with focused consumption of seawater sulfate at base of sulfate reduction zone.

consistent with diffusion of dissolved CO_2 toward the sediment-water interface. (2) Highly negative $\delta^{13}C_{CO_2}$ values would imply that carbon is derived from methane, but we could not measure $\delta^{13}C_{CO_2}$ for these cores. However, existing Deep Sea Drilling Project data from nearby Site 533 show $\delta^{13}C_{CO_2}$ as negative as $-31.4‰$ at the base of the sulfate reduction zone (Claypool and Threlkeld, 1983). (3) Ammonium is produced by oxidation of nitrogen-containing sedimentary organic matter through sulfate reduction (e.g., Gieskes, 1981), but not by anaerobic methane oxidation. Ammonium profiles in Carolina Rise and Blake Ridge cores are usually linear, and in core 11-8, the profile shows no inflection at the base of the sulfate-reduction zone (Fig. 2). Thus, the major source of ammonium is not concentrated near the interface, nor within the sulfate-reduction zone, but must occur well below the sulfate-reduction zone. Any ammonium produced by sulfate reduction of sedimentary organic matter is a minor component and its signature is overwritten by diffusion of ammonium from below. (4) $\delta^{34}S$ values of total solid phase sulfide show little variation (mean $-38.1‰ \pm 6‰$, $N = 5$) with depth within the sulfate-reduction zone, but increase to $+23.6‰$ immediately below the sulfate-reduction zone. This suggests focused sulfate consumption at the base of the sulfate-reduction zone as sulfur in seawater sulfate ($\delta^{34}S = +20.0‰ \pm 0.1‰$; Rees et al., 1978) is reduced to ultimately reside in solid-phase sulfide (Goldhaber and Kaplan, 1980).

Role of Organic Carbon in Sulfate Depletion

Sulfate depletion is usually controlled by the quantity and quality of sedimentary organic matter, supplied by depositional processes, which is essentially a function of sedimentation rate (Toth and Lerman, 1977; Berner, 1978; Canfield, 1991). However, at the Carolina Rise and Blake Ridge, the linearity and factor of 16 variation of sulfate gradients (Fig. 1) cannot be explained by sulfate reduction utilizing in situ sedimentary organic matter. Sedimentation rate varies little over the region or downcore (~22 cm/k.y.; Buelow, 1994), indicating that organic-matter flux has been relatively uniform in both space and time. Thus, sulfate gradients are not correlated with sedimentation rate. In addition, variations in sedimentary total organic carbon (TOC) appear to exert little control on sulfate depletion. TOC varies by only a factor of two (mean TOC = 0.67% $\pm$ 0.38%, $N = 683$) in the piston-core sediments, and cores with the highest TOC values have the lowest sulfate depletion relative to seawater sulfate concentration.

Importance of Anaerobic Methane Oxidation

We infer that anaerobic methane oxidation is responsible for the bulk of sulfate depletion observed at the Carolina Rise and Blake Ridge. Anaerobic methane oxidation links sulfate and methane consumption at the base of the sulfate reduction zone (approximately the depth of no sulfate) and should result in the 1:1 stoichiometric consumption of methane and sulfate (see reaction above).

A simple one-dimensional, finite-difference diagenetic model was used to test the effect of a sulfate sink at the base of the sulfate reduction zone on sulfate concentration profiles. The model, based on Berner's (1980) diagenetic equation for sulfate depletion, assumes steady state, and that compaction, sediment burial, and diffusion are the only mass-transport processes. Focused sulfate consumption at the base of the sulfate reduction zone (representing sulfate depletion due only to anaerobic methane oxidation) results in linear model profiles that mimic the linear sulfate gradients observed in piston core sediments.
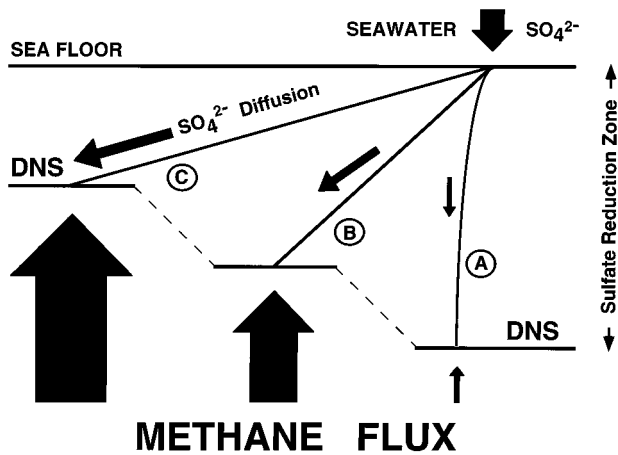
Figure 3. Schematic diagram shows how upward methane flux controls sulfate profiles and depth of no sulfate (DNS). Arrow size is proportional to upward methane flux. Typical sulfate profiles display convex-up curvature (A) reflecting sulfate reduction of in situ organic sedimentary matter. Linear sulfate profiles (B and C) result when focused sulfate consumption, driven by methane flux from below, occurs at DNS at rates substantially greater than those for sulfate reduction of in situ sedimentary organic matter. In these cases, sulfate diffuses into sediments and is consumed by reaction with methane at base of sulfate reduction zone. Rate of sulfate consumption and steepness of sulfate gradients are thus controlled by flux of methane from below.

Sulfate and Methane Flux

Linear sulfate profiles indicate that sulfate consumption is primarily driven by upward-diffusing methane rather than by flux of organic matter to the sediment. At steady state, sulfate and methane fluxes should be balanced so that interstitial sulfate concentrations will be determined by the upward flux of methane from below (Fig. 3).

The sulfate flux (J) for the largest observed sulfate gradient (core 11-8; 2.9 mM m^{-1}) is 1.8×10^{-3} mmol cm^{-2} yr^{-1} calculated using Fick's First Law (Berner, 1980):

$$J = D_O \phi^3 \frac{\partial C}{\partial x}$$

where D_O is the diffusion coefficient of SO$_4$$^{2-}$ in water (5.8×10^{-6} cm^2 s^{-1} at 5 °C; Li and Gregory, 1974), and ϕ is porosity (mean porosity over the upper 10 m is 0.70; Paulus, 1972). This estimate is based on bottom-water temperatures of 3 to 5 °C (Luyten, 1977), a geothermal gradient of 40 °C km^{-1} (Ruppel et al., 1995), and sediment strength data from the piston cores. Assuming that downward sulfate flux is stoichiometrically balanced by upward methane flux (i.e., $J_{SO_4} = J_{CH_4}$) at the depth of no sulfate, the proxy methane flux for core 11-8 is also 1.8×10^{-3} mmol cm^{-2} yr^{-1}. Using the measured sulfate gradients, proxy methane flux varies by at least a factor of 16 over the Carolina Rise and Blake Ridge.

Methane Gradients

Bottom-simulating reflectors may be produced by gas bubbles at the base of gas hydrate stability (Bangs et al., 1993; MacKay et al., 1994), where gas hydrate begins to dissociate so that methane gas, methane-saturated water, and gas hydrate coexist. Methane concentration at the base of gas hydrate stability can be calculated (Paull et al., 1994) using the methane solubility model of Duan et al. (1992). Methane gradients calculated from proxy methane fluxes

can be compared to gradients required by methane saturation at the base of gas hydrate stability (Paull et al., 1994) to determine if diffusive equilibrium exists between the base of gas hydrate stability and the base of the sulfate-reduction zone. For example, the methane saturation concentration at core site 11-8 at the base of gas hydrate stability is ~188 mM (hydrostatic conditions; water depth = 3000 m; base of gas hydrate stability = 600 m subbottom; geothermal gradient ~40 °C km^{-1}; Ruppel et al., 1995) and predicts a diffusive, steady-state methane gradient of 0.3 mM m^{-1}. The proxy methane flux (1.8×10^{-3} mmol cm^{-2} yr^{-1}) for core 11-8 predicts a methane gradient of 2 mM m^{-1} using Fick's First Law ($\phi = 0.60$; Paulus, 1972; $D_O^{CH_4} = 1.31 \times 10^{-5}$ cm^2 s^{-1} at 15 °C; Lerman, 1979). At core site 11-8, the proxy methane flux is more than a factor of six larger than that required by diffusive equilibrium with methane at the base of gas hydrate stability.

Implications

Steeper methane gradients imply significant dissolved methane concentrations well above the base of gas hydrate stability, closer to the methane-sulfate boundary. At steady state, steep gradients may occur because (1) intensified microbial methane production occurs with depth, or (2) dissolved methane is associated with gas hydrate below. Linear concentration gradients of sulfate and other dissolved species imply steady-state processes. The first scenario is unlikely because the most labile organic matter should be consumed by sulfate reducers before methane production begins. In addition, TOC changes little with depth at these sites (Boyce, 1972; Sheridan et al., 1983; Buelow, 1994), implying that there is no increased amount of substrate available for increased methane production. Methane associated with gas hydrates is the simplest explanation.

CONCLUSION

Linear sulfate profiles in piston cores from Carolina Rise and Blake Ridge sediments imply that anaerobic methane oxidation is the dominant sulfate-consuming process. Variations in linear sulfate gradients are controlled by differences in upward methane flux (Fig. 3). Methane flux, calculated from sulfate profiles, varies by at least a factor of 16, which suggests lateral variation in methane concentrations at depth. We infer that this methane is associated with underlying gas hydrate deposits, indicating laterally heterogeneous hydrate distribution. Wherever sulfate profiles are linear, sulfate gradients may be used to estimate the in situ methane flux from other continental-margin sediments.

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