

8. MODEL, STABLE ISOTOPE, AND RADIOTRACER CHARACTERIZATION OF ANAEROBIC METHANE OXIDATION IN GAS HYDRATE-BEARING SEDIMENTS OF THE BLAKE RIDGE¹

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ABSTRACT

Anaerobic methane oxidation (AMO) was characterized in sediment cores from the Blake Ridge collected during Ocean Drilling Program (ODP) Leg 164. Three independent lines of evidence support the occurrence and scale of AMO at Sites 994 and 995.

First, concentration depth profiles of methane from Hole 995B exhibit a region of upward concavity suggestive of methane consumption. Diagenetic modeling of the concentration profile indicates a 1.85-m-thick zone of AMO centered at 21.22 mbsf, with a peak rate of 12.4 nM·d⁻¹.

Second, subsurface maxima in tracer-based sulfate reduction rates from Holes 994B and 995B were observed at depths that coincide with the model-predicted AMO zone. The subsurface zone of sulfate reduction was 2 m thick and had a depth integrated rate that compared favorably to that of AMO (1.3 vs. 1.1 nmol·cm⁻²·d⁻¹, respectively). These features suggest close coupling of AMO and sulfate reduction in the Blake Ridge sediments.

Third, measured $\delta^{13}\text{CH}_4$ values are lightest at the point of peak model-predicted methane oxidation and become increasingly ¹³C-enriched with decreasing sediment depth, consistent with kinetic isotope fractionation during bacterially mediated methane oxidation. The isotopic data predict a somewhat (60 cm) shallower maximum depth of methane oxidation than do the model and sulfate reduction data.

INTRODUCTION

Continental margin sediments contain a large reservoir of methane and thus represent a potentially significant contribution to the global methane budget. This is particularly true of methane hydrate-bearing sediments. Despite this large reservoir, the oceans as a whole contribute only about 2% of the annual global flux of methane to the atmosphere (Cicerone and Oremland, 1988). This is largely due to anaerobic methane oxidation (AMO), which consumes upwardly diffusing methane before it can escape the sediments and contribute to the global flux (Reeburgh and Alperin, 1988).

A wealth of geochemical evidence now supports the conclusion that anaerobic methane oxidation is important in marine sediments. The first such evidence came from geochemical models that showed that "concave up" methane concentration profiles observed in many marine sediments can only be accounted for by consumption of methane in anoxic depth intervals (Barnes and Goldberg, 1976; Martens and Berner, 1977; Reeburgh, 1976; Scranton, 1988). The model predictions have been corroborated by radiotracer experiments that show that ¹⁴CH₄ is converted to ¹⁴CO₂ in anoxic systems (Alperin and Reeburgh, 1984; Devol, 1983; Hoehler et al., 1994; Iversen and Jørgensen, 1985; Reeburgh, 1980). Distributions of naturally occurring stable isotopes provide further evidence of methane oxidation. The presence of ²H- and ¹³C-enriched CH₄ is consistent with kinetic fractionation arising from methane consumption (Albert and Martens,

1995; Alperin et al., 1988; Oremland and DesMarais, 1983; Whiticar and Faber, 1986), whereas the presence of ¹³C-depleted CO₂ implies oxidation of an isotopically "light" substrate (methane) (Blair and Aller, 1995). Finally, time-series incubations have shown decreasing methane concentrations in contained anoxic samples (Lidstrom, 1983).

Despite the lack of a concretely proven mechanism for anaerobic methane oxidation, several features are consistently observed. Most importantly, from the standpoint of marine sediments, is an apparent link to sulfate reduction:



In many marine sediments where the process has been characterized, a secondary maximum in sulfate reduction rates coincides with the peak in methane oxidation rates. Often, the methane oxidation rate represents a relatively small fraction of the secondary maximum in sulfate reduction rates (Alperin and Reeburgh, 1984; Devol, 1983; Devol and Ahmed, 1981), suggesting that most of the electrons used to reduce sulfate are derived from organic matter fermentation. In at least one instance, however, methane apparently fueled as much as 80% of the secondary maximum in sulfate reduction rates (Iversen and Jørgensen, 1985). The contribution of anaerobic methane oxidation to the overall depth-integrated sulfate reduction rate is typically quite low.

Most studies of anaerobic methane oxidation have focused on nearshore sedimentary environments that are relatively rich in organic matter. Ocean Drilling Program (ODP) Leg 164 thus provided a unique opportunity to study the process in more oligotrophic continental margin sediments. The goal of this study was to characterize anaerobic methane oxidation in sediments overlying methane hydrates on the Blake Outer Ridge. The question was addressed using three independent techniques:

1. Diagenetic modeling of high-resolution methane concentration data,
2. Analysis of methane stable-carbon isotope chemistry, and

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3. Direct measurement of methane oxidation and sulfate reduction rates via a radiotracer approach.

With the exception of tracer-based methane oxidation rates (for which the detection limit was too high), each independent line of evidence indicated the occurrence of methane oxidation in the zone of overlap between methane and sulfate. Although these results bear qualitative analogy to many of the previous nearshore studies, the rates and depth scales involved differ by orders of magnitude.

METHODS

Storage and Sampling of Cores

Selected 1.5-m sections of intact core from Holes 994B and 995B were cut from the standard 9-m segments, capped immediately, and transferred to a cold room (6°C) for storage. The sections were placed into PVC tubes that were capped on both ends and fitted with gas inlet and outlet ports. These ports allowed for continuous flushing with nitrogen gas to ensure anoxia of the cores during storage.

Cores from Hole 994B were subsampled aboard the *JOIDES Resolution* approximately one week after they were obtained. Cores from Hole 995B were transported to a shore-based lab and subsampled approximately two weeks after they were obtained. Subsampling of the cores was conducted in similar fashion for both ship- and shore-based measurements. Desired depth ranges were sampled by hack sawing through the core liner and sediment (perpendicular to the axis of the core). The selected intervals were at least 10 cm from either end of the original core section so that relatively undisturbed samples were assured. Immediately after sawing, the freshly exposed sediment surface was sampled by inserting cut-off 3-mL plastic syringes along the axis of the core (thus sampling a depth interval of ~4 cm). The syringe plunger was held fixed at the sediment surface while the barrel was pushed into the sediment, in an overall procedure that is analogous to piston coring. This sampling method produced sediment-filled syringes that were free from atmospheric gas bubbles. The syringes were then removed from the sediment and treated as described below for the concentration/isotope and rate measurements.

Concentration and $\delta^{13}\text{C}$ of Methane

Pore-water methane gas was sampled by advancing the plunger of the open-ended plastic syringe to extrude a small quantity of sediment, then shaving off this excess (with a razor blade) so that the surface of the remaining sediment was flush with the open end of the syringe barrel. This allowed for precise determination of the sediment volume contained in the (graduated) syringe. The sediment in the syringe was then extruded into a 20-mL glass serum vial that contained 5.00 mL of 1.0 M NaOH (designed to terminate any bacterial activity). The vial was then capped immediately with a red rubber septum. The internal volume of each sample vial was carefully determined and recorded beforehand, taking into account the effect of the rubber septum.

Each vial was shaken vigorously for several minutes and then left to stand for >1 hr. This process slurried the sediment pellet into a high-porosity suspension that promoted equilibration of pore-water methane with the vial headspace. We have previously found that suspensions of similar porosity achieve aqueous-gas equilibrium within minutes. The headspace gas was sampled by syringe: a small volume (1 mL or less) of distilled water was injected into the sealed vial and an equivalent volume of gas was withdrawn. The methane concentration in the headspace gas was analyzed by gas chromatography with flame ionization detection. Standards were prepared minutes before use by diluting precisely known volumes of pure methane gas into glass serum vials similar to those used for the sediment samples. The pore-water methane concentration was then calculated from the headspace gas concentration as follows:

$$[\text{CH}_4] = \frac{P_{\text{ATM}} \cdot V_{\text{H}}}{R \cdot T \cdot \Phi \cdot V_{\text{S}}},$$

where V_{H} and V_{S} are the volume of the sample vial headspace and whole sediment sample, respectively; P_{ATM} is the pressure of the vial headspace (assumed to be the measured atmospheric pressure at the time the vials were sealed); R is the universal gas constant; T is the temperature of the vial headspace; and Φ is the sediment porosity (determined in our lab for three depth intervals over the sampled length of core).

Once the vials had been sampled for methane concentration analysis, they were subsequently sampled for stable carbon isotope analysis. Distilled water (5 mL) was injected into the vial by syringe and an identical volume of headspace gas was removed. Methane in the sample was concentrated in-line via cryogenic focusing (Popp et al., 1995). The $^{13}\text{C}/^{12}\text{C}$ ratio was determined on a Mat-252 isotope ratio mass spectrometer (Finnigan Mat). Reported isotope ratios are corrected for the contribution of atmospheric methane in the headspace gas to the overall methane isotope signature. The isotopic composition of atmospheric methane was measured for "lab air" at the time the sample vials were sealed.

Sulfate Reduction and Methane Oxidation Rate Measurements

For rate measurements, the sediment-filled syringes were sealed with black-butyl rubber stoppers. These stoppers had one hole that had previously been filled with silicone caulk to provide a septum for injecting tracer. The filled syringes were incubated overnight in a constant temperature bath at the in situ sediment temperature. Each syringe was then injected with an aliquot of either aqueous $\text{H}_2^{35}\text{SO}_4$ (specific activity = 1500 Ci-mmol⁻¹; 10- μL injection; 3×10^8 dpm for samples in the 0–17 mbsf interval or 3×10^7 dpm for those below 17 mbsf) or gaseous $^{14}\text{CH}_4$ (specific activity = 55 mCi-mmol⁻¹; 25- μL injection; 7×10^6 dpm). In the case of ^{35}S , the added sulfur was negligible with respect to the ambient pool. The ^{14}C addition enhanced the ambient CH_4 concentration by ~3 μM (equivalent to a 30% increase at the top of the sediment column and a 1%–5% increase in the apparent zone of methane oxidation). The enhanced methane concentration was taken into account in all rate calculations. The injected samples were incubated for 4 days at in situ sediment temperature in the dark. Incubations were terminated by extruding the sediment pellet into a 20-mL glass serum vial containing 5.0 mL of 1.0 M NaOH and immediately capping and shaking the vial.

The ^{35}S tracer was obtained as $\text{H}_2^{35}\text{SO}_4$ from a commercial source and used as is. Because there was no commercially available source of $^{14}\text{CH}_4$ at the time of cruise preparations, tracer was obtained as $^{14}\text{CH}_3\text{I}$ and reacted to methane. This was accomplished by adding an excess of Superhydride (Aldrich Chemical Co.) to the CH_3I under anhydrous and anoxic conditions. Reductive dehalogenation of the CH_3I produced methane, which was transferred to a vial containing an anoxic solution of 0.1 M NaOH (ensuring that any $^{14}\text{CO}_2$ present would be removed from the tracer gas). Significant dilution of the methane with nitrogen gas occurred during the overall process, such that the activity of the resultant tracer gas was limited to 7×10^6 dpm per 25- μL injection. The synthesized gas was free of ^{14}CO (by GC/HgO detection) and $^{14}\text{C}_2$ or higher hydrocarbons (by GC/FID), ensuring that any $^{14}\text{CO}_2$ formed during the sediment incubations must have derived entirely from $^{14}\text{CH}_4$.

For the sulfate reduction rate samples, the quantity of H_2^{35}S formed during the incubation was measured by a previously described acidic-chrome technique (Fossing and Jørgensen, 1989). This was used to calculate sulfate reduction rates (SRR) as follows:

$$\text{SRR} = [\text{SO}_4^{2-}] \cdot \frac{\alpha}{t} \cdot \frac{{}^{35}\text{S}_{\text{red}}}{{}^{35}\text{SO}_4^{2-}},$$

where α is the kinetic isotope fractionation factor (^{35}S vs. ^{32}S) observed for sulfate reduction (assumed to be 1.045; Jørgensen, 1978); t is the incubation time; $^{35}\text{S}_{\text{red}}$ is the recovered activity of reduced sulfur forms; and $^{35}\text{SO}_4^{2-}$ is the added activity of $^{35}\text{SO}_4^{2-}$.

During the initial stages of our analysis, the acidic-chrome technique was found to produce a slow but constant chemical reduction of the tracer $^{35}\text{SO}_4^{2-}$ during sample analysis, thus contributing to a high and somewhat variable blank. This chemical reduction is made problematic by the necessity to measure sulfate reduction rates that are 2–4 orders of magnitude lower than those typically observed in coastal sediments. To address this problem one of the two replicate samples from each depth was treated with a procedure intended to remove tracer $^{35}\text{SO}_4^{2-}$ prior to analysis. The sediment sample was slurried with a large quantity of distilled water (~50 mL), allowed to settle for several hours, and then decanted (retaining the solid phase). This procedure was repeated, and the solid phase was then subjected to the acidic-chrome procedure. Because of the potential for loss of reduced sulfur during the above described procedure, these values are probably best viewed as minimum estimates. This potential loss, combined with possible blank-induced variability in the nondecanted samples contributes to considerable noise between replicates. Despite this noise, relative depth-variations in sulfate reduction rates can be clearly discerned.

For methane oxidation rate samples, the quantity of $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ in each sample at the end of the incubation was determined via the method described in Hoehler et al. (1994). These values were used to calculate methane oxidation rates (MOR) as follows:

$$\text{MOR} = [\text{CH}_4] \cdot \frac{\alpha}{t} \cdot \frac{^{14}\text{CO}_2}{^{14}\text{CH}_4},$$

where α is the kinetic isotope fractionation factor (^{14}C vs. ^{12}C) observed for methane oxidation (assumed to be 1.02; Alperin et al., 1988); t is the incubation time; and $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ are recovered radioactivities.

RESULTS

Concentration and Isotopic Composition of Methane

Pore-water methane concentrations measured for Hole 995B (Table 1) are plotted in Figure 1, along with pore-water sulfate concentrations from Holes 994B and 995B obtained shipboard (Paull, Matsumoto, Wallace, et al., 1996). The methane concentration profile displays the concave-up curve shape typical of marine sediments, though on a depth scale 10–100 times greater than is generally observed in coastal sediments. The upward concavity is consistent with methane consumption in a depth interval near 21–22 mbsf. Inverse numerical advection-diffusion-reaction modeling (Berner, 1980) of the profile in this region (described by Borowski et al., Chap. 9, this

volume) predicts a peak methane oxidation rate of about 13 nM-d⁻¹ (Fig. 2). The zone of apparent methane oxidation is coincident with the region in which sulfate and methane co-occur, suggesting the process is closely coupled to sulfate reduction. This is consistent with an apparent link between the two processes observed in a number of coastal marine sediments (Alperin and Reeburgh, 1984; Devol, 1983; Hoehler et al., 1994; Iversen and Jørgensen, 1985; Reeburgh, 1980).

The behavior of methane stable carbon isotopes in sediments from Hole 995B (Table 1; Fig. 3) also suggests that AMO is occurring near the sulfate depletion depth. Methane is most depleted in ^{13}C (lightest) at 21.45 mbsf. Above this depth, the methane becomes increasingly enriched in ^{13}C (heavier), suggesting preferential consumption of $^{12}\text{CH}_4$ as methane diffuses up towards the sediment-water interface. This trend is consistent with kinetic isotope fractionation during methane oxidation (Alperin et al., 1988; Oremland and DesMarais, 1983; Whiticar and Faber, 1986).

Theoretically, the trend towards heavier methane $\delta^{13}\text{C}$ should begin at the base of the methane-oxidizing zone. Hence, the isotopic evidence suggests that methane oxidation occurs down to a depth of 21.45 mbsf, while the model predicts an AMO zone that extends about 60 cm deeper. This discrepancy may result from “smoothing” the cubic spline fit used in the model (Borowski et al., Chap. 9, this volume). It is interesting to note in this context, however, that measured sulfate reduction rates are consistent with an AMO zone that closely matches that predicted by the model (as described below and in Fig. 4).

Sulfate Reduction Rates

Tracer-based sulfate reduction rates measured in sediments from Holes 994B and 995B (Table 2; Fig. 4) have two clear features.

First, sulfate reduction occurs at clearly discernible rates in the upper portion of the sediment column. These rates decrease with depth, reaching near-baseline levels below 10 mbsf (Fig. 4A). This is consistent with organic matter-fueled sulfate reduction, which slows as the sediments become increasingly depleted in utilizable organic matter (with increasing depth).

Second, a subsurface maximum in sulfate reduction rates is evident in the apparent zone of methane oxidation. The pore-water chemistry in Holes 994B and 995B is quite comparable, as evidenced by similar sulfate concentration profiles (Fig. 1). Hence, sulfate reduction rates in sediments from Hole 994B may be compared to the modeled methane oxidation rates in Hole 995B with relative confidence. The penetration of sulfate in Hole 994B may be deeper than in Hole 995B by a few tens of centimeters (Fig. 1), so it is possible that other features of the pore-water chemistry (e.g., methane oxidation) are likewise offset. In sediments from Hole 995B, the subsurface peak in sulfate reduction occurred at 21.13 mbsf, whereas the model predicts a peak in methane oxidation at 21.22 mbsf (Fig. 4B). In Hole

Table 1. Concentration and isotopic composition of pore-water methane at Site 995B.

Core, section	Interval (cm)	Depth (mbsf)	CH ₄ conc. (μM)*	CH ₄ conc. (μM)†	δ ¹³ CH ₄ (‰ vs. PDB)*	δ ¹³ CH ₄ (‰ vs. PDB)†
164-995B-						
1H-3	66-76	3.685	7.5	8.2	-62.4	-64.1
2H-1	122-132	17.245	6.0	6.3	-79.3	-80.6
2H-3	100-110	20.025	16.2	15.9	-93.3	-92.9
2H-3	120-130	20.225	17.2	17.7	-93.9	-93.4
2H-4	10-20	20.625	18.6	17.0	-95.4	-95.5
2H-4	30-40	20.825	16.2	19.5	-80.1	-89.4
2H-4	72-82	21.245	52.8	56.0	-98.5	-99.8
2H-4	92-102	21.445	103.2	105.3	-101.1	-101.3
2H-4	122-132	21.745	180.4	173.9	-97.5	-98.0
2H-5	10-20	22.125	281.2	267.6	-93.4	-93.4
2H-5	30-40	22.325	372.8	362.0	-92.3	-92.4
2H-5	60-70	22.625	428.5	413.9	-90.3	-90.8
2H-5	80-90	22.825	453.2	431.7	-90.7	-90.6

Notes: Conc. = concentration. * and † represent two different samples from the same depth interval.

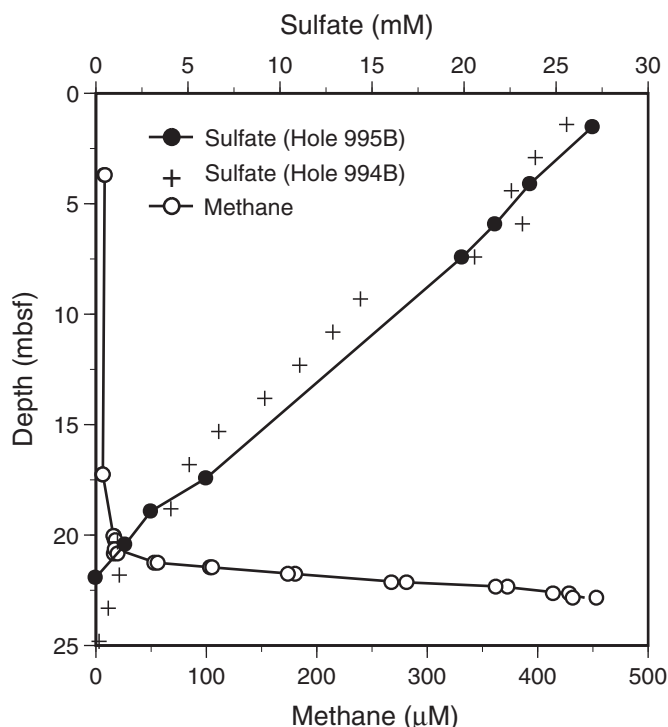


Figure 1. Pore-water concentrations of methane and sulfate vs. depth in Hole 995B. Sulfate concentrations from Hole 994B are also plotted to show that the two sites are comparable with respect to the depth of sulfate depletion. Note the upward concavity of the methane concentration profile (indicating methane consumption) near the base of the sulfate-containing zone. Sulfate concentration data are from Paull, Matsumoto, Wallace, et al. (1996).

994B, this sulfate reducing zone is offset by ~ 0.2 m (deeper in the sediment column) relative to the model-predicted zone in Hole 995B. Interestingly, the subsurface sulfate reducing zone in Hole 994B spans a depth (~ 2 m) that is quite similar to the model-predicted AMO zone in Hole 995B (1.85 m).

The highest sulfate reduction rate within the secondary maximum in Hole 995B is approximately twice the maximum model-predicted rate (Fig. 4B). The integrated sulfate reduction rate over the entire 2-m span of the subsurface maximum (pooling the data from Holes 994B and 995B) is quite comparable to the integrated model-derived methane oxidation rate, at approximately 1.3 and 1.1 $\text{nmol}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, respectively. Given the uncertainty in the tracer-based sulfate reduction rates, the close agreement between these values may be largely fortuitous, but it is probably not unreasonable to suggest that they agree within a factor of 2–3.

The integrated sulfate reduction rate at the top of the core is substantially higher than in the subsurface maximum. A minimum estimate, based on the few available data points, is ~ 40 $\text{nmol}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, roughly 30-fold higher than the quantity of sulfate apparently used to oxidize methane.

Tracer-Based Methane Oxidation Rates

The samples incubated with $^{14}\text{CH}_4$ did not produce $^{14}\text{CO}_2$ at significant levels. This is likely due to a combination of very low in situ AMO rates (model-predicted rates are 1–2 orders of magnitude lower than rates previously measured in coastal sediments) and an inadequate tracer activity. The detection limit for methane oxidation rates can be calculated given the activity of the tracer, the procedural blank for the overall rate measurement, and the in situ methane concentra-

tion. This limit was above the model-predicted rates for Hole 995B (Fig. 2A). Hence, the lack of measurable methane oxidation rates should not be taken to indicate a lack of activity; rather, this can be viewed as setting an upper limit on methane oxidation rates that corresponds to the detection limit for the process.

DISCUSSION

The results provide three independent forms of evidence to indicate the occurrence of anaerobic methane oxidation: diagenetic modeling, stable isotope, and radiotracer. Each of these places the zone of methane oxidation in an ~ 2 -m interval that coincides with the overlap of sulfate- and methane-containing pore waters. Further, the model-predicted methane oxidation and tracer-based sulfate reduction rates suggest a similar magnitude for AMO rates.

In a qualitative sense, the behavior of methane oxidation in Blake Ridge sediments is very similar to what has previously been observed for nearshore environments; however the absolute scale on which the process occurs differs markedly. Where methane oxidation has previously been characterized in sediment environments, it generally occurs within a zone of, at most, a few tens of centimeters in thickness and at depths seldom greater than 2 mbsf (Alperin and Reeburgh, 1984; Devol, 1983; Hoehler et al., 1994; Iversen and Jørgensen, 1985; Reeburgh, 1980). In the Blake Ridge sediments, the AMO zone itself spans nearly 2 m and is located more than 20 mbsf. In addition, the methane oxidation rates (suggested by the model and measured sulfate reduction rates) are 2–3 orders of magnitude lower than in most coastal settings. Effectively, methane oxidation in Blake Ridge sediments is “stretched out” relative to nearshore environments.

The “stretching out” is characteristic of the entire process of organic matter remineralization, as illustrated by a simple comparison. In organic-rich sediments from nearshore Cape Lookout Bight, North Carolina (which has among the highest rates of overall remineralization reported for marine sediments), sulfate reduction rates as high as 2000 $\mu\text{M}\cdot\text{d}^{-1}$ (Crill and Martens, 1987) lead to sulfate depletion within 10 cm of the sediment-water interface (Martens and Klump, 1980). Sulfate-coupled methane oxidation at this site is limited to a zone of 5–10 cm (Hoehler et al., 1994). In the more oligotrophic Blake Ridge sediments, measured sulfate reduction rates near the sediment-water interface are four orders of magnitude lower than in Cape Lookout Bight, permitting penetration of sulfate to 20 mbsf (deeper by two orders of magnitude). The AMO in Blake Ridge sediments occurs at rates 2 orders of magnitude lower than in Cape Lookout and over a 20-fold broader zone.

The presence of measurable sulfate reduction in the upper portion of the sediment column at Site 994B brings to light an interesting discrepancy. Borowski et al. (1996) note that pore-water sulfate concentrations in the sediments of this region typically exhibit a linear decrease with depth and suggest that this indicates a lack of organic matter-driven sulfate reduction. Similar geochemistry was recently observed in sediments of the upwelling region off western Africa (Niewöhner et al., 1998). To reconcile these observations with the measured sulfate reduction rates, it is critical to note that linear sulfate concentration profiles can only demonstrate a lack of *net* sulfate reduction. It has been repeatedly shown that sulfides resulting from sulfate reduction can be reoxidized to sulfate in situ by ferric and manganic oxides (Aller and Rude, 1988; Fossing and Jørgensen, 1990; Sørensen and Jørgensen, 1987). If such a process occurred in the Blake Ridge sediments, any evidence of organic matter-driven sulfate reduction would be lost from the pore-water sulfate concentration profiles (because, in effect, no *net* reduction of sulfate has occurred if the sulfides are reoxidized).

In such a case, the consumption of sulfate via methane oxidation at depth might represent a much smaller fraction of the total sulfate reduction than suggested by pore-water concentration gradients

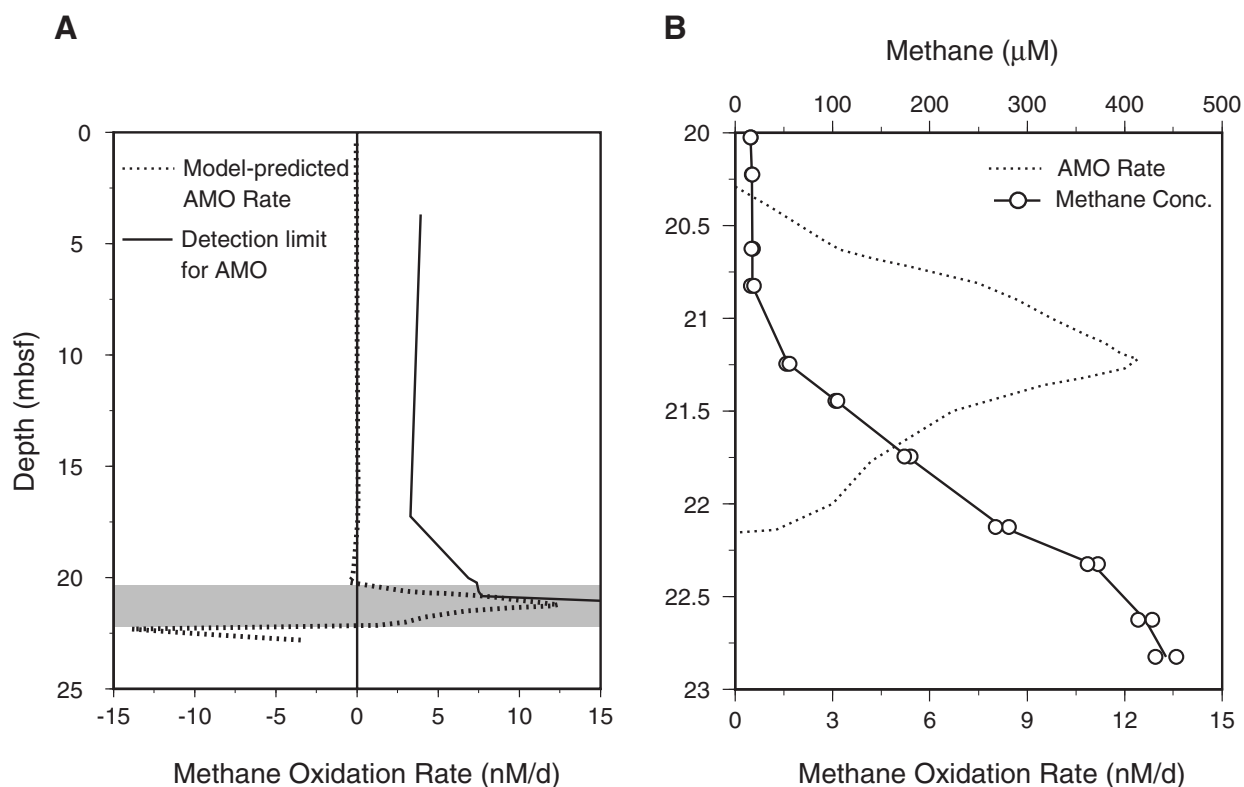


Figure 2. Rates of anaerobic methane oxidation vs. depth in sediments from Hole 995B. **A.** Methane oxidation rates derived from inverse numerical advection-diffusion-reaction modeling of the methane concentration profile, along with the calculated detection limit of the ^{14}C -tracer-based AMO rate measurement. Note that over the entire sediment column, the model predicts rates that are lower than or at the detection limit. Negative values for model-derived methane oxidation rates indicate methane production. **B.** Blow-up of the 20–23 mbsf depth interval showing the relationship of the model-derived AMO rates to the region of upward concavity in the methane concentration profile. The model and parameters are described in detail by Borowski et al. (Chap. 9, this volume). The shaded region in A is used to denote the depth interval over which the model predicts the occurrence of AMO, as applied in Figures 3 and 4. SR = sulfate reduction; AMO = anaerobic methane oxidation.

alone. Borowski et al. (Chap. 9, this volume) calculate methane and sulfate fluxes for Hole 995B based on pore-water concentration gradients. These calculations indicate that ~35% of the downward sulfate flux can be accounted for by upward diffusing methane. Measured sulfate reduction rates ascribe a lesser importance to methane oxidation: the depth-integrated sulfate reduction rate in the subsurface, AMO-associated zone (which is approximately equal to the integrated methane oxidation rate) is only about 2%–5% of the depth-integrated rate in the upper 10 m of the sediment column.

It is clearly reasonable to expect at least some organic matter-driven sulfate reduction in these sediments. Biogenic production of methane in the region immediately underlying the apparent AMO zone is indicated both by the diagenetic model (Fig. 2A) and by the extremely light (^{13}C -depleted) isotopic signature of methane in the depth interval surrounding the sulfate-methane transition depth (Fig. 3). The biogeochemical processes (i.e., fermentation of organic matter) that drive biogenic methane production will preferentially fuel sulfate reduction when sulfate is present (Lovley et al., 1982). Hence, the evidence of in situ biogenic methane formation in the sediments of Hole 995B indirectly suggests the occurrence of sulfate reduction in the upper 20 m of the sediment column.

A small contribution of AMO to *absolute* sulfate reduction rates does not necessarily imply a small contribution to *net* sulfate reduction rates. If the suggested metal-based oxidizing capacity of the sediments is exhausted at a depth shallower than the zone of methane oxidation, then AMO could in theory represent the entire contribution to *net* consumption of sulfate. In such a case, the upward flux of

methane would strongly influence the downward sulfate flux and corresponding sulfate concentration gradient, as proposed by Borowski et al. (1996).

SUMMARY

Anaerobic methane oxidation in Blake Ridge sediments overlying methane hydrates was characterized by three independent techniques. Pore-water methane concentration profiles from Hole 995B exhibit a region of upward concavity suggestive of methane consumption. Diagenetic modeling of the concentration profile indicates a 1.85-m-thick zone of AMO centered at 21.22 mbsf, with peak rate of $12.4 \text{ nM}\cdot\text{d}^{-1}$. The thickness and locality of the model-predicted AMO zone are corroborated by a subsurface maximum in sulfate reduction rates. Depth-integrated rates of methane oxidation and sulfate reduction in the model-predicted AMO zone compare favorably, suggesting that nearly all of the sulfate reduction in the subsurface maximum is fueled by AMO. Methane stable carbon isotope chemistry provides further evidence of AMO. Methane $\delta^{13}\text{C}$ values are lightest at the point of peak model-predicted methane oxidation and become increasingly ^{13}C enriched with decreasing sediment depth, consistent with kinetic isotope fractionation during methane oxidation. The isotopic evidence suggests the deepest occurrence of methane oxidation is about 60 cm shallower than that predicted by the model. The contribution of methane oxidation to the overall sulfate cycle in these sediments is difficult to assess; however, it is clear that

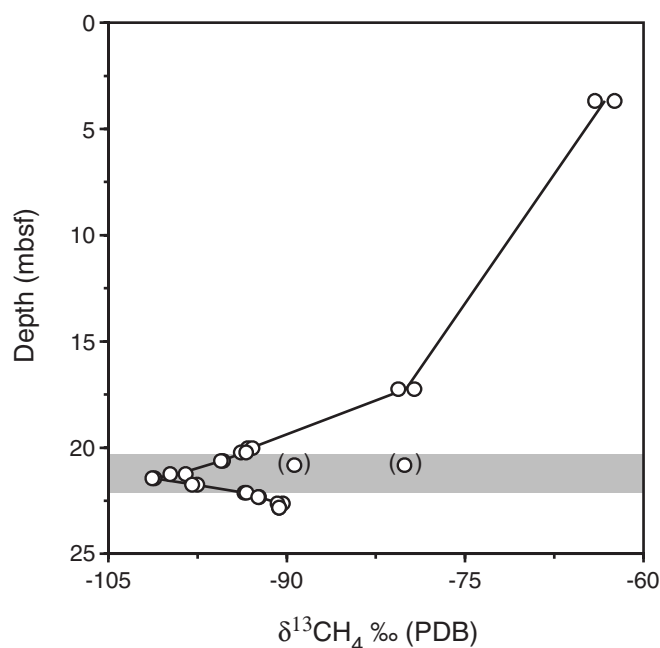


Figure 3. $\delta^{13}\text{CH}_4$ vs. depth in sediments from Hole 995B. The shaded region represents the model-predicted zone of anaerobic methane oxidation. The points in parentheses are duplicate samples that are part of the methane isotope data set. The large deviation between the two samples and from the general trend suggest an error that was introduced during sample processing or analysis rather than a real variation in the data. Lacking direct evidence of such a problem, however, the points are included but left off the trendline.

the process represents an essentially quantitative sink for upwardly diffusing methane.

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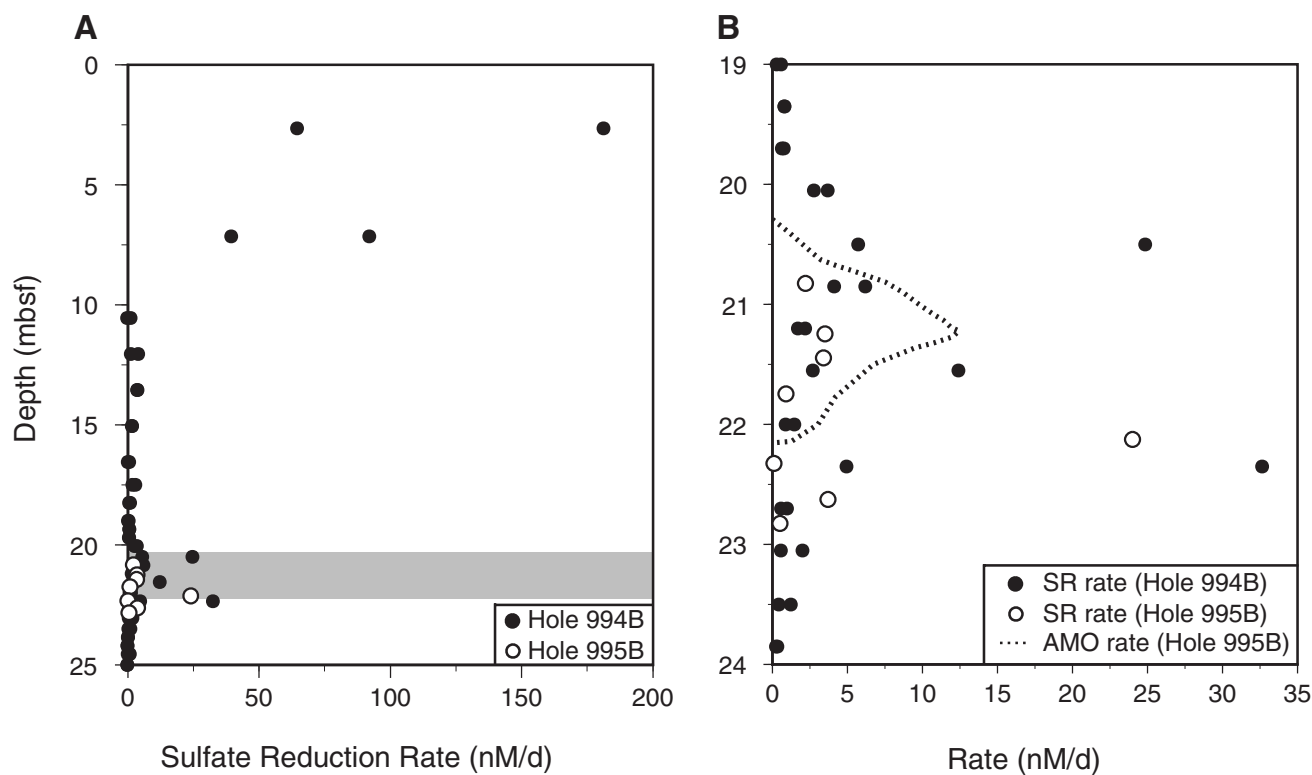


Figure 4. The relationship of sulfate reduction and methane oxidation. **A.** ^{35}S -tracer-based rates of sulfate reduction in sediments from Holes 994B and 995B. Note the subsurface maximum in rates that coincides with the model-predicted methane oxidation zone (shaded region). **B.** Blow-up of the 19–24 mbsf depth interval showing the relative localization and magnitude of measured sulfate reduction rates in Holes 994B and 995B to model-derived methane oxidation rates in Hole 995B. AMO = anaerobic methane oxidation.

Table 2. Sulfate reduction rates in Holes 994B and 995B.

Core, section	Interval (cm)	Depth (mbsf)	SRR (nM-d ⁻¹)*	SRR (nM-d ⁻¹)†
164-994B-				
1H-2	100-110	2.65	64.7	181.4
1H-5	100-110	7.15	39.6	92.2
2H-2	100-110	10.55	1.3	0
2H-3	100-110	12.05	1.4	4.2
2H-4	100-110	13.55	4.0	3.8
2H-5	100-110	15.05	3.8	1.8
2H-6	100-110	16.55	1.8	0.2
3H-1	10-20	17.5	0.2	2.0
3H-1	80-95	18.25	2.0	0.7
3H-2	10-25	19.0	0.7	0.3
3H-2	45-60	19.35	0.8	0.8
3H-2	80-95	19.7	0.8	0.7
3H-2	115-130	20.05	2.8	3.7
3H-3	10-25	20.5	5.8	24.9
3H-3	45-60	20.85	6.3	4.1
3H-3	80-95	21.2	1.7	2.2
3H-3	115-130	21.55	2.7	12.4
3H-4	10-25	22.0	0.9	1.5
3H-4	45-60	22.35	5.0	32.7
3H-4	80-95	22.7	1.0	0.6
3H-4	115-130	23.05	0.6	2.0
3H-5	10-25	23.5	1.3	0.5
3H-5	45-60	23.85	0.4	0.3
3H-5	80-95	24.2	0.1	0.2
3H-5	115-130	24.55	0.2	1.0
3H-6	10-25	25.0	0.1	0.1
3H-6	45-60	25.35	0.3	0.1
3H-6	80-95	25.7	0.1	0.6
164-995B-				
2H-4	30-40	20.825	2.2	
2H-4	72-82	21.245	3.5	
2H-4	92-102	21.445	3.4	
2H-4	122-132	21.745	0.9	
2H-5	10-20	22.125	23.9	
2H-5	30-40	22.325	0.2	
2H-5	60-70	22.625	3.7	
2H-5	80-90	22.825	0.5	

Notes: SRR = sulfate reduction rate. * and † represent two different samples from the same depth interval.