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7. Oxygen Isotope Composition of Dissolved Sulfate in Deep-Sea Sediments: Eastern Equatorial Pacific Ocean[1]

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ABSTRACT

High-resolution analyses of the oxygen isotope ratio ($^{18}O/^{16}O$) of dissolved sulfate in pore waters have been made to depths of >400 meters below seafloor (mbsf) at open-ocean and upwelling sites in the eastern equatorial Pacific Ocean. $\delta^{18}O$ values of dissolved sulfate ($\delta^{18}O$-SO_4) at the organic-poor open-ocean Site 1231 gave compositions close to modern seawater (+9.5‰ vs. Vienna-standard mean ocean water, providing no chemical or isotopic evidence for microbial sulfate reduction (MSR). In contrast, the maximum $\delta^{18}O$ values at Sites 1225 and 1226, which contain higher organic matter contents, are +20‰ and +28‰, respectively. Depth-correlative trends of increasing $\delta^{18}O$-SO_4, alkalinity, and ammonium and the presence of sulfide indicate significant oxidation of sedimentary organic matter by sulfate-reducing microbial populations at these sites. Although sulfate concentration profiles at Sites 1225 and 1231 both show similarly flat trends without significant net MSR, $\delta^{18}O$-SO_4 values at Site 1225 reveal the presence of significant microbial sulfur-cycling activity, which contrasts to Site 1231. This activity may include contributions from several processes, including enzyme-catalyzed equilibration between oxygen in sulfate and water superimposed upon bacterial sulfate reduction, which would tend to shift $\delta^{18}O$-SO_4 toward higher values than MSR alone, and sulfide oxidation, possibly coupled to reduction of Fe and Mn oxides and/or bacterial disproportionation of sulfur intermediates. Large isotope enrichment factors

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observed at Sites 1225 and 1226 (ε values between 42‰ and 79‰) likely reflect concurrent processes of kinetic isotope fractionation, equilibrium fractionation between sulfate and water, and sulfide oxidation at low rates of sulfate reduction. The oxygen isotope ratio of dissolved pore water sulfate is a powerful tool for tracing microbial activity and sulfur cycling by the deep biosphere of deep-sea sediments.

INTRODUCTION

Cycling of sulfur compounds is a ubiquitous process in marine sediments that supports a range of microbial metabolic strategies. The occurrence of sulfur over a wide range of oxidation states (–2 to +6) allows sulfur species to serve as both electron acceptors and electron donors. In reduced form as sulfide ($\Sigma H_2S = H_2S_{(aq)} + HS^-$), sulfur is also an important sink for reactive iron (Berner, 1971; Goldhaber and Kaplan, 1974). The reduction of sulfate to sulfide is by far the most important pathway for sedimentary organic matter oxidation in anoxic marine sediments, and there is increasing evidence that anaerobic oxidation of methane controls microbial sulfate reduction (MSR) in many marine systems (Niewöhner et al., 1998; Aharon and Fu, 2000; Hensen et al., 2003; D'Hondt, Jørgensen, Miller, et al., 2003).

The stable isotope ratios of oxygen ($^{18}O/^{16}O$) and sulfur ($^{34}S/^{32}S$) in dissolved sulfate may provide information about specific biogeochemical pathways for sulfur in marine sediments, such as bacterial sulfate reduction, sulfide oxidation, sulfur disproportionation, and transport processes of sulfur species (Rees, 1973; Goldhaber and Kaplan, 1980; Zak et al., 1980; Canfield et al., 1998; Böttcher et al., 1998a, 1998b, 1999, 2001, 2004; Jørgensen et al., 2004; Brunner et al., 2005). Sulfate containing the lighter isotope ^{32}S is utilized preferentially during MSR, resulting in an enrichment of ^{34}S in the residual pore water sulfate. In seawater-derived pore waters, an enrichment of ^{18}O is also observed during ongoing MSR (Zak et al., 1980; Böttcher et al., 1998a, 1998b, 1999, 2004). The magnitudes of isotope fractionation accompanying MSR and the degree of heavy isotope enrichment in residual sulfate seem to depend on a number of environmental factors, including temperature, sulfate concentration, microbial community composition, the rate of sulfate reduction, and the type and amount of sedimentary organic matter being oxidized (Jørgensen, 1979; Berner, 1980; Boudreau and Westrich, 1984; Aharon and Fu, 2000). Isotopic fractionation of oxygen and sulfur in residual sulfate during MSR has been measured in pure laboratory cultures, sediment incubations, and natural systems and ranges from 4‰ to 29‰ for oxygen and from 4‰ to 46‰ for sulfur (e.g., Kaplan et al., 1963; Lloyd, 1967, 1968; Kemp and Thode, 1968; Mizutani and Rafter, 1973; Chambers and Trudinger, 1979; Fritz et al., 1989; Ku et al., 1999; Böttcher et al. 2001; Aharon and Fu, 2000; Mandernack et al., 2003). Whereas sulfur isotope fractionation upon dissimilatory sulfate reduction is usually interpreted as primarily kinetic in nature (e.g., Kaplan and Rittenberg, 1964; Rees, 1973), an intracellular isotope exchange between water and sulfur intermediates is proposed to lead to a partial oxygen isotope exchange between overall extracellular sulfate and pore waters (Fritz et al., 1989; Böttcher et al., 1998a, 1999; Aharon and Fu, 2000). Under oxygen isotope exchange equilibrium conditions, dissolved sulfate should be enriched in ^{18}O compared to Vienna-standard mean ocean water (V-SMOW) by more than 30‰ (Böttcher et al., 1998a).

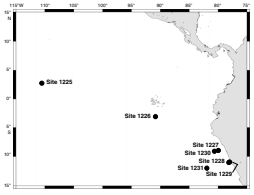
Much of the sulfide produced during dissimilatory MSR in marine sediments is oxidized back to sulfate by a variety of biological and abiotic pathways (Jørgensen, 1990; Goldhaber and Kaplan, 1980; van Stempvoort and Krouse, 1994; Canfield and Thamdrup, 1994; Böttcher and Thamdrup, 2001), and sulfate produced by oxidation of sulfide may have variable $\delta^{18}O$ values reflecting the nature and complexity of the abiotic and biological oxidation pathways and relative contributions from different oxidants (water and dissolved oxygen) (Taylor et al., 1984; Böttcher et al., 2001; Brunner et al., 2005). These pathways often include the production of intermediate sulfur species such as elemental sulfur and thiosulfate, which can undergo further bacterial disproportionation reactions that may lead to further fractionations of both sulfur and oxygen isotopes in secondary sulfate (Canfield and Thamdrup, 1994; Canfield et al., 1998; Cypionka et al., 1998; Habicht et al., 1998; Böttcher et al., 2001, 2004; Böttcher and Thamdrup, 2001). Under circumneutral and low-temperature sedimentary conditions, an abiotic oxygen isotope exchange between water and sulfate does not take place (Lloyd, 1967, 1968; Zak et al., 1980). Therefore, changes in $\delta^{18}O$ values of sulfate under anoxic conditions provide clear evidence for the enzyme-catalyzed processes. Thus, the stable isotope ratio of oxygen in dissolved sulfate may be a valuable indicator for tracing microbial activity and sulfur transformations by a deep biosphere in marine sediments.

Only a few studies on marine pore water systems have included the analysis of the stable oxygen isotopic composition of dissolved sulfate to date (Zak et al., 1980; Böttcher et al., 1998a, 1998b, 1999; Bottrell et al., 2000), and most have focused on shallow pore water systems (Pierre, 1985; Böttcher et al., 1998b; Ku et al., 1999; Aharon and Fu, 2000). The sites drilled during Ocean Drilling Program (ODP) Leg 201 provide a unique opportunity to study oxygen isotope fractionation by the deep biosphere in pore waters of deep sediment sections averaging several hundred and as much as ~400 meters below sea floor (mbsf) and cover a wide range of water depths and sedimentary conditions (e.g., organic carbon content and sedimentation rate).

GEOLOGIC SETTING

Leg 201 was the first ODP leg devoted exclusively to the characterization of microbial communities in the deep biosphere of marine sediments. Seven drilling sites in the eastern equatorial Pacific Ocean and along the Peru continental margin (Fig. F1) were targeted to cover a broad spectrum of electron acceptor, electron donor, organic substrate, and sedimentary conditions, including sites with and without methane hydrate. Previously drilled sites (Deep Sea Drilling Project and ODP Sites 321, 846, and 851) located near the targeted sites provided baseline data for interstitial water chemistry, lithology, and sediment properties. Data reported here are from one open-ocean site (1231) and two equatorial upwelling sites (1225 and 1226) that are characterized by relatively low total organic carbon content (0%–0.9%) and moderate to low rates of sediment accumulation (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004). Previous geochemical studies indicate that modern seawater flows through the basaltic basement underlying all three of the sites (Baker et al., 1991; Oyun et al., 1995). Sediments at the sites comprise variable mixtures of primarily nannofossil and diatom oozes with volcanic glass and hydrothermal input at Site 1231.

F1. Study sites, p. 14.



Sediments at Site 1225 (Site 851) were deposited on ~11-Ma basaltic crust in a relatively high productivity region between the South Equatorial Current and the North Equatorial Counter Current. This site is located at 3760 m water depth and is representative of the eastern equatorial region. Site 1226 (Site 846) is ~2300 km east-southeast of Site 1225 and 300 km south of the Galapagos Islands. This site is influenced by the South Equatorial and Peru currents and overlies ~16.5-Ma basement at 3297 m water depth. Open-ocean Site 1231 (Site 321) is located at 4827 m water depth in the Peru Basin. The Pleistocene- to Eocene-aged organic-poor sediments at Site 1231 are representative of most of the world ocean (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004).

METHODS

Interstitial water was squeezed from 645 whole-round cores immediately after core retrieval using hydraulic pressure and standard ODP titanium-stainless steel squeezers (Manheim and Sayles, 1974). Pore waters were filtered (0.45 µm) and subsequently analyzed for concentrations of major and minor dissolved components, including sulfate, chloride, sulfide, alkalinity, and nutrients (ammonium, phosphate, and nitrate) on board the *JOIDES Resolution* (D'Hondt, Jørgensen, Miller, et al., 2003) using standard ODP methods (Gieskes et al., 1991). From 112 of the 645 samples, ~10 mL of filtered pore water was immediately fixed with zinc acetate to precipitate zinc sulfide and to prevent artifactual oxidation of sulfide to sulfate. Following gravity settling of zinc sulfide over several days, ~5 mL of the supernatant containing dissolved sulfate was transferred to high-density polyethylene containers and stored at 4°C for subsequent shore-based analyses of oxygen (this study) and sulfur (**Böttcher et al.,** this volume) isotopic composition of dissolved sulfate.

Dissolved sulfate was precipitated quantitatively as barium sulfate according to standard gravimetric procedures (Clesceri et al., 1989). Briefly, 10% barium chloride solution was added to diluted pore water samples that were acidified to ~pH 4 to preclude formation of barium carbonate. Precipitated barium sulfate was filtered (0.2 µm), washed, and dried. Dried barium sulfate samples were thoroughly homogenized and ~5–10 mg of sample was loaded into a quartz vessel and baked at 650°–700°C for 1 hr to remove residual water and organic matter from the barium sulfate crystals. Next, 150 µg of sample was loaded into a 3.5 mm × 5 mm pressed silver foil capsule and placed in a Costech Zero-Blank autosampler for oxygen isotope analysis using a Finnigan Delta^{plus}XP with TC/EA module (High Temperature Conversion) and Conflo III interface operating in continuous-flow mode (Earth System Center for Stable Isotope Studies of the Yale Institute for Biospheric Studies, USA). Barium sulfate samples are reacted at 1450°C in a graphite reactor crucible to release oxygen, which in turn reacts with the graphite to produce carbon monoxide (CO) (Kornexl et al., 1999). The CO is entrained in He carrier gas, passed through a gas chromatograph, and introduced into the mass spectrometer. Oxygen isotope ratios were determined by integrating the areas under CO peaks of masses m/z 28, 29, and 30. All oxygen isotope data are reported as δ-values in permil and referenced to the V-SMOW standard. Two internal laboratory $BaSO_4$ standards with $\delta^{18}O$ values of +0.1‰ and +16.9‰ and the International Atomic Energy Agency-National Bureau of Standards 127

$BaSO_4$ standard ($\delta^{18}O$ = +9.3‰) were used for data calibration and correction. The precision of the method based on replicate measurement of standards is ±0.5‰.

RESULTS AND DISCUSSION

Pore water $\delta^{18}O$-SO_4 values determined for Sites 1225, 1226, and 1231 are shown in Tables **T1, T2,** and **T3** along with concentrations of dissolved sulfate, ammonium, sulfide, alkalinity, and metals. Methane was present at all of the sites, but only at low- to near trace-level amounts (<0.25 µM). The approach to normal seawater sulfate concentrations at depth is observed at all three of the sites, consistent with previous reports of basin-scale flow of modern seawater through basement and upward into the base of the sediment column (Baker et al., 1991; Oyun et al., 1995).

T1. Isotope data, Site 1231, p. 21.

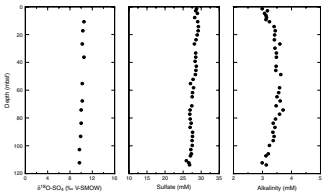
T2. Isotope data, Site 1225, p. 22.

T3. Isotope data, Site 1226, p. 23.

Peru Basin Site 1231

Site 1231 is the most organic carbon poor of all the Leg 201 sites and had the lowest measured microbial activity (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004). As expected, Site 1231 also shows the smallest changes in concentration of dissolved constituents and $\delta^{18}O$-SO_4 values (Table **T1;** Fig. **F2**). Pore water sulfate concentrations decreased only slightly with depth, ranging from near bottom water values of ~29 mM over the uppermost 48-m interval, to ~27 mM over the lower 60-m interval of the core (Fig. **F2**). This slight decrease in sulfate concentration with depth may suggest some small amount of sulfate-reducing activity; however, sulfide ($\Sigma H_2S = H_2S_{(aq)} + HS^-$) was below detection limits (0.0002 mM) in pore waters at Site 1231. $\delta^{18}O$ values of dissolved sulfate at Site 1231 remained essentially constant with depth (Fig. **F2**) and averaged about +10‰. These values are close to the currently accepted seawater value of +9.5‰ (Longinelli and Craig, 1967; Longinelli, 1989). Variations in alkalinity and ammonium concentrations with depth (Fig. **F2**) are attributed to chemical exchange processes (i.e., sinks) at both the sediment/seawater and sediment/basement interface (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004). The isotopic composition of sulfur in dissolved sulfate ($\delta^{34}S$-SO_4) at this site also reflects pore waters that are isotopically unmodified by MSR (**Böttcher et al.,** this volume). Thus, several lines of chemical and stable isotopic evidence—sulfate and sulfide concentrations and $\delta^{18}O$-SO_4—clearly point to the absence of sulfate-reducing activity at open-ocean Site 1231.

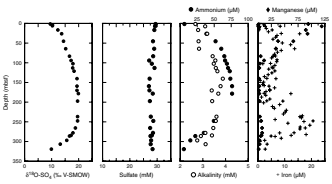
F2. Pore water profiles, Site 1231, p. 15.



Equatorial Upwelling Site 1225

There is chemical and isotopic evidence for increased microbial activity at Site 1225 when compared to Site 1231 that is consistent with the abundance of higher amounts of organic matter found at this higher-bioproductivity site (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004). Pore water sulfate concentrations decrease with depth from ~29 mM at 7.3 mbsf to a minimum of 27 mM at 159.3 mbsf, then rise again to 28 mM at the sediment/basement interface near 319 mbsf (Fig. **F3**). $\delta^{18}O$-SO_4 values increase gradually with depth from +9.5‰ at 1.5 mbsf to a plateau of +20‰ between ~178 and 250 mbsf, indicating

F3. Pore water profiles, Site 1225, p. 16.



significant activity of sulfate-reducing bacteria (Table T2; Fig. F3). Below this plateau, $\delta^{18}O\text{-}SO_4$ values decrease more rapidly with depth and approach a normal seawater value (+9.9‰) at ~319 mbsf. The sulfate concentration profile mirrors the $\delta^{18}O\text{-}SO_4$ vs. depth profile in its overall shape, and the maximum $\delta^{18}O\text{-}SO_4$ plateau coincides with the zone of minimum sulfate concentration (~27 mM). The return of $\delta^{18}O\text{-}SO_4$ values and pore water sulfate concentrations to normal seawater values at the base of the sediment column further supports previous findings that indicate the flow of modern seawater through underlying basaltic basement rocks in the eastern equatorial region.

Although high $\delta^{18}O\text{-}SO_4$ values (as high as +20‰) are a strong indication of MSR at Site 1225, pore water sulfate concentration and alkalinity vs. depth profiles at this site are nearly identical to those at the low-activity open-ocean Site 1231, which had typical seawater $\delta^{18}O\text{-}SO_4$ values and showed no evidence of MSR.

The process of dissimilatory MSR should result in increased concentrations of sulfide, bicarbonate (i.e., alkalinity; Equation 1), and products of organic matter degradation such as ammonium.

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S. \quad (1)$$

Alkalinity increased very little with depth from normal seawater values (~3–4 mM); however, ammonium concentrations increased from 6 µM at 1.5 mbsf to a maximum of 76 µM at 159 mbsf, which is twice the maximum value observed at Site 1231 (Table T2; Fig. F2). One explanation for the difference in $\delta^{18}O\text{-}SO_4$ behavior at Sites 1225 and 1231, despite similar sulfate and alkalinity profiles, is that sulfide produced from MSR at Site 1225 has been oxidized completely back to sulfate without diffusional loss of sulfide. This would result in diminished net reduction in the concentration of pore water sulfate (Ku et al., 1999). Dissolved sulfide was below detection at Site 1225, which supports its removal by iron sulfide formation, sulfide oxidation, and/or some alternative process occurring within the sediments at this site. However, sulfur isotope discrimination in dissolved residual sulfate is consistent with minor net MSR taking place in the pore waters at Site 1225 (**Böttcher et al.,** this volume).

The oxygen in sulfate produced by oxidation of sulfide may be acquired from dissolved oxygen, water, or a mixture of the two, depending on the oxidation pathway (biotic vs. abiotic) and superimposed by contributions from intermediate processes of sulfur disproportionation, which in turn may depend on the involvement of reactive mineral oxidants (e.g., Fe or Mn oxides) present in the sediments (Taylor et al., 1984; van Stempvoort and Krouse, 1994; Böttcher et al., 2001, 2004; Böttcher and Thamdrup, 2001). The $\delta^{18}O$ values of sulfate derived from sulfide oxidation depend further on the fractionation of oxygen isotopes between sulfate and the oxidant source (i.e., water or O_2) (Taylor et al., 1984; van Stempvoort and Krouse, 1994). Controlled experiments on the oxidation of various sulfur compounds (e.g., elemental sulfur, sulfite, and pyrite) indicate that water is the dominant source of oxygen in sulfate derived from oxidation of sulfide and elemental sulfur (van Stempvoort and Krouse, 1994; Böttcher et al., 2001, 2004; M. Böttcher and A. Schippers, unpubl. data).

Dissolved sulfate $\delta^{18}O$ values at Site 1225 seem to reflect a mixture of sulfate contributed from several different sources/processes, including sulfate diffusing upward from the sediment/basement interface and

downward from the sediment/water interface, residual sulfate remaining after MSR, sulfate derived from sulfide oxidation, and sulfate that has undergone enzyme-catalyzed exchange with ambient pore water. Sulfate diffusing into the sediment column from either above or below is derived from normal seawater and, thus, has a $\delta^{18}O$ value of about +9.5‰ (Fig. **F3**). The $\delta^{18}O$ value of residual sulfate following MSR is determined by the fractionation during MSR. Apparent fractionation factors, α, for oxygen isotopes in sulfate have been determined for pure cultures of sulfate-reducing bacteria and from enrichments of marine sediments (e.g., Kemp and Thode, 1968; Mizutani and Rafter, 1973; Ku et al., 1999; M.E. Böttcher and J. Detmers, unpubl. data, 2001; M.E. Böttcher, J. Benecke, and H. Cypionka, unpubl. data). The oxygen isotope fractionation factor is estimated in the present study assuming a closed system and using a simplified Rayleigh equation (Rayleigh, 1896; Mizutani and Rafter, 1973; Goldhaber and Kaplan, 1974; Aharon and Fu, 2000)

$$\Delta\delta = \delta_t - \delta_0 = 10^3(\alpha - 1)\ln(f), \quad (2)$$

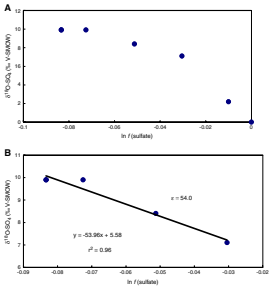
where

δ_t = $\delta^{18}O$ value of residual sulfate at time t,
δ_0 = initial $\delta^{18}O$ value of sulfate before any MSR, and
f = fraction of sulfate remaining at time t (f = 1 at t = 0).

The apparent fractionation is obtained from the slope of this equation, $10^3(\alpha - 1)$, which is expressed in terms of the isotope enrichment factor, ε (in permil).

Data from the upper 170-m zone of Site 1225, plotted according to Equation 2, show nonlinear behavior that suggests variable fractionations and that more than simple MSR is affecting $\delta^{18}O$-SO_4 values at this site (Fig. **F4A**). The ε-SO_4 determined for this zone is +54‰ (Fig. **F4B**), which is significantly larger than previously reported ε-SO_4 for MSR of +4‰ to +29‰ (e.g., Lloyd, 1967; Fritz et al., 1989). The multiple and potentially complex pathways for sulfide oxidation (e.g., Böttcher et al., 2001) make it difficult to constrain ε-SO_4. Accordingly, very few values for ε-SO_4 have been reported in the literature (Ku et al., 1999; Aharon and Fu, 2000), and to date none have been determined for sediment depths >50 mbsf. The total range of reported ε-SO_4 is –8.7‰ to +29‰ and includes biotic and abiotic pathways for oxidation of sulfide, sulfite, and elemental sulfur, using both water and dissolved oxygen as the oxygen source (van Stempvoort and Krouse, 1994; Ku et al., 1999; Aharon and Fu, 2000; Böttcher et al., 2001, 2004; Böttcher and Thamdrup, 2001). The ε-SO_4 determined for Site 1225 (+54‰) is higher than previously reported values by almost more than a factor of two. This very steep slope (+54‰) is accompanied by a small amount (~2 mM) of net sulfate removal (i.e., high f [sulfate] values) and further supports the occurrence of sulfide oxidation at this site as an explanation for both the heavy sulfate $\delta^{18}O$ values and the relative lack of change in sulfate concentration. The present results make clear that no constant apparent fractionation factor exists and that specific sets of biogeochemical conditions may be superimposed to produce different relations between the oxygen isotope composition of dissolved sulfate and net sulfate reduction.

F4. Isotopic fractionation, p. 17.



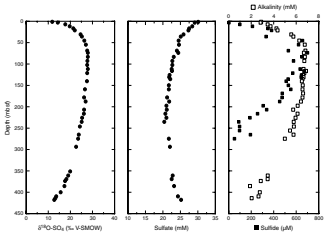
Several potential oxidants for sulfide are present in both the upper and lower regions of the sediment column at Site 1225 and include iron, manganese, nitrate, and dissolved oxygen. These oxidants may form an upper and lower oxidizing boundary for sulfide diffusing away from the MSR zone. For example, there is a broad peak in the concentration of dissolved iron (Fe^{2+}) between 175 and 275 mbsf, which coincides with the zone of maximum $\delta^{18}O\text{-}SO_4$ and, presumably, maximum MSR, and a less pronounced peak centered at ~20 mbsf (Fig. F3). Sulfide produced from MSR may have reduced sedimentary reactive Fe^{3+} oxide phases to Fe^{2+}, which subsequently removed additional sulfide (not detected at Site 1225) as iron-sulfide phases. There is also a large peak in dissolved Mn between 1.5 and 64.3 mbsf and a smaller peak below the MSR zone between ~237 and 278 mbsf that could have served as a reaction sink for sulfide at this site (Fig. F3).

A quantitative evaluation of the results is complicated by the fact that sulfate reduction in the deep sediments takes place under partly open conditions (**Böttcher et al.,** this volume), with sulfate diffusing from the top and the base into the sediment section. The downcore trend in oxygen isotope values is also consistent with an enzymatically catalyzed isotope exchange upon bacterial sulfate reduction, finally leading to an isotopic equilibration. The observed enrichment of the heavy oxygen isotope, however, is of unusual magnitude when compared to the small net amount of sulfate reduced. This may be explained by a superimposition of MSR by disproportionation processes that are associated with an enrichment of ^{18}O in the secondary sulfate formed (Böttcher et al., 2001). A second explanation has been introduced by Böttcher et al. (1998a), who suggested that the relative degree of oxygen isotope equilibration may be controlled by microbial sulfate reduction rates. Therefore, at lower cellular rates, more time is provided for intracellular oxygen isotope exchange. Maximum oxygen isotope values of sulfate are still below the exchange equilibrium values (Fritz et al., 1989; Böttcher et al., 1998a) expected at maximum temperatures of 7°C observed at Site 1225 (D'Hondt, Jørgensen, Miller, et al., 2003). This indicates that the low MSRs, mixing of sulfate from different extents of equilibration, and/or sulfide oxidation did not lead to complete stable isotope exchange equilibrium. However, the observed oxygen isotope data make it possible to clearly distinguish the activity of the biosphere in the deep sulfur cycles of Sites 1225 and 1231.

Equatorial Upwelling Site 1226

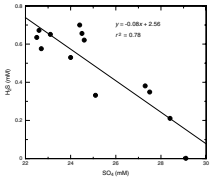
Site 1226 is the most organic rich of the eastern equatorial Pacific sites and is also located at the shallowest water depth (3297 m). Pore water $\delta^{18}O\text{-}SO_4$ and sulfate concentration profiles are clearly more influenced by sulfate reduction at this site (Table T3; Fig. F5). $\delta^{18}O\text{-}SO_4$ values increase with depth from +11.8‰ at 1.3 mbsf to a plateau of +28‰ between ~70 and 140 mbsf, and then decline toward the bottom of the hole due to introduction of seawater that flows through the underlying basaltic basement without obvious modification by bacterial sulfate reduction. $\delta^{18}O\text{-}SO_4$ values reach +12.7‰ at the maximum depth drilled of 418 mbsf (Fig. F5). Higher maximum $\delta^{18}O\text{-}SO_4$ values at Site 1226 compared with Site 1225 are consistent with greater extents of MSR at Site 1226 facilitated by a higher amount of sedimentary organic matter. Dissolved sulfate concentrations generally mirror the $\delta^{18}O\text{-}SO_4$ profile, declining from 30.1 mM at 1.3 mbsf to a minimum of 19.8 mM at 246.2

F5. Pore water profiles, Site 1226, p. 18.



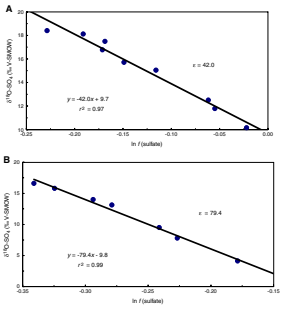
mbsf and then rising with depth to reach 25.2 mM at 418 mbsf (Fig. F5). Both increased alkalinity and significant amounts of dissolved sulfide were detected in the uppermost ~250 m at Site 1226 (Fig. F5). Dissolved sulfide formed a broad maximum peak of 600–700 µM between 45 and 130 mbsf (Fig. F5). A plot of dissolved sulfate vs. sulfide (Fig. F6) shows a negative linear correlation, which suggests that sulfide is forming at the expense of sulfate; however, the slope of this line is an order of magnitude smaller than the slope of one expected for a MSR-dominated system. Data points are concentrated far below a 1:1 slope line, indicating significant loss of sulfide, most likely due to formation of iron sulfides, and probably a partial diffusion out of the maximum MSR zone and subsequent oxidation at shallower depths. The isotopic and chemical profiles at Site 1226 indicate, similar to Site 1225, that dissolved sulfate enters the sediment column from both above (sediment/water interface) and below 418 mbsf (sediment/basement interface) and is reduced by microbial activity within the sediments.

F6. Sulfate vs. sulfide, p. 19.



Sulfate oxygen isotope enrichment factors (ε-SO_4) at Site 1226 are +42.0‰ in the upper MSR zone and +79.4‰ in the lower zone (below ~200 mbsf) (Fig. F7). Similar to Site 1225, these ε-SO_4 values are higher than the previously reported range of values, –8.7‰ to +29‰, and likely reflect bacterial sulfate reduction at low cellular sulfate reduction rates, probably superimposed by sulfide oxidation and disproportionation reactions of sulfur intermediates. Assuming normal seawater $\delta^{18}O$ values of 0‰ for the pore waters, the theoretical equilibrium value between sulfate and water is still not reached at Site 1226 but is more closely approximated than at Site 1225. Besides the higher extent of net sulfate reduction observed at this site, the enhanced temperatures may have additionally influenced the overall shape of the isotope profiles. The higher temperatures may enhance microbial sulfate reduction rates (J. Kallmeyer and T.G. Ferdelman, unpubl. data, 2004), and in addition a lower $\delta^{18}O$-SO_4 value is expected under equilibrium conditions (e.g., Fritz et al., 1989). A complete quantitative evaluation of the observed stable oxygen isotope fractionation, however, requires additional consideration of system openness and associated differential transport processes in the pore waters, as already shown for the stable isotopes of sulfur (Chanton et al., 1987; Jørgensen, 1979; Jørgensen et al., 2004) and the combination of oxygen isotope measurements with results for sulfur isotope compositions (**Böttcher et al.,** this volume).

F7. Isotope enrichment factors, p. 20.



CONCLUSIONS

Oxygen isotope compositions of dissolved sulfate in pore waters at open-ocean and equatorial upwelling sites drilled during Leg 201 indicate the presence of microbial sulfur transformations in the deep-sea sediments of Sites 1225 and 1226 to depths of 418 mbsf and clearly reflect different degrees of MSR activity in sediments. The open-ocean Site 1231 had $\delta^{18}O$-SO_4 values that were close to normal seawater values (~10‰) throughout the entire ~114-m sediment column and showed no evidence for MSR, consistent with chemical compositions of pore water and low organic matter contents. Evolution of $\delta^{18}O$-SO_4 values and MSR activity increased progressively from Site 1225 to Site 1226, reaching maximum values of +20‰ and +28‰, respectively. Combined sulfate concentration and $\delta^{18}O$-SO_4 data at Sites 1225 and 1226 suggest the presence of a sulfate-reducing microbial community and

oxidation of sulfide with further disproportionation of sulfur intermediates. Results from this study show that the isotopic composition of oxygen in pore water sulfate is an important tool in revealing processes of dynamic sulfur transformations by the biosphere of deep-sea sediments.

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Figure F1. Leg 201 open-ocean and equatorial upwelling study sites.

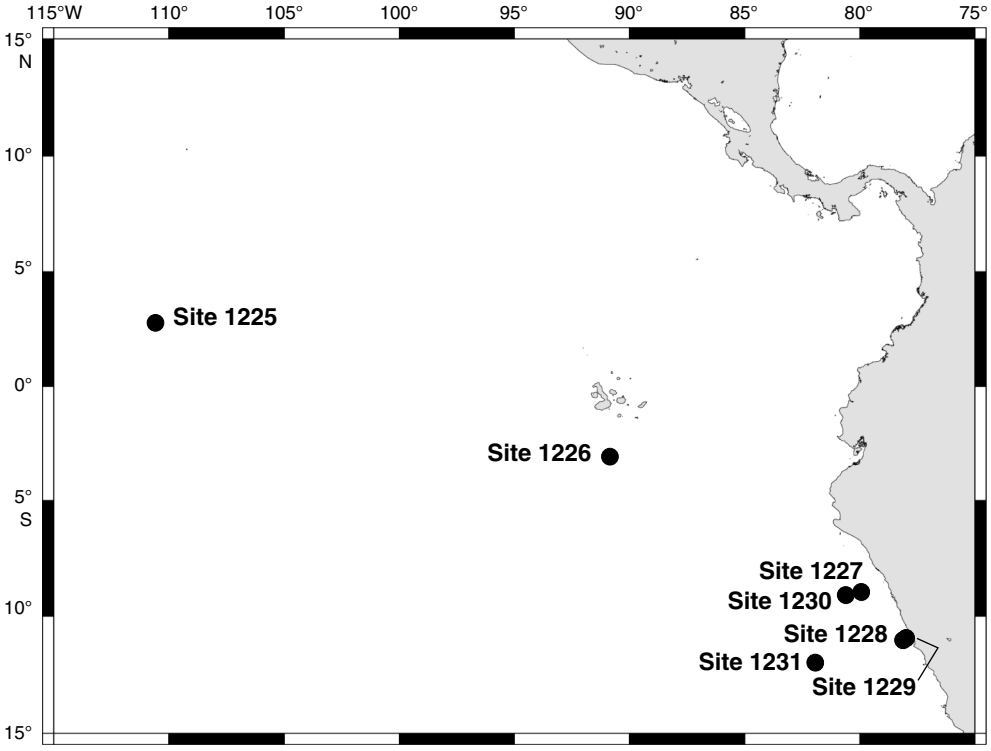

Figure F2. Site 1231 pore water profiles of $\delta^{18}O\text{-}SO_4$, dissolved sulfate, and alkalinity vs. depth. $\delta^{18}O\text{-}SO_4$ data are from this study. All other data are from D'Hondt, Jørgensen, Miller, et al. (2003). V-SMOW = Vienna-standard mean ocean water.

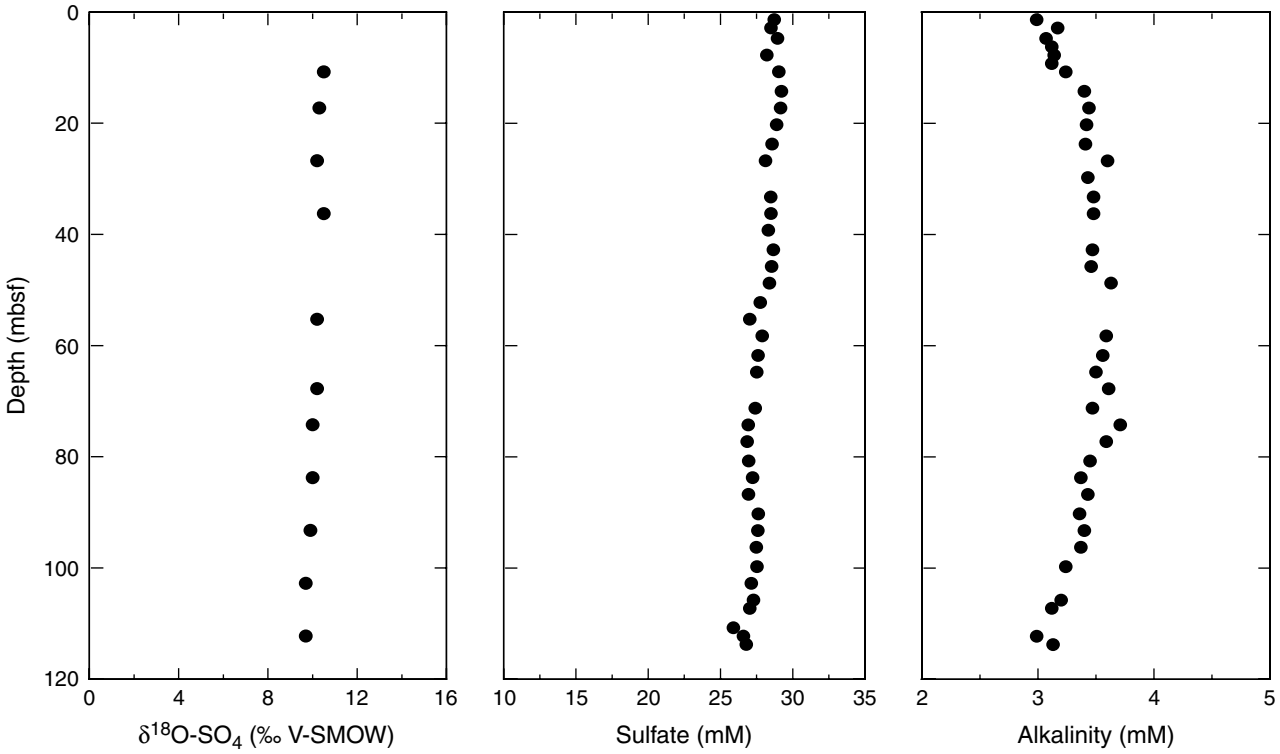

Figure F3. Site 1225 pore water profiles of $\delta^{18}O\text{-}SO_4$, dissolved sulfate, ammonium and alkalinity, and dissolved manganese and iron vs. depth. $\delta^{18}O\text{-}SO_4$ data are from this study. All other data are from D'Hondt, Jørgensen, Miller, et al. (2003). V-SMOW = Vienna-standard mean ocean water.

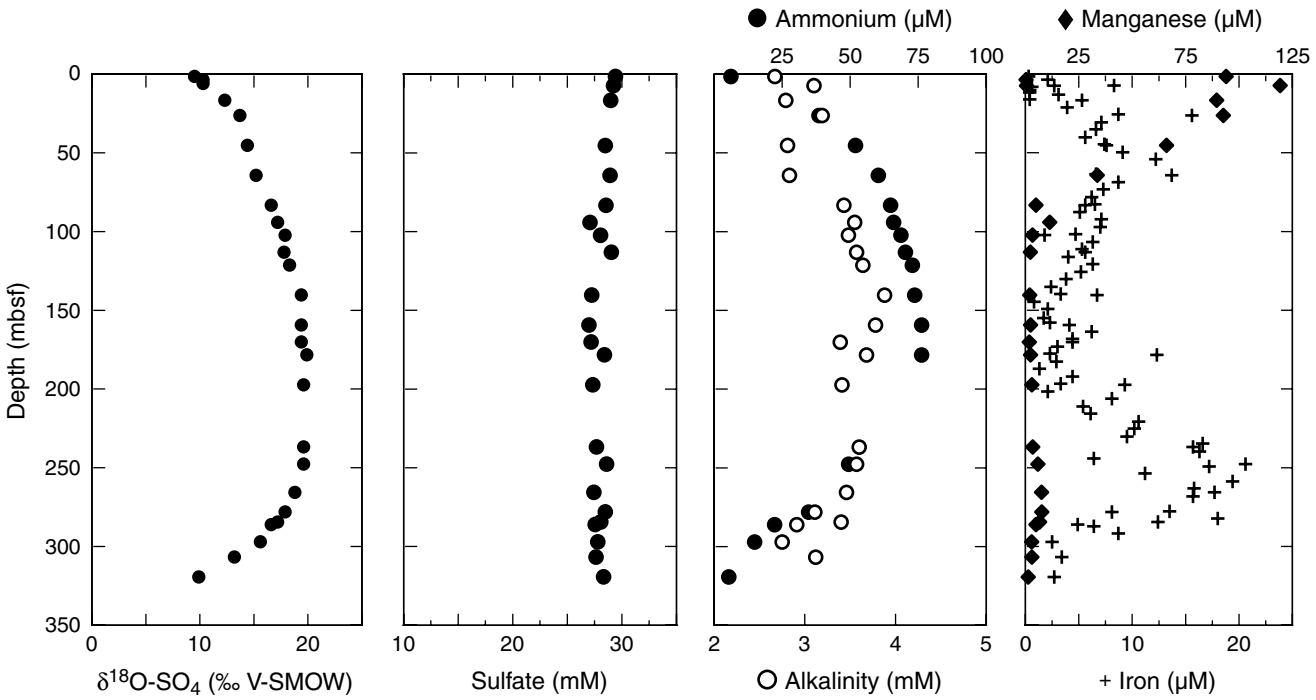

Figure F4. Isotopic fractionation during MSR at Site 1225. **A.** $\delta^{18}O\text{-}SO_4$ vs. fraction of SO_4 remaining (ln *f*) in the upper MSR zone (0–200 mbsf) showing nonlinear behavior. **B.** Sulfate oxygen isotope enrichment factor, $\varepsilon\text{-}_{SO4}$, for linear region of A. V-SMOW = Vienna-standard mean ocean water.

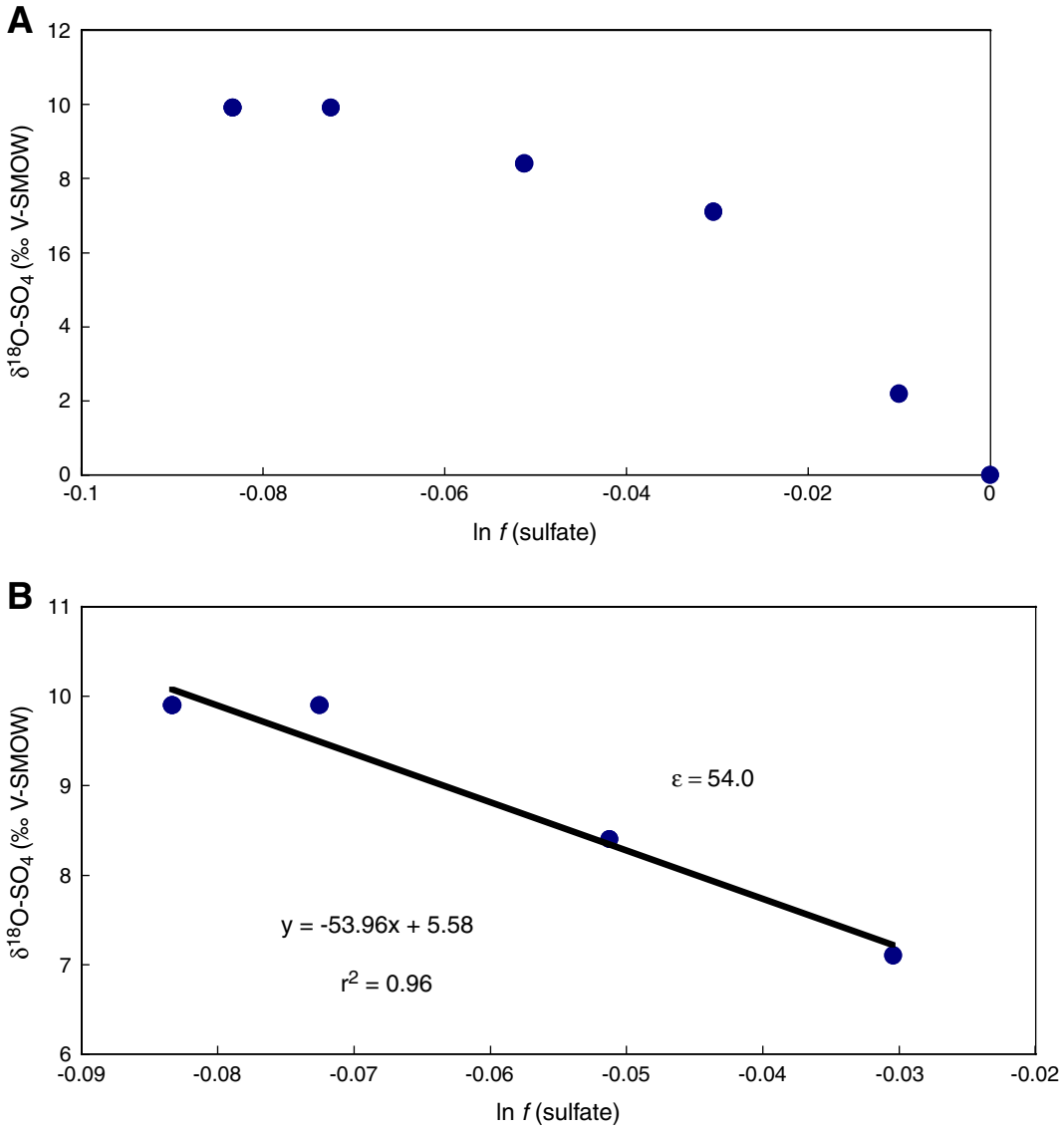

Figure F5. Site 1226 pore water profiles of $\delta^{18}O\text{-}SO_4$, dissolved sulfate, and dissolved sulfide ($\Sigma H_2S = HS^-_{(aq)} + H_2S$) and alkalinity vs. depth. $\delta^{18}O\text{-}SO_4$ data are from this study. All other data are from D'Hondt, Jørgensen, Miller, et al. (2003). V-SMOW = Vienna-standard mean ocean water.

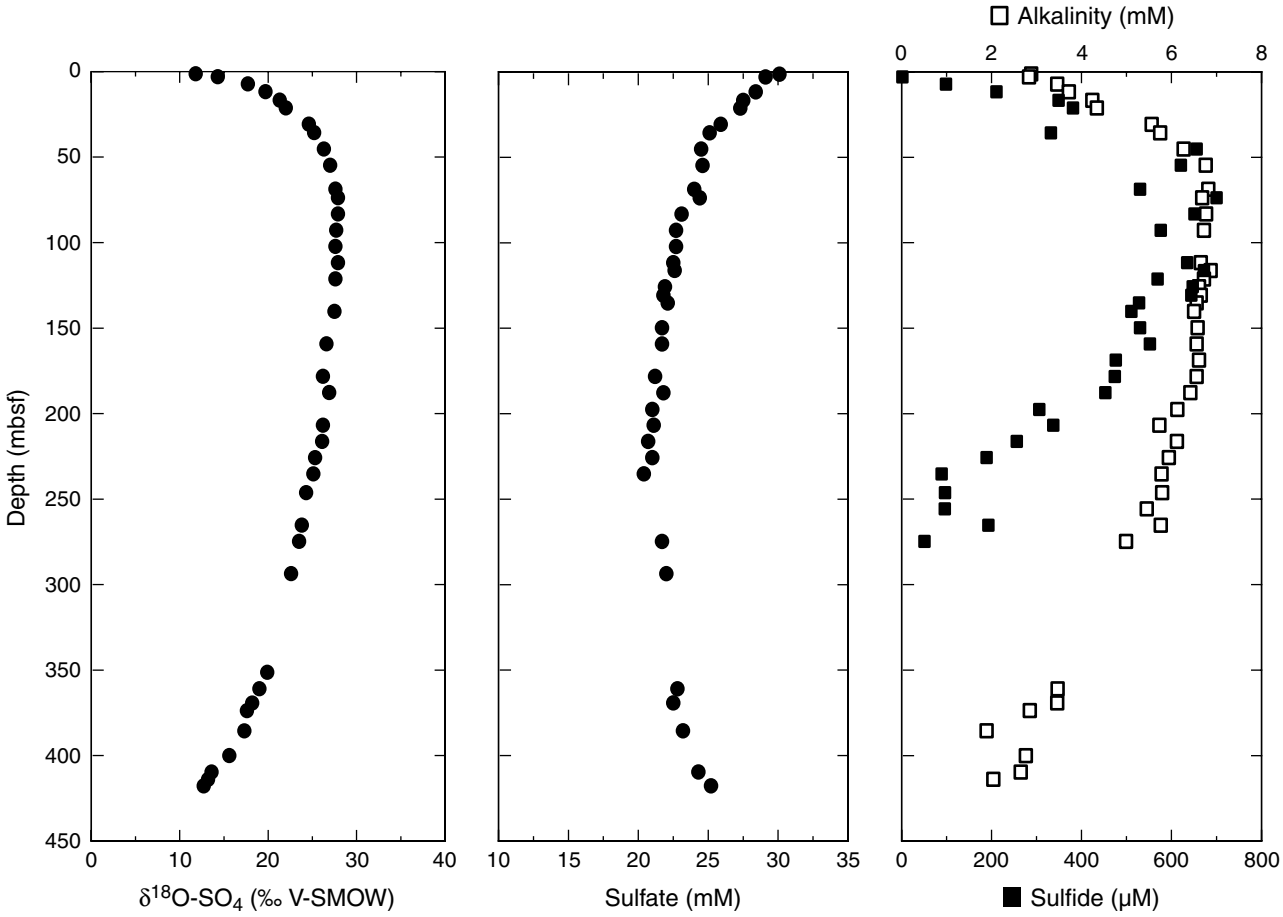

Figure F6. Site 1226 sulfate vs. sulfide. Negative linear correlation suggests sulfide formation at the expense of sulfate. Data plot far below 1:1 slope for MSR-dominated systems. Data are from D'Hondt, Jørgensen, Miller, et al. (2003).

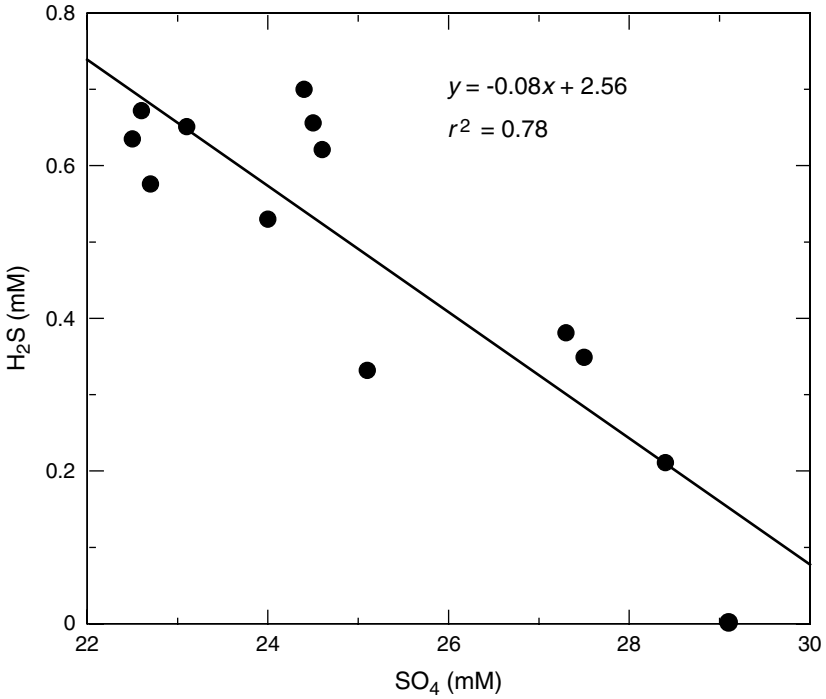

Figure F7. Site 1226 oxygen isotope enrichment factors for (**A**) upper and (**B**) lower MSR zones. V-SMOW = Vienna-standard mean ocean water.

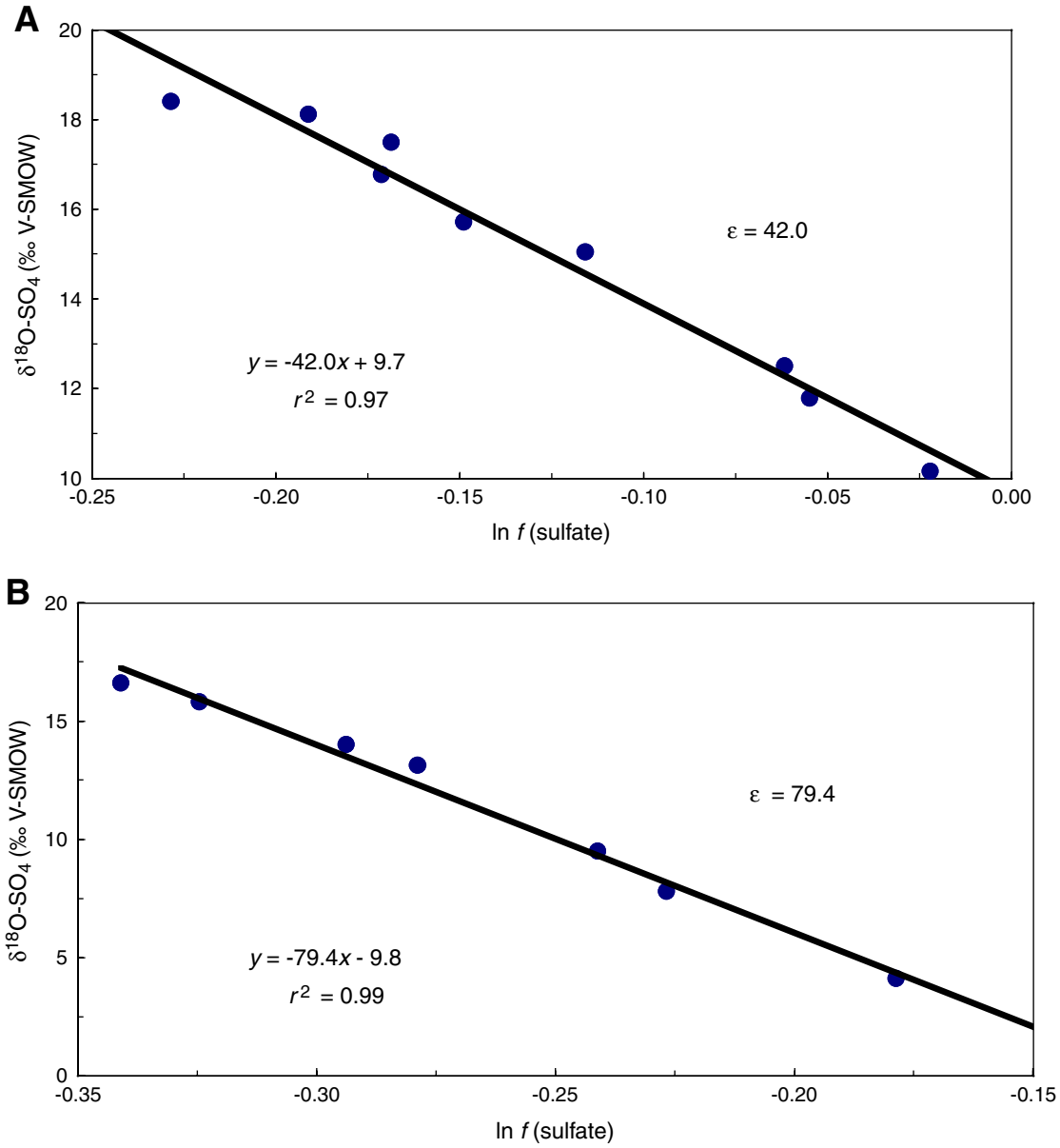

Table T1. Pore water chemical and sulfate oxygen isotope data, Site 1231.

Depth (mbsf)	SO_4 (mM)	H_2S (mM)	Alkalinity (mM)	NH_4 (μM)	$\delta^{18}O$-SO_4 (‰ V-SMOW)
1.4	28.7		3.0	7.6	
2.9	28.5		3.2	17.0	
4.8	29.0		3.1		
6.3			3.1	30.5	
7.8	28.2		3.1	34.8	
9.3			3.1	32.7	
10.8	29.0	<0.2	3.2		10.5
12.3					
14.3	29.2		3.4	34.2	
17.3	29.2	<0.2	3.4		10.3
20.3	28.9		3.4	35.9	
23.8	28.6		3.4	32.6	
26.8	28.1	<0.2	3.6	29.8	10.2
29.8			3.4	33.4	
33.3	28.5		3.5	30.9	
36.3	28.5	<0.2	3.5	30.5	10.5
39.3	28.3		2.3	31.3	
42.8	28.6		3.5	29.4	
48.8	28.4		3.6	28.4	
52.3	27.8			30.2	
55.3	27.0	<0.2	4.0	27.8	10.2
58.3	27.9		3.6	23.8	
61.8	27.6		3.6	22.7	
64.8	27.5	<0.2	3.5	19.5	
67.8			3.6	21.8	10.2
71.3	27.4		3.5		
74.3	26.9	<0.2	3.7	9.0	10.0
77.3	26.9		3.6	10.0	
80.8	26.9		3.4	11.5	
83.8	27.2	<0.2	3.4	13.2	10.0
86.8	26.9		3.4	9.4	
90.3	27.6		3.4	10.5	
93.3	27.6	<0.2	3.4		9.9
96.3	27.5		3.4	5.3	
99.8	27.5		3.2	2.0	
102.8	27.1	<0.2	3.8	1.4	9.7
105.8	27.3		3.2	0.1	
107.3	27.0		3.1	4.1	
110.8	25.9			0.1	
112.3	26.6	<0.2	3.0	1.6	9.7
113.8	26.8		3.1	1.2	

Note: V-SMOW = Vienna-standard mean ocean water.

Table T2. Pore water chemical and sulfate oxygen isotope data, Site 1225.

Depth (mbsf)	SO_4 (mM)	Alkalinity (mM)	NH_4 (μM)	Fe (μM)	Mn (μM)	$\delta^{18}O$-SO_4 (‰ V-SMOW)
1.5	29.4	2.7	6.2	0.3	94	9.5
7.3	29.2	3.1		8.3	119.3	9.8
16.7	29.0	2.8		5.3	89.5	12.3
26.3	29.9	3.2	38.5	15.6	92.7	13.7
45.3	28.5	2.8	51.9	7.6	66.1	14.4
64.3	28.9	2.8	60.4	13.7	33.6	15.2
83.3	28.6	3.4	64.8	5.6	4.9	16.6
94.2	27.1	3.6	65.9		11.4	
102.3	28.0	3.5	68.6	1.8	3.3	17.9
113.2	29.0	3.6	70.3	5.6	2.3	
121.3		3.6	72.8	6.7	2	18.3
140.3	27.2	3.9	73.7	4.1	2.4	19.4
159.3	27.0	3.8	76.2	4.4	1.8	19.4
170.2	27.2	3.4		12.3	2.4	
178.3	28.4	3.7	76.2	9.3	3	19.9
197.3	27.3	3.4		15.7	3.4	19.6
236.8	27.7	3.6		17.7	7.5	19.6
247.7	28.6	3.6	49.4	8.1	7.6	19.6
265.6	27.4	3.5		12.4	6.6	
278.1	28.5	3.1	34.7	4.9	4.9	
284.4	28.1	3.4		2.5	2.9	17.2
286.1	27.5	2.9	22.2	3.4	3	
297.1	27.8	2.8	14.9	2.7	1.3	15.6
306.7	27.6	3.1		2.1	0.3	
319.3	28.3		5.4	2.7	0.5	9.9

Note: V-SMOW = Vienna-standard mean ocean water.

Table T3. Pore water chemical and sulfate oxygen isotope data, Site 1226.

Depth (mbsf)	SO_4 (mM)	Alkalinity (mM)	NH_4 (μM)	H_2S (mM)	$\delta^{18}O$-SO_4 (‰ V-SMOW)
1.3	30.1	2.9	51.7	ND	11.8
3.0	29.1	2.8	95.0	0.0	14.3
7.2		3.5	217.3	0.1	17.7
11.7	28.4	3.7		0.2	19.7
16.7	27.5	4.2		0.3	21.3
21.2	27.3	4.3		0.4	22.0
30.7	25.9	5.6	412.5	ND	24.6
35.7	25.1	5.8	433.5	0.3	25.2
45.2	24.5	6.3		0.7	26.3
54.7	24.6	6.8		0.6	27.0
68.7	24.0	6.8	570.2	0.5	27.6
73.7	24.4	6.7		0.7	27.9
83.2	23.1	6.8		0.7	27.9
92.7	22.7	6.7	621.6	0.6	27.7
102.2	22.7			ND	27.6
111.7	22.5	6.7	621.9	0.6	27.9
116.2	22.6	6.9	622.2	0.7	
121.2		6.7	640.9	0.6	27.6
125.7	21.9	6.6		0.6	
130.7	21.8	6.7		0.6	
135.2	22.1	6.6		0.5	
140.2		6.5	639.8	0.5	27.5
149.7	21.7	6.6	623.3	0.5	
159.2	21.7	6.6		0.6	26.6
168.7		6.6	605.8	0.5	
178.2	21.2	6.6	596.9	0.5	26.2
187.7	21.8	6.4		0.5	26.9
197.5	21.0	6.1	582.9	0.3	
206.7	21.1	5.7	577.8	0.3	26.2
216.2	20.7	6.1		0.3	26.1
225.7	21.0	5.9	555.4	0.2	25.3
235.2	20.4	5.8	568.1	0.1	25.1
246.2	19.8	5.8		0.1	24.3
255.7		5.4	517.5	0.1	
265.2		5.8	502.0	0.2	23.8
274.7	21.7	5.0		0.1	23.5
293.6	22.0		476.7		22.6
351.3			386.8		19.9
360.9	22.8	3.5			19.0
369.2	22.5	3.5			18.2
373.7		2.9			17.6
385.5	23.2	1.9			17.3
400.0		2.8			15.6
409.6	24.3	2.6			13.6
413.9		2.0			13.2
417.7	25.2				12.7

Notes: V-SMOW = Vienna-standard mean ocean water. ND = not determined.