6. Sulfur Isotope Fractionation by the Deep Biosphere within Sediments of the Eastern Equatorial Pacific and Peru Margin[1]

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ABSTRACT

Fifty-seven interstitial water samples from six sites (Ocean Drilling Program Sites 1225–1229 and 1231) in the eastern equatorial Pacific Ocean and the Peru margin were analyzed for the stable sulfur isotopic composition ($^{34}S/^{32}S$) of dissolved sulfate along with major and minor ions. With the exception of Site 1231, sulfate from the interstitial fluids ($\delta^{34}S$ values as much as 89‰ vs. the SF_6-based Vienna-Canyon Diablo troilite standard) is found at depth to be enriched in ^{34}S with respect to modern seawater sulfate ($\delta^{34}S$ = ~21‰), indicating that microbial sulfate reduction (MSR) took place to different extents at all investigated sites. Deeper sediments at Sites 1228 and 1229 are additionally influenced by diffusion of a sulfate-rich brine that has already undergone sulfate reduction. The intensity of MSR depends on the availability of substrate (organic matter), sedimentation conditions, and the active bacterial community structure. Formation of isotopically heavy diagenetic barite at the sulfate–methane transition zone is expected at Sites 1227 (one front), 1229 (two fronts), and probably Site 1228. At Site 1231, the constant sulfur isotopic composition of sulfate and concentrations of minor pore water ions indicate that suboxic (essentially iron and manganese oxide based) diagenesis dominates and no net MSR occurs.

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INTRODUCTION

Leg 201 of the Ocean Drilling Program (ODP), which took place in year 2002, was the first ocean drilling expedition completely dedicated to the study of microbial life and its impact on sediment biogeochemistry deep beneath the seafloor (D'Hondt, Jørgensen, Miller, et al., 2003). In the present study, interstitial waters from six sites (Sites 1225–1229 and Site 1231) from the eastern equatorial Pacific Ocean and the Peru margin (Fig. F1) were retrieved during Leg 201 (Table T1). The positions of the sites were chosen to be close to previously analyzed sites drilled during Deep Sea Drilling Project (DSDP) Leg 34 (Yeats, Hart, et al., 1976) and ODP Leg 112 (Suess, von Huene, et al., 1988) (Table T1). Site 1231 represents a deep-sea setting characteristic of much of the world's open ocean, and organic-poor Neogene deep-sea clays and Paleogene nannofossil ooze were recovered in the Peru Basin. Miocene to Holocene carbonate and siliceous oozes and chalk were recovered at deep-sea Sites 1225 and 1226 in the eastern equatorial Pacific. Both sites are influenced by the relatively high productivity equatorial ocean. The shallow-water Sites 1227, 1228, and 1229 are from the Peru continental margin (Fig. F1) (D'Hondt, Jørgensen, Miller, et al., 2003), and Miocene to Holocene biogenic oozes and terrigenous sediments were cored. The composite section of recovered sediments spans a time interval from the late Eocene to the Holocene (D'Hondt, Jørgensen, Miller, et al., 2003). Organic matter contents differ significantly between sites as a function of water depth and surface water productivity (Table T1). Downcore variation in the sedimentary column of the Peru margin sites (Table T1) demonstrate that sedimentation conditions changed over time. Sedimentary in situ temperatures between 1° and 20°C (Table T1) provide environmental conditions selecting for psychrophilic and mesophilic bacteria. Whereas dissolved methane was observed in the pore waters of a number of settings, none of the investigated sites presented here contained gas hydrates.

Sulfur isotope fractionation in dissolved sulfate of pore waters is an important indicator for the occurrence of microbial sulfate reduction (MSR) in marine sediments (e.g., Hartmann and Nielsen, 1969; Jørgensen, 1979; Jørgensen et al., 2004), and stable sulfur isotope studies were among the first to show by indirect evidence that bacterial sulfate reduction takes place even in deep marine sediments (Zak et al., 1980; Brumsack et al., 1992; Böttcher et al., 1998, 2003, 2004b; Rudnicki et al., 2001). In agreement with the stable isotope evidence, microbial activity in the deep biosphere of marine sediments was found by pore water modeling (Canfield, 1991) and was later directly confirmed by microbiological and radiotracer studies (Bale et al., 1997; Parkes et al., 1994; D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2002, 2004; Parkes et al., 2005).

In the present study, pore waters recovered during Leg 201 were analyzed for stable isotope ratios in dissolved sulfate ($^{34}S/^{32}S$), together with major and minor ions to identify the activity of sulfate-reducing bacteria in the sediment-pore water system. The covariation of dissolved sulfate concentrations and mass-dependent sulfur isotope discrimination is used to calculate apparent closed-system (Rayleigh) fractionation factors (Hartmann and Nielsen, 1969; Goldhaber and Kaplan, 1974; Claypool, 2004). In most sediments, however, bacterial sulfate reduction takes place under conditions that are at least partly open with respect to dissolved sulfate (e.g., Jørgensen, 1979; Jørgensen et al., 2004). There-

F1. Sampling sites, p. 13.

T1. Site data, p. 19.

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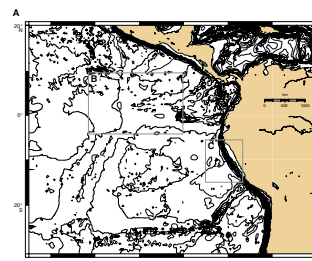
fore, the Rayleigh-type fractionation factors are combined with a relationship recently derived by Claypool (2004) for DSDP and ODP cores to estimate for the Leg 201 sites the open system diffusional supply of dissolved sulfate. It is found that stable isotope variations indicate net microbial sulfate reduction in all sites, with the exception of the open-ocean deep-sea Site 1231, and that all sites are at least partially open to diffusional supply of sulfate from the bottom waters and partly from underlying brines. Sulfate supply from underlying brines is additionally found at selected sites. The oxygen isotope geochemistry of dissolved sulfate is discussed in an accompanying publication (Blake et al., this volume).

METHODS

Interstitial water samples were squeezed from whole-round cores immediately after retrieval of the cores with the standard titanium-stainless steel ODP squeezer (Manheim and Sayles, 1974). Care was taken to minimize contamination from drill fluids by the removal of the outer sediment rim. The retrieved pore waters were subsequently analyzed on board the *JOIDES Resolution* for concentrations of major and minor constituents, including sulfate, sulfide, and chloride, using methods described by Gieskes et al. (1991) and D'Hondt, Jørgensen, Miller, et al. (2003). Pore water samples were immediately fixed after filtration with Zn acetate. After removing the ZnS by membrane filtration (0.45 µm), dissolved sulfate was precipitated quantitatively as $BaSO_4$ by the addition of a barium chloride solution. The precipitate was washed several times with deionized water, dried at 110°C, and baked (600°C) to remove residual organic matter and water. Sulfur isotope ratios ($^{34}S/^{32}S$) were analyzed by combustion isotope ratio monitoring mass spectrometry (Giesemann et al., 1994; Böttcher and Schnetger, 2004). After combustion of barium sulfate to SO_2 in an elemental analyzer (Eurovector), sample and calibration gas were introduced alternately in a He stream into a ThermoElectron Finnigan MAT Delta$^+$ gas mass spectrometer through a ThermoElectron Finnigan MAT Conflo II interface. Stable isotope ratios $^{34}S/^{32}S$ are given in the δ-notation with respect to the SF_6-based Vienna-Canyon Diablo troilite (V-CDT) standard (Ding et al., 1999) according to the following equation:

$$\delta^{34}S[\text{‰}] = (R_{sample}/R_{V\text{-}CDT} - 1) \times 10^3, \tag{1}$$
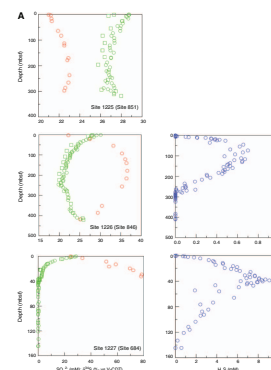
where $R = {}^{34}S/^{32}S$. Analytical stable isotope results are compiled in Table T2.
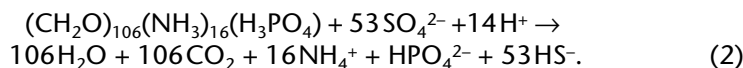
RESULTS AND DISCUSSION

From the downhole variation of dissolved sulfate concentrations in the interstitial waters it is evident that bacterial sulfate reduction takes place in the sediment column of all sites investigated during Leg 201, with the exception of the open-ocean deep-sea Site 1231 (Fig. F2). The high-resolution sulfate measurements carried out during Leg 201 agree remarkably well with the less-resolved data obtained during the previous Leg 112 (Fig. F2). MSR associated with the degradation of organic matter leads to the liberation of carbon dioxide, ammonium, and hy-

drogen sulfide (e.g., Froelich et al., 1979) according to the overall reaction

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\,SO_4^{2-} + 14\,H^+ \rightarrow$$
$$106\,H_2O + 106\,CO_2 + 16\,NH_4^+ + HPO_4^{2-} + 53\,HS^-. \qquad (2)$$

Additionally, bicarbonate and bisulfide are produced upon sulfate reduction associated with anaerobic oxidation of methane (e.g., Hoehler et al., 1994; Boetius et al., 2000). By these two microbially catalyzed processes, sulfate reduction in Leg 201 cores is associated with an increase in pore water concentrations, such as dissolved sulfide, alkalinity, and ammonium (D'Hondt, Jørgensen, Miller, et al., 2003; D'Hondt et al., 2004). The intensity of net sulfate reduction, however, differs among sampling sites depending on the availability of organic substrates for microbial activity and sediment age. Thus, very low total organic carbon (TOC) contents characterize the sediments of Site 1231, which corresponds to Leg 34 Site 321 (Table T1).

Essentially constant sulfate concentrations with depth at the open-ocean Site 1231 (Fig. F2) (see also Brady and Gieskes, 1976, for preliminary results from Site 321) indicate that no net sulfate reduction occurs. This is confirmed by the sulfur isotopic composition of dissolved sulfate throughout the whole sediment column (see below) and is in agreement with results from oxygen isotope analysis of dissolved sulfate (**Blake et al.,** this volume). Some net sulfate reduction is, however, observed at the equatorial deep-sea Sites 1225 and 1226, which receive a higher flux of organic matter because of enhanced productivity (D'Hondt, Jørgensen, Miller, et al., 2003). Sulfate concentrations increase toward the bottom of the sediment column following an initial decrease to a minimum value at ~200 meters below seafloor (mbsf). This increase suggests diffusion of sulfate from seawater that is flowing through underlying basaltic crust (D'Hondt, Jørgensen, Miller, et al., 2003). In contrast to the deep-sea sites, sulfate is completely exhausted at the Peru margin sites within the upper 30–40 mbsf (Fig. F2) because of higher amounts of reactive organic matter and enhanced sedimentation rates, which lead to the burial of a higher relative fraction of organic matter that may be easily consumed by microorganisms (Suess, 1980; Berner, 1980).

The experimental measurements of sulfate in the upper sulfate zone of Sites 1226–1229 gave depth-integrated gross sulfate reduction rates between 14 and 681 mmol/m²/yr (J. Kallmeyer and T.G. Ferdelman, pers. comm., 2004) (Table T3). These values indicate a dependence of the sulfate reduction rate on water depth, bottom water redox conditions, and, therefore, availability of organic matter. Sulfate reduction is typically less significant in the deep sea as compared to Peru margin sediments (Jørgensen, 1982; Canfield, 1991). The measured rates are lower than those typically measured on the continental margin (Jørgensen, 1982; Ferdelman et al., 1999; Fossing et al., 2000; Parkes et al., 2005; J. Kallmeyer and T.G. Ferdelman, pers. comm., 2004), but are higher than the modeled net sulfate reduction (e.g., Fossing et al., 2000; Böttcher et al., 2004b). The latter may be due to the fact that the activity of sulfate-reducing bacteria as deduced from pore water sulfate profiles tends to underestimate gross rates. Because of reoxidation of sulfide and enhanced transport processes in marine surface sediments, gross sulfate reduction rates there are typically much higher than the net rates reflected by dissolved sulfate (e.g., Fossing et al., 2000). Reduc-

tion of dissolved sulfate in the sediment is linked with the availability of metabolizable organic matter or hydrocarbons (mainly CH_4) (Berner 1980; Borowski et al., 1996; Boetius et al., 2000). The sulfate profiles at Peru margin Sites 1227, 1228, and 1229 show a convex-upward curvature (Fig. F2), which, together with the downhole variations in alkalinity and dissolved ammonium (D'Hondt, Jørgensen, Miller, et al., 2003), indicate that sulfate reduction associated with in situ microbial degradation of organic matter plays a significant role in the upper part of the sedimentary column at these sites (Borowski et al., 1996). Downcore changes in sulfate gradients are observed at Sites 1228 and 1229 and suggest a nonsteady-state contribution of sulfate reduction, probably due to changes at the beginning of the Holocene. The different sulfate gradients seem to be related to changes in sedimentation rates and corresponding changes in lithology (D'Hondt, Jørgensen, Miller, et al., 2003). In the different lithologic units of the Peru margin sites, changes in sedimentation rates (Table T1) are associated with different organic matter contents, leading to changes in substrate availabilities. High methane concentrations were not observed at Sites 1225 and 1226, due to the availability of dissolved sulfate throughout the sediment core. Therefore, no contribution from anaerobic oxidation of methane is expected at these sites.

The saline brines found at depth at Sites 1228 and 1229 are enriched in sulfate compared to modern seawater (as much as 40 mM) (Fig. F2) but still have isotope signatures that exceed the modern seawater value. Based on the composition of the fluids it is assumed that seawater was the source of sulfate and that microbial sulfate reduction already modified these brines in their sulfate contents and associated stable isotopic composition.

Stable Sulfur Isotope Fractionation

Microbial reduction of dissolved sulfate causes a kinetic isotope effect and an enrichment of the lighter sulfur isotope ^{32}S in the formed hydrogen sulfide (Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979). Both open- and closed-system diagenesis lead to a corresponding accumulation of the heavy isotope (^{34}S) in the residual sulfate (Hartmann and Nielsen, 1969; Jørgensen, 1979; Jørgensen et al., 2004). Dissolved sulfate in the modern ocean has a sulfur isotopic composition of ~21‰ (Böttcher et al., 2000b), which does not differ significantly from the seawater composition within the past 50 m.y. (Paytan et al., 1998). This value is closely reflected by dissolved sulfate throughout the complete pore water profile at Site 1231, indicating that no net sulfate reduction takes place. The very low activity of sulfate-reducing bacteria parallels the very low TOC contents (Table T1). Pore water constituents, however, indicate some suboxic diagenesis (D'Hondt et al., 2004; D'Hondt, Jørgensen, Miller, et al., 2003). All other investigated sites showed a downcore increase in pore water sulfate $^{34}S/^{32}S$ ratios, mirroring the net decrease in dissolved sulfate (Fig. F2) and indicating that the changes in sulfate concentrations are because of bacterial activity. Isotope results obtained at Site 1228 are in general agreement with previous measurements carried out on sulfate at Site 680 (Fig. F2) (G. Claypool, unpubl. data). The maximum isotope values observed in the residual dissolved sulfate decrease with increasing water depth. This trend corresponds to a decrease in the overall activity of the sulfate reducing community (Table T3).

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Minimum stable sulfur isotope fractionation during MSR was esti-
mated in a first step using a (closed system) Rayleigh fractionation
model (Goldhaber and Kaplan, 1974; Claypool, 2004). Measured sulfate
concentrations [SO₄] and isotope ratios (R) were modeled according to
the following equation:

$$\log(R) = (1 - \alpha_R^{-1}) \log [SO_4] + \log(R°) - (1 - \alpha_R^{-1}) \log [SO_4]°, \qquad (3)$$

where

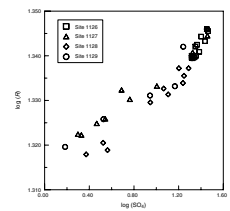   ° = conditions at the sediment/water interface and
   α_R = the fractionation factor.

In agreement with Equation 3, the pore water data gave essentially
straight lines in a Rayleigh plot (Fig. F3). The resulting α_R values obtained
from linear regression of the data at each site are between 1.014 and
1.040 (Table T3). These results are in the range previously calculated for
marine sediments (e.g., Hartmann and Nielsen, 1969; Rudnicki et al.,
2001; Böttcher et al., 2004b; Claypool, 2004). Because of the influence
of transport processes (as diffusion) on pore water profiles, the actual in
situ isotope fractionation factors are typically underestimated by the ap-
plication of Equation 3 (Jørgensen, 1979; Goldhaber and Kaplan, 1980;
Rudnicki et al., 2001; Jørgensen et al., 2004). For example, for the span
of α_R values compiled in Table T3, model calculations of Rudnicki et al.
(2001) for deep-ocean sediments of the Cascadia Basin gave actual iso-
tope fractionations as much as 10‰ higher than closed-system simula-
tions. These magnitudes of sulfur isotope discrimination obtained from
pore water sulfate are within the range observed in experiments with
pure cultures of mesophilic and psychrophilic sulfate-reducing bacteria,
where a maximum of –47‰ has been observed (Kaplan and Rittenberg,
1964; Chambers et al., 1975; Canfield, 2001; Bolliger et al., 2001;
Brüchert et al., 2001). It has additionally been found that sulfur isotope
discrimination associated with anaerobic methane oxidation (Böttcher
et al., 2000a) is similar to isotope effects using other electron donors (Ka-
plan and Rittenberg, 1964; Chambers and Trudinger, 1979; Detmers et
al., 2001). Depending on the actual cellular rates of sulfate reduction
(D'Hondt et al., 2002), isotope discrimination associated with this pro-
cess may change (Kaplan and Rittenberg, 1964; Chambers and
Trudinger, 1979; Chambers et al., 1975) and reactions from the oxida-
tive part of the sulfur cycle may contribute to the overall isotope effects
(Habicht and Canfield, 2001). Hydrogen sulfide may be reoxidized to
sulfur species with intermediate oxidation states, such as elemental sul-
fur or thiosulfate. It has been found that the bacterial disproportion-
ation of sulfur intermediates is associated with the production of ³²S-
enriched sulfide (Canfield and Thamdrup, 1994; Canfield et al., 1998;
Cypionka et al., 1998; Habicht et al., 1998). It should be noted, however,
that in deep hypersulfidic sediments from the Australian continental
margin (Wortmann et al., 2001) and in deep-sea sediments of the Casca-
dia Basin (Rudnicki et al., 2001), sulfur isotope discrimination even ex-
ceeding –70‰ during bacterial reduction of dissolved sulfate was related
to the metabolic activity of natural bacterial populations without imply-
ing further recycling by sulfur intermediates.

Claypool (2004) used results from a number of previous DSDP and
ODP pore waters to derive a relationship between the openness of a sed-
iment with respect to diffusional supply of dissolved sulfate and the cal-

culated Rayleigh isotope fractionation factors. Results on modeled isotope discrimination from the present study (Table T3) together with recent published data from the southwest Pacific (Böttcher et al., 2004b) have been converted by the use of the relationship proposed by Claypool (2004) to derive the fraction between the diffusional flux (J_d) and the total flux (diffusional and burial) of sulfate ($J_d + J_b$). Results are compiled in Table T3 and indicate that all sediments considered here are at least partially open with respect to dissolved sulfate from the bottom waters with a minimum value for the fraction $J_d/(J_d + J_b)$ in Leg 201 sediments of 0.46 (Table T3). Results range up to an 82% contribution of the diffusional flux and cover the range estimated for Leg 181 sediments from the southwest Pacific (Table T3).

Sedimentary reduced sulfur as a product of dissimilatory sulfate reduction was found in the Peru margin sites and is essentially present as pyrite with minor contributions from organic sulfur (Emeis and Morse, 1990; Mossmann et al., 1990). However, sedimentary sulfur may also occur in oxidized form as biogenic barite (e.g., Paytan et al., 1998), which is used as a proxy for paleoproductivity (Paytan et al., 1996) and typically contains the isotope signature of sulfate from the water column or in surface sediments (Paytan et al., 1998). In the zone of complete sulfate depletion, biogenic barite may redissolve and barium may diffuse upward in the sediment column toward the lower part of the sulfate zone. Because of the low solubility of barium sulfate, barite may precipitate at a "diagenetic front" (Brumsack et al., 1992; Torres et al., 1996; Böttcher et al., 2003; D'Hondt, Jørgensen, Miller, et al., 2003). Based on the pore water profiles observed in the sediments recovered during Leg 201 (Fig. F2) (D'Hondt, Jørgensen, Miller, et al., 2003), the dissolution of biogenic barite and the development of a diagenetic barite front can be inferred at Sites 1227, 1229, and probably 1228 (Fig. F2). The position of the barite front is expected to be at 30–40, 40, and 30 mbsf at Sites 1227, 1228, and 1229, respectively. The occurrence of a sulfate-rich brine at depth at Sites 1228 and 1229 can lead to the parallel development of a second, deeper-seated barite front at ~50 (Site 1228) and ~90 (Site 1229) mbsf. Based on the present isotopic composition of dissolved sulfate (~80‰–90‰ V-CDT), the diagenetic barite should be highly enriched in [34]S with respect to modern biogenic barite (Paytan et al., 1998) and Pacific Ocean water sulfate (Longinelli, 1989; Böttcher et al., 2000a, 2004b). As introduced by Böttcher et al. (2004a), the magnitude of heavy (sulfur and oxygen) stable isotope enrichments in diagenetic barite may serve as an indicator for the steepness of paleo-sulfate gradients during the development of barite fronts. Investigations in cooperation with Glen Snyder have been initiated to look at the stable sulfur isotopic composition of barite in the diagenetic fronts that developed in sulfate-depleted Leg 201 sediments. At Sites 1225, 1226, and 1231, interstitial water sulfate does not decrease to an extent that biogenic barite remobilization and formation of diagenetic barite is expected.

CONCLUSIONS

The analysis of stable sulfur isotope ratios in dissolved sulfate from interstitial waters recovered from sediments of the eastern equatorial Pacific and the Peru margin demonstrate that net dissimilatory reduction of sulfate by a deep biosphere takes place to different extents at all investigated sites, except for the open-ocean deep-sea Site 1231. Maxi-
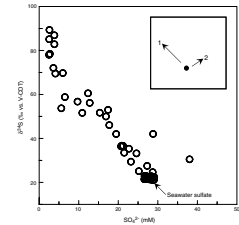
mum $\delta^{34}S$ values are also consistent with both modeled and measured sulfate reduction rates, which show decreasing rates with increases in water depth. Observed sulfur isotope discrimination indicates different degrees of openness of the sediment column with respect to dissolved sulfate. The dominant processes controlling sulfur isotope fractionation in dissolved sulfate are dissimilatory bacterial sulfate reduction and mixing with deep sulfate-rich brines (Fig. F4). Sulfate in these deep brines seems to be derived from seawater that was evaporated and already subjected to microbial sulfate reduction.

Therefore, the results from Leg 201 show that sulfur isotope fractionation in interstitial water sulfate is an extremely powerful tool in the evaluation of sinks, sources, and especially microbiological transformation reactions upon sulfur diagenesis by the deep biosphere in different types of marine sediments.

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Figure F1. A. Sampling sites of Leg 201 compared to previous sites drilled during DSDP Leg 34 and ODP Leg 112 (from D'Hondt, Jørgensen, Miller, et al., 2003). (Continued on next page.)
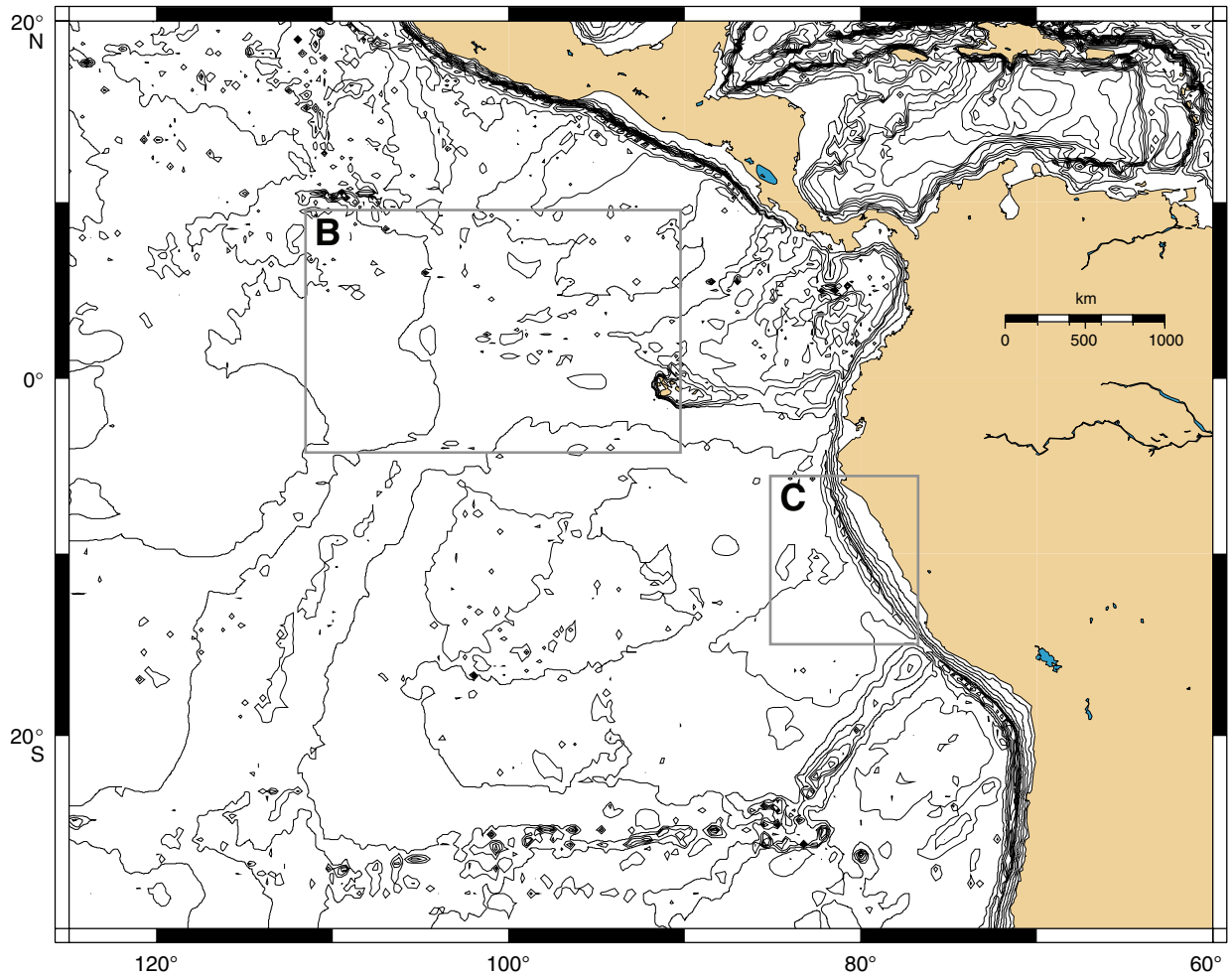
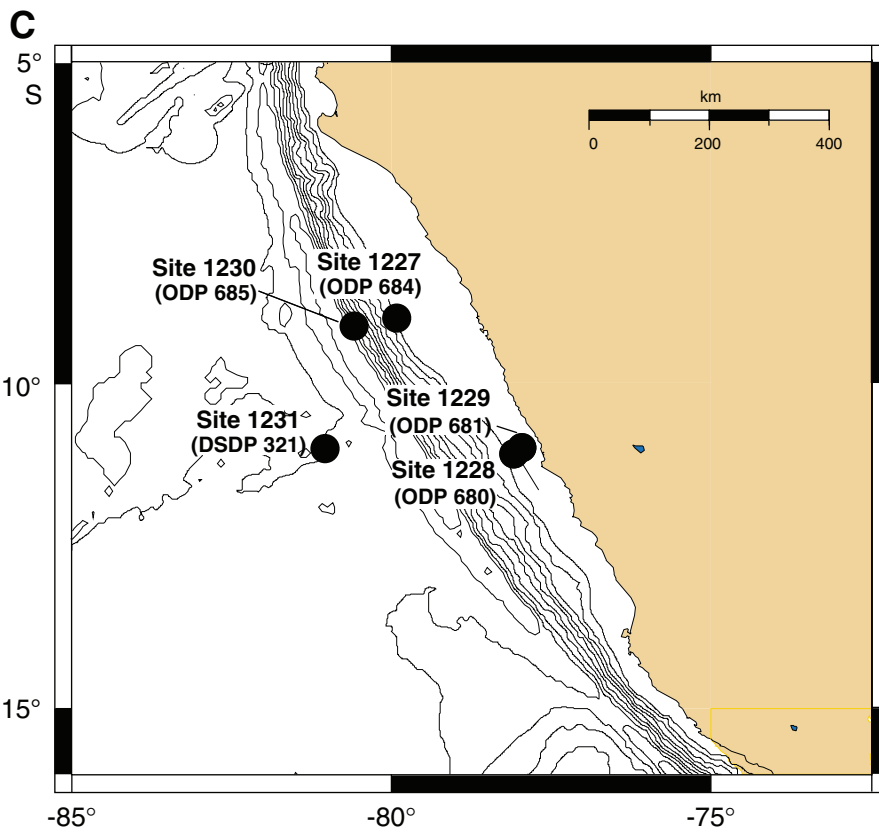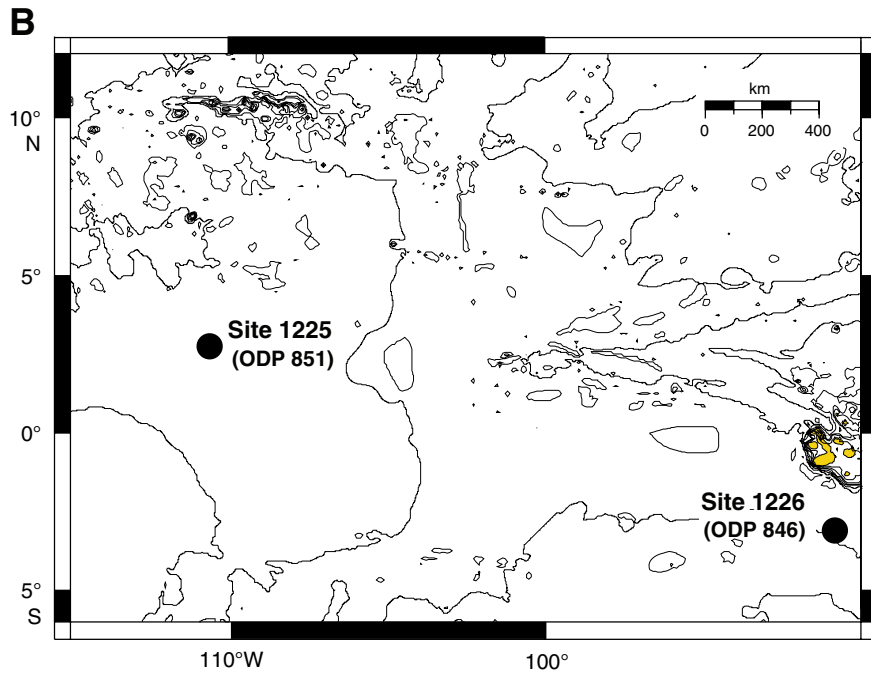**Figure F1 (continued). B.** Location of Sites 1225 and 1226. **C.** Location of Sites 1227 through 1231.

Figure F2. Leg 201 pore water sulfate concentrations (green circles) and $\delta^{34}S$ values (red circles) vs. depth. Green squares indicate sulfate concentrations measured in pore waters from previous sites drilled on almost identical positions during DSDP Leg 34 and ODP Leg 112 (Yeats, Hart, et al., 1976; Suess, von Huene, et al., 1988). H_2S data are total dissolved sulfide data and taken from D'Hondt, Jørgensen, Miller, et al. (2003). **A.** Sites 1225, 1226, and 1227. Sulfide was below detection limit in Site 1225 pore water. V-CDT = Vienna-Canyon Diablo troilite. (Continued on next page.)
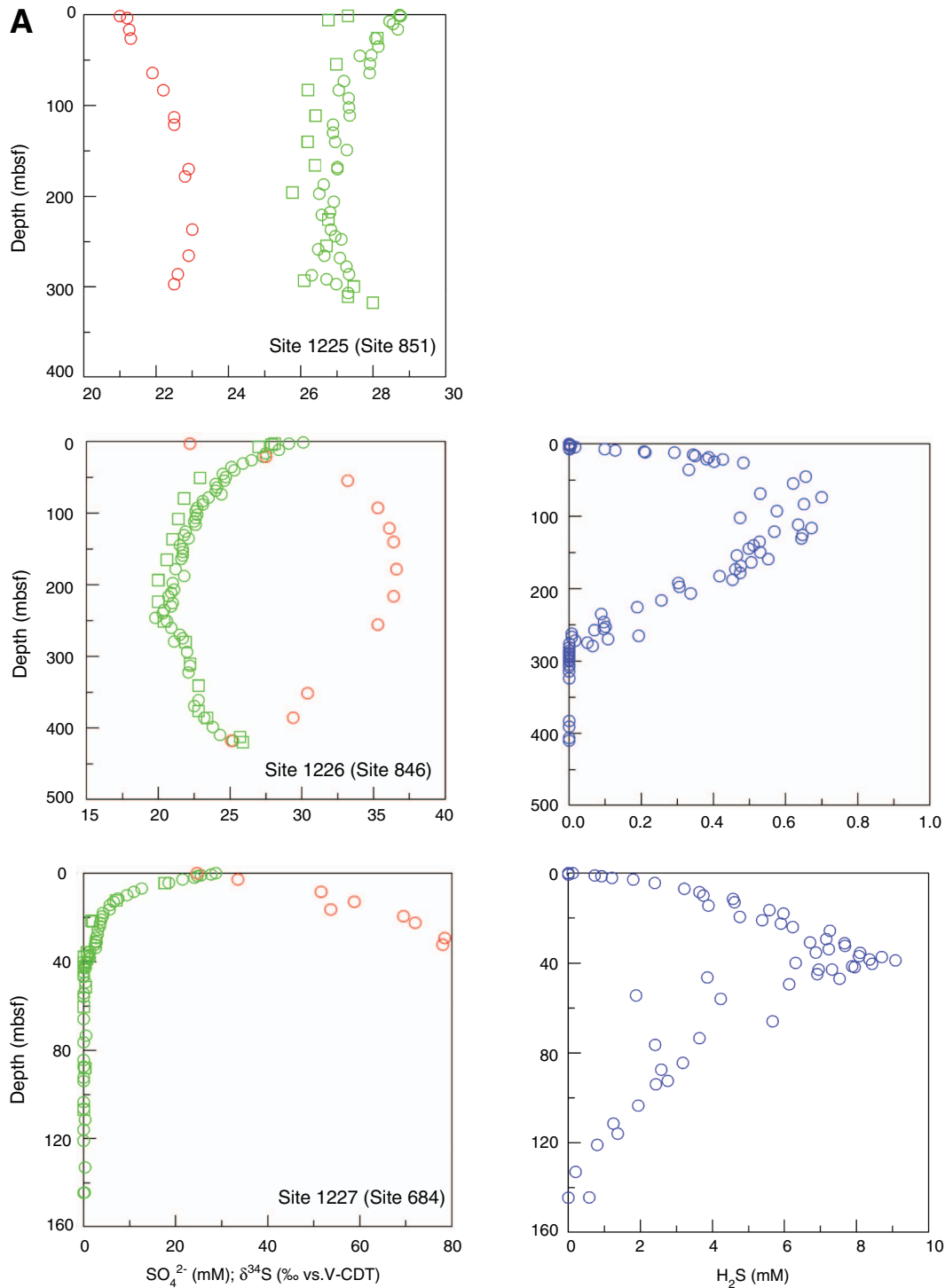
Figure F2 (continued). B. Sites 1228, 1229, and 1231. Red squares indicate the sulfur isotopic composition of dissolved sulfate measured in pore water at Site 680 (G. Claypool, unpubl. data). Sulfide was below detection limit in Site 1231 pore water. V-CDT = Vienna-Canyon Diablo troilite.
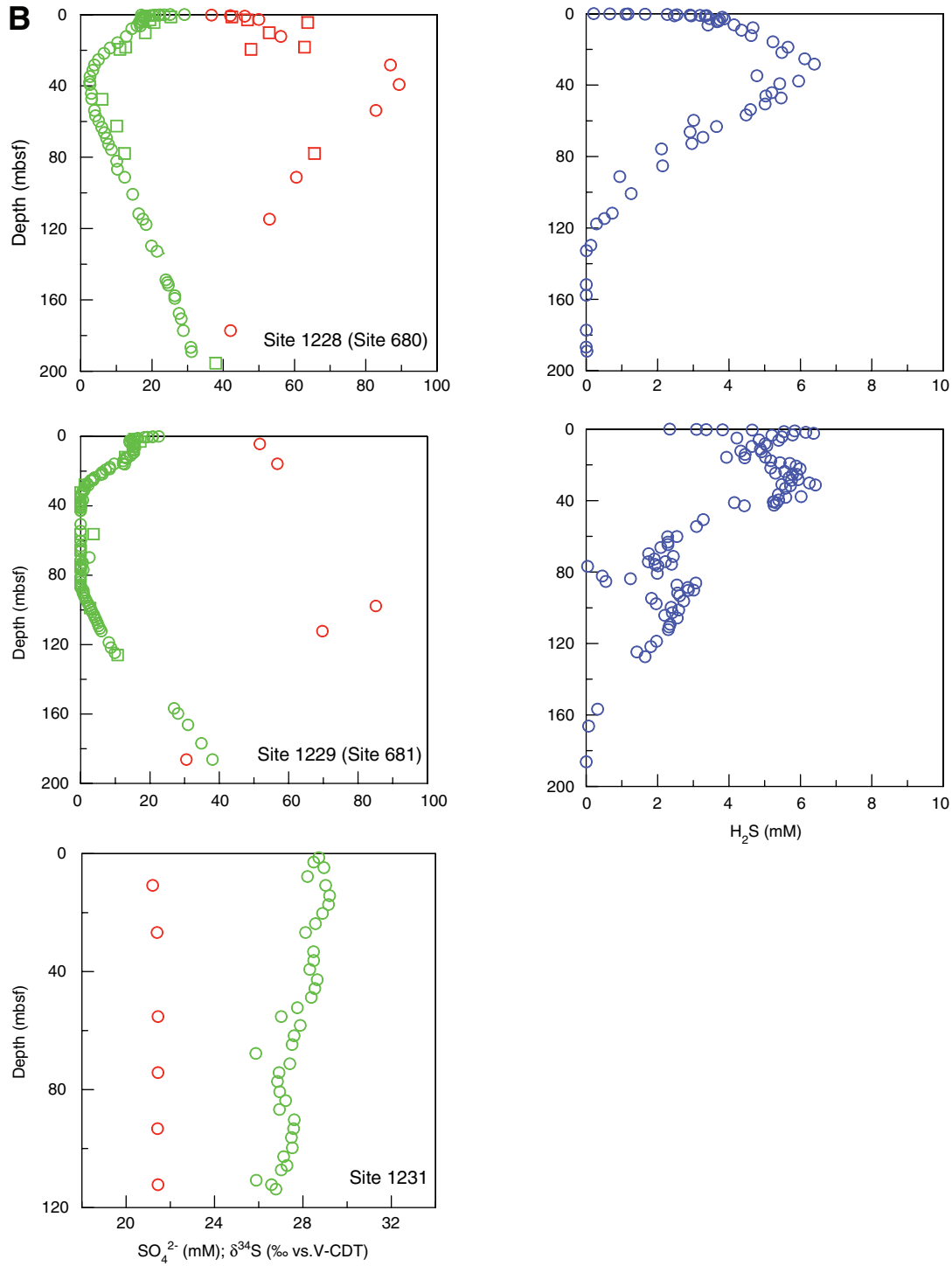
Figure F3. Rayleigh plots for pore water at Leg 201 sites (except Sites 1225 and 1231). Isotope ratios (*R*) were calculated using the measured isotope data based on the isotope ratio for the V-CDT standard (Ding et al., 1999). Based on chloride concentrations, all sulfate concentrations are normalized to the respective shallowest pore water sample of a given profile. Linear regression coefficients (*r*²) are 0.83, 0.97, 0.94, and 0.90 for Sites 1226, 1227, 1228, and 1229, respectively.

Figure F4. Sulfate concentrations vs. sulfur isotopic composition for all measured pore water sulfate samples from the Leg 201 sites compiled in Table T1, p. 19. The insert shows how different processes may influence the composition of dissol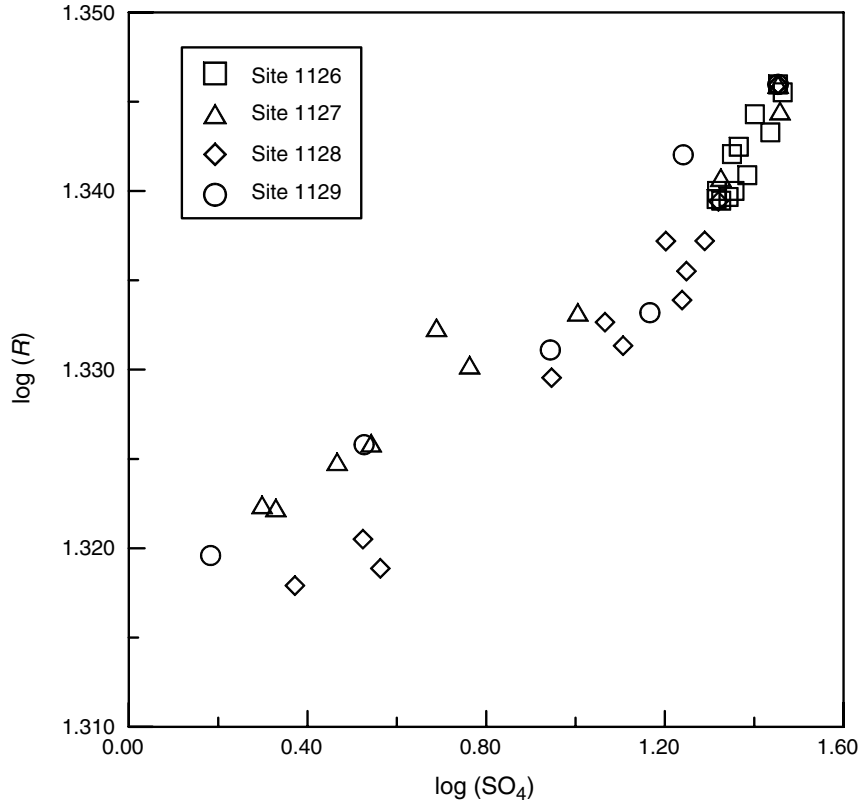ved sulfate. 1 = bacterial sulfate reduction, 2 = mixing with sulfate-rich deep brine. V-CDT = Vienna-Canyon Diablo troilite.
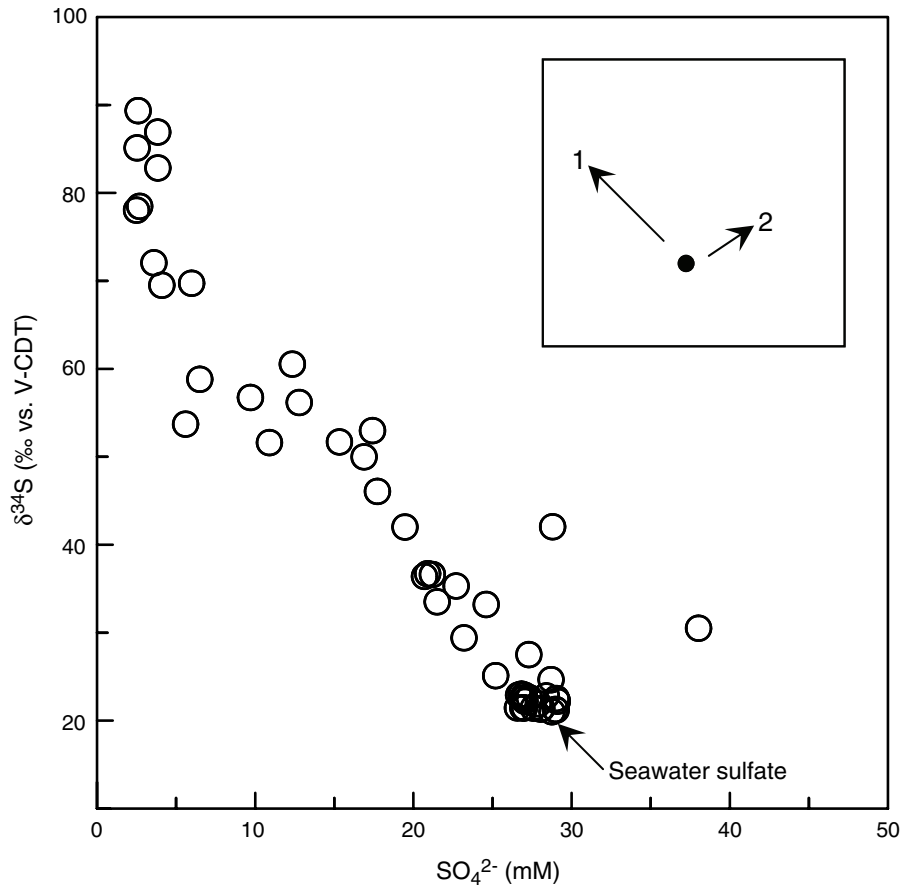
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Table T1. Leg 201 sites.

Site	PS	Description	Water depth (m)	Latitude	Longitude	Temperature range (°C)	TOC (wt%)	Sedimentation rate (m/m.y.)
1225	851	Equatorial upwelling	3760	2°46.22′N	110°34.31′W	1.4–7.0	0–0.9	10–68
1226	846	Equatorial upwelling	3297	3°05.70′S	90°49.08′W	1.7–24.4	0–2	10–50
1227	684	Ocean margin; Peru shelf	427	8°59.49′S	79°54.35′W	8.6–6.4	0.6–10.6	8–50
1228	680	Ocean margin; Peru shelf	252	11°03.90′S	78°04.67′W	12.5–19.3	0.1–13	22–55
1229	681	Ocean margin; Peru shelf	151	10°58.60′S	77°57.46′W	13.4–20.2	0.8–4	80
1231	321	Ocean margin; Peru Basin	4827	12°01.29′S	81°54.24′W	1.7–8.6	0–0.6	ND

Notes: PS = previous ODP/DSDP site drilled at essentially the same position as the Leg 201 site. TOC = total organic carbon. In situ temperature range between the sediment/water interface and the estimated base of drilled sediment column after D'Hondt, Jørgensen, Miller, et al. (2003). TOC data and sedimentation rates are taken from Cameron (1976), Suess, von Huene, et al. (1988), von Breymann et al. (1990), and D'Hondt, Jørgensen, Miller, et al. (2003). ND = not determined.

Table T2. Sulfur isotope data for dissolved sulfate measured in Leg 201 pore water.

Core, section, interval (cm)	$\delta^{34}S$ (‰ V-CDT)		Core, section, interval (cm)	$\delta^{34}S$ (‰ V-CDT)
201-1225A-			201-1227D-	
1H-2, 0–15	21.0		1H-1, 0–1	24.7
3H-2, 135–150	21.3		4H-2, 135–150	78.5
4H-3, 0–15	21.3		4H-4, 135–150	78
8H-3, 0–15	21.9		201-1228A-	
10H-3, 0–15	22.2		1H-2, 135–150	50
13H-3, 135–150	22.5		2H-5, 135–150	56.2
14H-3, 0–15	22.5		4H-3, 135–150	86.9
19H-3, 135–150	22.9		5H-4, 135–150	89.4
20H-3, 0–15	22.8		7H-1, 135–150	82.8
26H-3, 0–15	23.0		11H-1, 85–100	60.5
30H-2, 0–15	22.9		14H-3, 135–150	53
32H-3, 0–15	22.6		21H-1, 135–150	42
33H-3, 135–150	22.5		201-1228C-	
201-1226B-			1H-1, 30–45	36.7
1H-3, 0–20	22.2		1H-1, 60–75	42
3H-5, 130–150	27.5		1H-1, 90–105	46.1
7H-2, 130–150	33.2		201-1229A-	
11H-2, 130–150	35.3		1H-3, 131–148	51.7
14H-2, 130–150	36.1		3H-1, 135–150	56.7
16H-2, 130–150	36.4		11H-6, 135–150	85.1
20H-2, 130–150	36.6		13H-3, 135–150	69.7
24H-2, 130–150	36.4		22H-1, 135–150	30.5
28H-2, 130–150	35.3		201-1231B-	
38X-2, 110–150	30.4		2H-5, 135–150	21.2
43X-4, 110–150	29.4		4H-3, 135–150	21.4
47X-1, 130–150	25.1		7H-3, 135–150	21.4
201-1227A-			9H-3, 135–150	21.4
1H-2, 135–150	33.5		11H-3, 135–150	21.4
2H-2, 135–150	51.6		13H-2, 135–150	21.4
2H-5, 135–150	58.8			
3H-1, 135–150	53.7			
3H-3, 135–150	69.5			
3H-5, 135–150	72.1			

Note: V-CDT = Vienna-Canyon Diablo troilite.

Table T3. Rayleigh sulfur isotope fractionation factor.

Site	Water depth (m)	α_R	$J_d/(J_d + J_b)$	SRR (mmol/m^2/yr)
Leg 201				
1225	3760	1.014	0.82	ND
1226	3297	1.040	0.46	14
1227	427	1.019	0.75	82
1228	252	1.023	0.67	573
1229	151	1.018	0.59	681
Leg 181				
1119	396	1.015	0.80	ND
1120	544	1.029	0.61	ND
1121	4490	1.009	0.88	ND
1122	4432	1.048	0.36	ND
1123	3290	1.045	0.40	ND
1124	3978	1.040	0.47	ND
1125	1350	1.014	0.81	ND

Notes: α_R = minimum isotope fractionation under apparent closed system, conditions calculated based on pore water sulfate profiles in the upper sulfate zone (see text). Estimated α_R values for the deep (brine influenced) sulfate zone were found to be 1.028 (Site 1228) and 1.022 (Site 1229). Openness of the sedimentary system toward dissolved sulfate ($J_d/[J_d + J_b]$) are calculated based on the relationship derived by Claypool (2004; see text). SRR = depth integrated sulfate reduction rates, measured with radiotracers in the whole sulfate zone (J. Kallmeyer and T.G. Ferdelman, pers. comm., 2004). Results are compared to sites from the southwest Pacific (ODP Leg 181; Böttcher et al., 2004b). ND = not determined.