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Sulfur isotope evidence for microbial sulfate reduction in altered oceanic basalts at ODP Site 801

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Abstract

The subsurface biosphere in the basaltic ocean crust is potentially of major importance in affecting chemical exchange between the ocean and lithosphere. Alteration of the oceanic crust commonly yields secondary pyrite that is depleted in ³⁴S relative to igneous sulfides. Although these ³⁴S depleted sulfur isotope ratios may point to signatures of biological fractionation, previous interpretations of sulfur isotope fractionation in altered volcanic rocks have relied on abiotic fractionation processes between intermediate sulfur species formed during basalt alteration. Here, we report results for multiple S-isotope (³²S, ³³S, ³⁴S) compositions of altered basalts at ODP Site 801 in the western Pacific and provide evidence for microbial sulfate reduction within the volcanic oceanic crust. *In-situ* ion-microprobe analyses of secondary pyrite in basement rocks show a large range of δ³⁴S values, between −45‰ and 1‰, whereas bulk rock δ³⁴S analyses yield a more restricted range of −15.8 to 0.9‰. These low and variable δ³⁴S values, together with bulk rock S concentrations ranging from 0.02% up to 1.28% are consistent with loss of magmatic primary mono-sulfide and addition of secondary sulfide via microbial sulfate reduction. High-precision multiple sulfur-isotope (³²S/³³S/³⁴S) analyses suggest that secondary sulfides exhibit mass-dependent equilibrium fractionation relative to seawater sulfate in both δ³³S and δ³⁴S values. These relationships are explained by bacterial sulfate reduction proceeding at very low metabolic rates. The determination of the S-isotope composition of bulk altered oceanic crust demonstrates that S-based metabolic activity of subsurface life in oceanic basalt is widespread, and can affect the global S budget at the crust–seawater interface.

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1. Introduction

Alteration of oceanic crust by seawater is one of the most important processes controlling the global fluxes of many elements (e.g. Staudigel and Hart, 1983) and microbes likely

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play a significant role in this process (Bach and Edwards, 2003). The evidence for a deep biosphere within oceanic basement includes primarily the alteration textures of volcanic glass, the potential presence of DNA or high C, N and P contents in altered glass, and the light isotopic composition of C in some carbonate veins (e.g. Thorseth et al., 1992; Fisk et al., 1998; Furnes et al., 2001). However, the study of an active biosphere in the basaltic ocean crust is currently limited and lags behind our current understanding of subsurface life in deep-sea sediments (Parkes et al., 1994; Wortmann et al., 2001; D'Hondt et al., 2002). This is mainly due to technical difficulties involved

in identifying and culturing indigenous microbes, as well as the lack of a visual record of microbial activity in crystalline rocks in contrast to volcanic glass.

Previous studies of sulfur isotope compositions of deep-sea sediments have shown that sulfate-reducing communities are active in the deeply buried sediments and that their cellular metabolic activities may differ from those observed in near-surface sediments or in the water column (Wortmann et al., 2001). Sulfur isotope values of secondary pyrite precipitated in oceanic basalt fractures have been reported in numerous studies (Field et al., 1976; Krouse et al., 1977; Andrews, 1979; Puchelt et al., 1996) and $\delta^{34}\text{S}$ values generally range from basaltic values at 0‰ to highly negative values down to -50‰ . Although these negative $\delta^{34}\text{S}$ values are consistent with an origin involving microbial reduction of seawater sulfate, as commonly observed in marine sediment settings (Canfield, 2002), previous researchers favored an abiotic isotope fractionation process due to the lack of a well-identified organic carbon source in the basalts (Field et al., 1976; Andrews, 1979; Puchelt et al., 1996). In a previous model, Andrews (1979) proposed that igneous sulfide minerals are partially oxidized to unstable intermediate sulfur species (e.g. sulfite, SO_3^{2-} , or thiosulfate, $\text{S}_2\text{O}_3^{2-}$) which can inorganically disproportionate into sulfate and sulfide. Sulfate is lost from the rock, whereas sulfide, which combines with iron in the host rock, is precipitated as secondary pyrite. Recently, elevated $\delta^{34}\text{S}$ values (26.2 to 29‰) of preserved gypsum in exposed ophiolitic oceanic crust have been inter-

preted as the result of *in-situ* microbial sulfate reduction (Alt et al., 2003) but questions remain concerning the origin (i.e. abiotic or biotic), mechanisms (i.e. sulfate reduction or disproportionation), and global significance of the low $\delta^{34}\text{S}$ values in secondary sulfides in altered basalts.

Drilling at Ocean Drilling Program (ODP) Site 801 penetrated more than 400 m into Jurassic oceanic basement in the western Pacific (Larson et al., 1992; Plank et al., 2000). This section represents the oldest *in-situ* oceanic basement ever drilled and presents an excellent opportunity to explore potential S-isotope biosignatures of the deep biosphere. In this paper, we use three S-isotope approaches to unravel the mechanisms of S-isotope fractionation associated with the alteration of the oceanic crust at ODP Site 801. First, *in-situ* ion-microprobe $\delta^{34}\text{S}$ analyses were undertaken to document isotopic heterogeneity and textural relationship for secondary sulfides in altered rocks and veins. Second, analyses of multiple S isotopes ($^{32}\text{S}/^{33}\text{S}/^{34}\text{S}$) for selected secondary sulfides in the altered basalts were used to constrain multiple sulfur-isotope relationships between primordial sulfur and seawater sulfate. Analysis of $\delta^{33}\text{S}$ combined with standard $\delta^{34}\text{S}$ analysis provides a new dimension in documenting reactions involving sulfur, such as reaction pathways during microbial sulfate reduction and S disproportionation (Farquhar et al., 2003; Johnston et al., 2005; Ono et al., 2006). Finally, bulk rock S-isotope analyses are used to assess the large-scale budget of sulfur isotopes in altered oceanic basement at ODP Site 801.

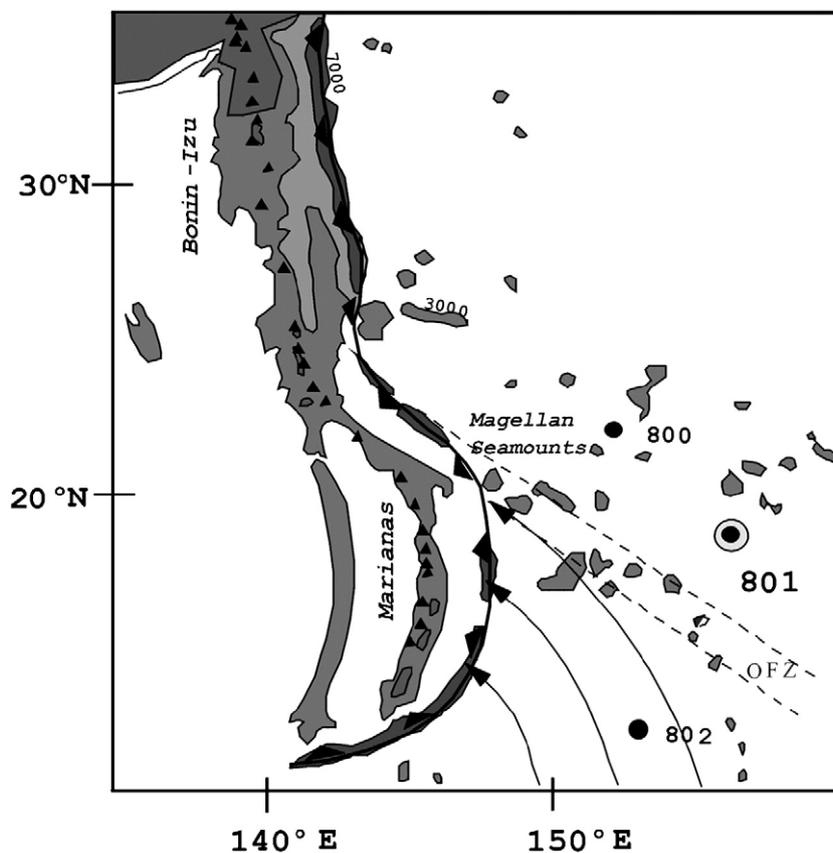


Fig. 1. Map of the West Pacific (Izu and Mariana arcs) and location of ODP Hole 801C drilled during Leg 129 and 185. Modified after Plank et al. (2000).

2. Geological setting and alteration history

ODP Site 801 is located in the Pacific plate several hundred kilometers east of the Marianas trench (Fig. 1). ODP Site 801 was drilled into Jurassic basement characterized by a lack of magnetic anomalies and a half-spreading rate of about 8 cm/yr (Larson et al., 1992; Plank et al., 2000). On the basis of flow morphology, geochemistry, and mineralogy, the basement section at Hole 801C, which was intersected at 461.6 meters below seafloor (mbsf), has been divided into four major sequences which include rocks drilled on both Leg 129 and Leg 185 (Larson et al., 1992; Plank et al., 2000; Kelley et al., 2003) (Fig. 2).

The uppermost basement (Unit ALK) is composed of alkaline basaltic to dolerite sills overlying a Si and Fe-oxyhydroxide-rich hydrothermal horizon (H.D. in Fig. 2). The alkali basalt section is younger (157 Ma; Pringle, 1992; Koppers et al., 2003)

than the underlying tholeiitic mid-ocean ridge basalt (MORB) section (~170 Ma). Below the hydrothermal deposit, the volcanic rocks (Unit MORB 0–110) comprise thin flows and pillows, lying above a series of thick lava flows. The upper 110 m of MORB (MORB 0–110 of Fig. 1) are thought to have erupted slightly off-axis (Pockalny and Larson, 2003). The on-axis MORB is divided into a middle (MORB 110–220) and a lower (MORB 220–420) unit, distinguished on the basis of a change in eruptive styles, with more massive flows in the lower unit. Between 600 and 720 mbsf the section is characterized by a pillow-dominated zone with a well-developed interpillow horizon (Unit MORB 110–220). A second Si–Fe-rich hydrothermal unit similar to the larger one uphole is present within Unit MORB 110–220 pillows (Fig. 2). From 720 mbsf to the bottom at 936 mbsf, the Unit MORB 220–420 comprises a tectonic breccia which separates a massive flow unit (720–890 mbsf) and a series of thin, generally <1-m thick, sheet flows and pillows (890–934 mbsf).

Three general types of low-temperature alteration can be observed (Alt and Burdett, 1992; Plank et al., 2000; Talbi and Honnorez, 2003): (1) replacement of igneous material in alteration halos and groundmass; (2) filling of void space by secondary phases; (3) development of breccia cements and cross-cutting veins. The latter are often filled with calcite, and can reopen and refill for millions of years, providing an important sink for carbon in the altered crust (Alt and Teagle, 1999). The most common secondary phases are saponite (Mg-smectite), calcite, celadonite, Fe-oxyhydroxide and pyrite (Alt and Teagle, 2003; Talbi and Honnorez, 2003). Most of the basalts are dark gray in color and have experienced 10 to 20% alteration (Alt and Teagle, 2003). In addition, both dark celadonite-rich, and brown Fe-oxyhydroxide alteration halos around fractures are observed. Secondary pyrite generally occurs within saponite-rich and carbonate veins but is also found at the boundary between the alteration halos and the host rock. Alteration of basalts at Site 801 took place at low temperatures (<100 °C), mainly off-axis, during aging of the oceanic crust (Plank et al., 2000; Alt and Teagle, 2003; Talbi and Honnorez, 2003). Fresh basaltic glass is locally preserved at Site 801C, demonstrating the heterogeneous distribution of low-temperature alteration. Volcanic glass recovered throughout the section is altered by invasive channels and tubes which are similar to other examples in basaltic glass in the deep ocean crust that have been attributed to microbial alteration (Plank et al., 2000).

3. Methodology

3.1. Sampling strategy

A comprehensive set of samples, covering the major Units at Site 801, were selected for this study (Table 1). All of the selected rocks have been affected by low-temperature alteration (<100 °C) resulting in various combinations of secondary minerals saponite (Mg-smectite), calcite, celadonite, Fe-oxyhydroxide and pyrite as replacements of igneous phases and as fillings of vesicles and cracks. A subset of samples was also selected for *in-situ* S-isotope analysis based on the occurrence

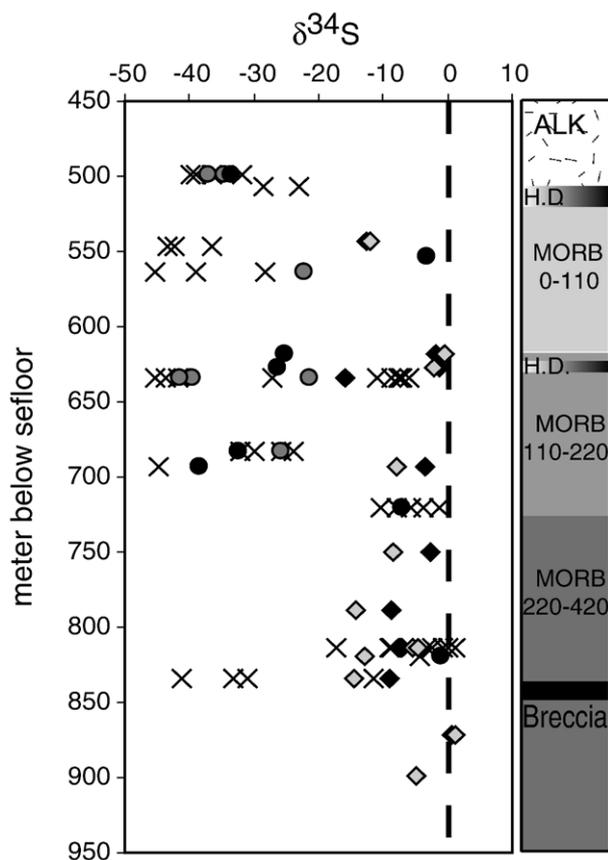


Fig. 2. Downhole $\delta^{34}\text{S}$ composition of sulfides in Hole 801C. Simplified stratigraphic column of basaltic basement is shown with the depth scale. S-isotope compositions obtained by ion microprobe for individual pyrite and marcasite minerals are marked by crosses while pyrite separates analyzed for multiple S isotopes and conventional gas-source mass spectrometers are marked by gray and black circles respectively. Gray and black diamonds correspond to bulk rock S-isotope analysis for AVS and Cr–S respectively. Dashed vertical line represents the S-isotope composition of fresh basalts. H.D. = Si–Fe-rich hydrothermal deposit. ALK = Alkaline basalts. MORB = Mid-ocean ridge basalts. Error bars for ion microprobe is 2‰ whereas the error bars on the gray and black symbols are 0.2‰.

Table 1
Major element chemistry, S concentration and S-isotope composition of altered basalts at Site 801

Sample	Depth	(wt.%)											(wt.%)			%			Description
		LOI	Al ₂ O ₃	CaO	Fe ₂ O ₃ T	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	ΣS	δ ³⁴ S	CrS/ΣS ^a	δ ³⁴ S	δ ³⁴ S	δ ³⁴ S	
													ΣS	CrS/ΣS ^a	AVS	CrS	SO ₄		
801C-06R3,18	543	6.4	22.1	8.0	3.6	2.6	1.7	<0.05	2.72	0.07	51.6	1.19	0.100	-12.0	97.3		-12.0	-5.6	Highly altered aphyric basalt
801C-06R3,42	544	9.9	21.9	14.1	6.0	0.8	2.4	0.15	3.04	0.07	50.0	1.14	0.049	-12.7	79.5		-12.7	-6.0	Medium altered basalt with carbonate veins
801C-15R4,69	618	4.7	14.8	11.0	12.6	0.1	5.7	0.16	2.79	0.20	46.1	1.85	0.039	-0.8	74.0	-1.9	-0.4	Medium altered basalt with thin saponite veins	
801C-15R7,1	621	7.1	19.5	8.2	5.5	0.9	1.5	0.03	3.65	0.20	51.0	2.44	0.051					Highly altered (bleached) basalt	
801C-15R7,31	622	9.9	18.4	12.9	5.1	0.5	1.8	0.13	3.44	0.24	46.1	2.17	0.082					Highly altered (bleached) basalt	
801C-16R3,82	627	8.3	16.6	6.2	12.1	0.5	2.5	0.10	3.19	0.38	45.3	3.78	0.220	-2.1	94.9	-1.4	-2.2	-2.5	Highly altered basalt
801C-17R1,100	634	3.1	12.7	11.3	15.9	0.1	5.5	0.26	2.53	0.28	46.1	2.71	0.270	-15.8	18.0	-15.8		-2.9	Least altered basalt with pyrite and carbonate-filled vesicles
801C-24R2,36	693	1.7	13.7	11.3	14.7	0.1	6.6	0.26	2.60	0.24	47.2	2.14	0.110	-7.7	95.7	-3.4	-7.9	-7.9	Least altered aphyric basalt
801C-25R1,10	701	1.7	13.7	11.7	14.1	0.0	6.9	0.25	2.68	0.2	48.6	2.0	0.016						Least altered aphyric basalt
801C-34R3,81	789	3.4	12.9	9.4	16.2	0.7	5.3	0.18	2.59	0.22	46.7	2.33	0.057	-13.3	85.6	-8.8	-14.1	-5.2	Medium altered basalt with alteration halos
801C-37R1,83	814	3.5	13.3	10.5	13.7	0.1	6.0	0.22	2.65	0.25	47.5	2.34	0.720	-4.9	84.2	-7.2	-4.5	-3.9	Least altered basalt with carbonate and saponite-filled vesicles
801C-37R1,83/V	814	10.8	6.2	2.0	46.8	0.5	4.8	0.07	0.47	0.11	27.5	1.02	0.026	-5.5			-5.5	1.2	Large celadonite and Fe-oxide vein with carbonate
801C-37R5,30	819	1.6	13.1	10.0	13.5	0.2	5.0	0.22	2.83	0.19	50.9	2.37	1.300	-12.9	47.4	-12.9	-12.9	-8.0	Least altered basalt
801C-39R2,28	834	1.9	13.8	10.8	14.2	0.1	6.9	0.27	2.62	0.23	46.8	2.34	0.110	-14.0	90.2	-9.0	-14.5	-1.9	Least altered aphyric basalt
801C-43R1,13	869	2.2	13.5	11.0	13.3	0.1	6.4	0.23	2.78	0.18	48.5	2.00	0.410						Least altered basalt
801C-43R2,75	871	0.3	14.6	10.7	12.7	0.2	6.5	0.22	3.02	0.26	48.6	2.10	0.210	0.9	29.5	0.8	1.3	-0.8	Least altered basalt with thin veins
801C-46R1,106	899	1.6	13.9	11.3	13.2	0.1	7.1	0.21	2.57	0.2	47.7	2.0	0.020	-5.0	61.4	-5.0	-5.0		Least altered basalt
801C-52M1,47	933	1.8	13.7	11.5	14.4	0.1	7.4	0.27	2.85	0.2	48.5	2.3	0.014						Least altered basalt
801 SUPER	750	7.7	11.1	12.0	12.7	0.6	5.7	0.21	2.12	0.15	45.4	1.54	0.092	-6.8	72.0	-2.7	-8.4	-3.8	Composite

^a CrS/ΣS corresponds to the proportion (in %) of Cr-reducible S (pyrite) relative to total S measured.

of macroscopic pyrite along veins and disseminated in the groundmass (Table 2).

We analyzed one composite sample (referred as SUPER) which represents a physical mixture of a subset of individual samples covering all basement lithologies identified at Site 801C (Plank et al., 2000; Revillon et al., 2002; Kelley et al., 2003). This SUPER composite was prepared by making a proportionate mixture of sub-composites (volcanic flows and volcanoclastites) from each of the three MORB intervals. These sub-composites were themselves prepared from 117 representative samples from each core segments from the basement section of Hole 801C (Kelley et al., 2003). Though detailed information about fine-scale variations can be obtained only

from the analysis of individual samples, the use of composites allows to estimate the average composition with very few analyses. Hence, we used S concentration and S-isotope composition of the SUPER composite to approximate the large-scale composition of the entire MORB section at Site 801.

3.2. S-isotope definitions and notations

Sulfur isotope values are reported using conventional delta notation:

$$\delta^x\text{S} = \left(\frac{^xR_{\text{sample}}}{^xR_{\text{reference}}} - 1 \right) \times 1000(\text{‰}) \quad (1)$$

Table 2
Individual $\delta^{34}\text{S}$ analysis of secondary sulfides in Hole 801C

Sample	Description	$\delta^{34}\text{S}$
<i>801B-43R1,29 — 499.4 mbsf</i>		
mar-1 ^a		−33.5
mar-2#1	Marcasite aggregate with minor pyrite disseminated	−31.8
mar-2#2	in thick carbonate-rich vein (5 mm thick)	−36.5
mar-3#1		−39.1
mar-3#2		−39.7
mar-3#3		−39.0
<i>801C-2R3,59 — 506.4 mbsf</i>		
py-1#1	Disseminated pyrite grain (0.5 mm) in carbonate-rich	−22.9
py-1#2	vein (2 mm thick)	−28.5
<i>801C-06R5,75 — 546.9 mbsf</i>		
py-1#1	Pyrite veinlet (0.5 mm thick) lining a carbonate-rich	−36.5
py-1#2	vein (2 mm thick), occurrence of pyrite aggregates locally	−42.3
py-1#3		−43.4
<i>801C-07R2,132 — 552.9 mbsf</i>		
py-1#1	Pyrite veinlet (0.1 mm thick) lining a carbonate-rich	−3.2
	vein (1 mm thick)	
<i>801C-09R1,32 — 563.5 mbsf</i>		
py-1#1	Polycrystalline marcasite aggregate disseminated in	−28.3
py-1#2	basalt groundmass	−38.9
py-2#3	Ditto, 2 mm from py-1	−45.3
<i>801C-15R4,69 — 618.3 mbsf</i>		
py-1 ^a	Hand-picked pyrite grains from carbonate and	−25.3
	saponite-rich vein (3 mm thick)	
<i>801C-16R4,9 — 627.5 mbsf</i>		
py-1 ^a	Hand-picked pyrite grains from saponite-rich vein	−26.3
	(2 mm thick)	
<i>801C-17R1,100 — 633.8 mbsf</i>		
py-1#1	Pyrite grains disseminated along fracture in basalt	−41.7
py-1#2	groundmass with minor carbonate and saponite	−45.3
py-1#3		−43.6
py-2#1	Ditto, 1 mm from py-1 along vein	−7.4
py-3#1	Ditto, 0.5 mm from py-2 along vein	−7.1
py-4#1	Ditto, 0.2 mm from py-3 along vein	−10.8
py-4#2		−5.9
py-5#1	Ditto, 1 mm from py-4 along vein	−27.1
py-6#1	Pyrite grain within basalt groundmass	−7.7
py-7#1	Pyrite grain within basalt groundmass	−43.7
py-8#1	Ditto	−8.8
<i>801C-23R1,45 — 682.4 mbsf</i>		
py-1 ^a		−32.5
py-2#1	Local pyrite enrichment (polycrystalline aggregates)	−25.7
py-2#2	associated with carbonate-rich vesicles (1–3 mm wide)	−32.1
py-2#3		−29.8
py-2#4		−23.9
<i>801C-24R2,36 — 693.0 mbsf</i>		
py-1 ^a	Pyrite associated with saponite-rich vein	−38.4
py-2#1	Thin pyrite veinlet (<0.1 mm)	−44.9
<i>801C-27R1,50 — 720.2 mbsf</i>		
py-1 ^a		−7.0
py-2#1	Disseminated pyrite grains lining non-mineralized fracture	−1.4
py-2#2	and extending 2 mm within basalt groundmass	−3.8
py-2#3		−5.8
py-2#4		−3.7

Table 2 (continued)

Sample	Description	$\delta^{34}\text{S}$
<i>801C-27R1,50 — 720.2 mbsf</i>		
py-3#1	Disseminated pyrite grains within basalt groundmass	−10.4
py-3#2		−7.8
<i>801C-37R1,83 — 814.1 mbsf</i>		
py-1#1	Pyrite grains with framboidal-like texture within porous	0.2
py-1#2	basalt groundmass	−3.3
py-1#3		−8.9
py-2#1	Polycrystalline pyrite aggregates within porous	−2.3
py-2#2	basalt groundmass	−3.2
py-3#1	Coarse pyrite grain lining basalt vesicle	1.3
py-3#2		−0.6
py-1#8	Coarse pyrite grain lining basalt vesicle	−8.6
py-1#9		−17.2
<i>801C-37R5,30 — 818.8 mbsf</i>		
py-1 ^a	Disseminated fine-grained pyrite within coarse-	−1.0
py-2#1	grained, porous basalt groundmass	−4.2
<i>801C-39R2,28 — 834.0 mbsf</i>		
py-1#1		−31.0
py-1#2	Pyrite-rich veinlet (0.5 mm thick) within fine-grained	−33.2
py-1#3	basalt	−41.3
py-1#4		−11.4

^a $\delta^{34}\text{S}$ values obtained on micro-drilled sulfide grains (gas-source mass spectrometer).

where xR is the isotope ratio, $^x\text{S}/^{32}\text{S}$ ($x=33$ or 34), of the sample compared to reference material. S-isotope data are reported on the Vienna-CDT scale (V-CDT) by defining $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ of IAEA S-1 (artificial Ag_2S) to be -0.055 and -0.300% , respectively (Coplen and Krouse, 1998; Ono et al., 2007).

We define *traditional* capital delta notation (Δ) as deviations of $\delta^{33}\text{S}$ from a reference line:

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}. \quad (2)$$

An alternative Δ definition has been preferred by recent studies (Hulston and Thode, 1965; Gao and Thiemens, 1991; Miller, 2002; Young et al., 2002), and we denote this as Δ^* :

$$\Delta^{33}\text{S}^* = \delta^{33}\text{S}^* - 0.515 \times \delta^{34}\text{S}^* \quad (3)$$

where

$$\delta^x\text{S}^* = \ln \left(\frac{^xR_{\text{sample}}}{^xR_{\text{ref}}} \right) \times 1000 = \ln \left(\frac{\delta^x\text{S}}{1000} + 1 \right) \times 1000. \quad (4)$$

Both definitions (Δ and Δ^*) are used in Table 3 for comparison. Note that the modified delta notations ($\delta^{34}\text{S}^*$ and $\Delta^{33}\text{S}^*$) are *fractionation-oriented* (i.e. linear relationships during mass-dependent isotope fractionation) whereas traditional delta coordinates ($\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) are *mass-balance oriented* (i.e. linear relationships during mixing) (Ono et al., 2007).

Mass-dependent sulfur isotope fractionation factors are described by the following power law (Hulston and Thode, 1965; Farquhar et al., 2003; Ono et al., 2007):

$$^{33}\alpha = ^{34}\alpha^{33}\theta \quad (5)$$

where fractionation factors (α) are defined as the ratio of $^{x}\text{S}/^{32}\text{S}$ between two pools of sulfur (e.g., A and B). That is,

$${}^x\alpha = ({}^x\text{S}/^{32}\text{S})_A / ({}^x\text{S}/^{32}\text{S})_B. \quad (6)$$

The $^{33}\theta$ value for equilibrium isotope fractionation factors between SO_4^{2-} and H_2S may also vary as a function of temperature, from 0.5145 at 0 °C to 0.5154 at 500 °C (Ono et al., 2007) while microbial sulfate reduction follows different $^{33}\theta$ value of ~ 0.512 (Farquhar et al., 2003; Ono et al., 2007).

3.3. Bulk rock analysis

Solid sample surfaces were cleaned with a sand-blaster and washed with distilled water. Sample powders for bulk rock analysis were prepared using agate grinding vessels. Major element chemistry was determined by ICP-AES at CRPG-CNRS (France) following the procedure described in Govindaraju and Mevelle (1987) and results are presented in Table 1. S concentrations were analyzed in 250 mg bulk rock samples using a LECO144DR carbon–sulfur analyzer. The precision is estimated at 5% for S content $> 0.05\%$ and the limit of detection is 0.005%.

Sulfur isotope compositions of bulk rocks were determined following the procedure of Rice et al. (1993) and Canfield et al. (1986) and data are reported in Table 1. Acid-volatile sulfides (AVS) were first extracted in HCl with SnCl_2 added to prevent oxidation. Chromium–reducible sulfides (Cr–S) were subsequently extracted using the Cr-reduction method (Table 1). Evolved H_2S for AVS and Cr–S were precipitated as Ag_2S , and acid soluble sulfate was reduced to H_2S with Thode's solution and precipitated as Ag_2S . Sulfur isotope analyses of Ag_2S were performed at Queen's University (Canada). Yields from the sulfur extractions average 90% of the bulk S concentrations from LECO C–S analyzer, but only the latter are reported. Total $\delta^{34}\text{S}$ composition is obtained by mass balance calculation between AVS and Cr–S.

3.4. Micro-drilled sulfide analysis

The $^{34}\text{S}/^{32}\text{S}$ analyses of micro-drilled sulfides (Table 2) were performed on a VG602D double-collector mass spectrometer

at CRPG and are given in conventional $\delta^{34}\text{S}$ notation relative to V-CDT (Coplen and Krouse, 1998). We used the NIST sulfide standard NZ-1 defined at -0.3% and we obtained $\text{NZ-2} = 21.6\% \pm 0.1\%$, $\text{NZ-3} = -31.6\% \pm 0.1\%$, $\text{NBS-123} = 17.4\% \pm 0.1\%$, $\text{NBS-127} = 20.4\% \pm 0.2\%$ based on replicate measurements. The precision for sulfide data is typically $\pm 0.2\%$ (2 sigma level) and is often better than 0.1%.

The $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ analyses were performed at the Carnegie Institution of Washington (USA). The fluorination manifold is coupled on-line with a two-stage gas chromatography purification system, which is critical for ultra-high-precision isotope ratios measurements. Multiple sulfur isotope ratios are analyzed by a gas-source mass spectrometer (Finnigan MAT 253) with SF_6 as analyte. Details of the analytical technique can be found in Hu et al. (2003) and Ono et al. (2006). For isotope analysis, Ag_2S (~ 1.5 mg) were prepared by conventional distillation (Cr-reduction) after precise micro-drilling of rock matrix containing large sulfide grains in polished section (Supplementary Materials). Precision and accuracy are 0.2 and 0.004‰ for $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$, respectively (Ono et al., 2006). Isotope results are reported in Table 3.

3.5. Ion-microprobe analysis

S-isotope compositions of pyrite and marcasite, ranging in size from 100 μm up to 2 mm in diameter, hosted in the basalt groundmass or occurring within vein fractures (Table 2 and Fig. 2) were determined using a modified CAMECA IMS 3F ion microprobe at the CRPG (Chaussidon and Demange, 1988). Rock chips were mounted in epoxy together with an internal pyrite S-isotope standard (GAV18), polished, and coated with gold. Sulfides were sputtered with a 10–15 nA O^- primary beam of 50 μm in diameter. Secondary $^{32}\text{S}^+$ and $^{34}\text{S}^+$ ions were analyzed in mono-collector mode without energy filtering at a mass resolution of 3000 as no sulfur hydrides were observed. The instrumental mass fractionation (the difference between $\delta^{34}\text{S}$ obtained with the ion probe and the true value) was determined at -47% using the internal standard GAV18 defined at 10.5‰ relative to V-CDT. Under normal conditions, the internal precision of S-isotope analysis is about 1.0‰. However, during the analytical period of

Table 3
Multiple sulfur isotope composition of secondary sulfide in ODP Hole 801C normalized to V-CDT scale

Sample	$\delta^{33}\text{S}$	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\delta^{33}\text{S}^*$	$\delta^{34}\text{S}^*$	$\Delta^{33}\text{S}^*$	Description
Sample 801C-17R1,100							
#2	-20.541	-39.665	-0.114	-20.755	-40.473	0.089	Polycrystalline pyrite grain disseminated along fracture in basalt groundmass with minor carbonate and saponite
#3	-20.656	-39.886	-0.115	-20.872	-40.703	0.090	
#4	-20.418	-39.422	-0.116	-20.629	-40.220	0.084	
#5	-21.529	-41.521	-0.146	-21.764	-42.408	0.076	
#6	-11.066	-21.385	-0.053	-11.128	-21.617	0.005	
Sample 801C-43R1,29/V							
#7	-19.178	-37.055	-0.095	-19.364	-37.759	0.082	Polycrystalline marcasite aggregate with minor pyrite disseminated in thick carbonate-rich vein
#8	-17.881	-34.556	-0.085	-18.043	-35.167	0.068	
Sample 801C-23R1,45							
#9	-13.356	-25.762	-0.089	-13.446	-26.100	-0.005	Local pyrite enrichment (polycrystalline aggregates) associated with carbonate-rich vesicles (1–3 mm wide)
Sample 801C-9R1,32							
#12	-11.496	-22.121	-0.104	-11.563	-22.369	-0.042	Polycrystalline marcasite aggregate disseminated in basalt groundmass

this study, reproducibility of the standard measured between each sample data point in the same polished section was somewhat poorer (2.0‰ at 95% confidence level for 40 analyses). This is mainly due to instability of the primary gun and/or change of instrumental bias during repositioning of the sample.

4. Results and discussion

4.1. ^{34}S – ^{32}S isotope profile through basaltic oceanic crust section

S-isotope analyses of bulk basalt and individual Fe-sulfide grains (pyrite and marcasite) display a large spread of $\delta^{34}\text{S}$ values from 1.3‰ down to -45 ‰ (Fig. 2). *In-situ* ion-microprobe analyses reveal that $\delta^{34}\text{S}$ values lower than -20 ‰ (e.g. sample 801B-43R1,29; 801C-39R2,28) are commonly found in pyrite and marcasite precipitated in open space of altered basalts, such as within mm thick carbonate veins, thin fractures lined with saponite or in vesicles (Fig. 3). In contrast, $\delta^{34}\text{S}$ values higher than -10 ‰ (e.g. sample 801C-27R1,50; 801C-37R1,83) are preferentially found for secondary sulfides disseminated within

the basalt matrix. Although significant isotopic variations of up to 10‰ occur at sub-mm scales, showing the existence of several generations of sulfide minerals having distinct S-isotope compositions (Fig. 3), no systematic $\delta^{34}\text{S}$ zonation within sulfide grains could be identified. As evident from Fig. 2, no clear trend can be drawn along the depth profile and highly negative $\delta^{34}\text{S}$ values analyzed by ion microprobe are found at the greatest depth (840 mbsf). As expected, S-isotope compositions of bulk rocks do not display the same degree of variability as for *in-situ* analysis and $\delta^{34}\text{S}$ values for both AVS and Cr-S vary between 0.9 and -15.8 ‰. In general, AVS yields higher $\delta^{34}\text{S}$ values than Cr-S by up to 5‰, although some samples (e.g. 801C-37R1,83) display inverse relationships. Less negative $\delta^{34}\text{S}$ values for AVS are explained by considering that AVS fraction preferentially sampled primary pyrrhotite having primordial isotope compositions ($\delta^{34}\text{S} \approx 0$ ‰). The SUPER composite yields negative $\delta^{34}\text{S}$ values of -2.7 ‰ for AVS and -8.4 ‰ for Cr-S, with the bulk sulfide-S (i.e., AVS+Cr-S) of the uppermost 440 m of volcanic basement at Site 801 having $\delta^{34}\text{S} = -6.8$ ‰.

Altered basalts at Site 801 are generally characterized by heterogeneous S concentrations (Table 1) ranging from values

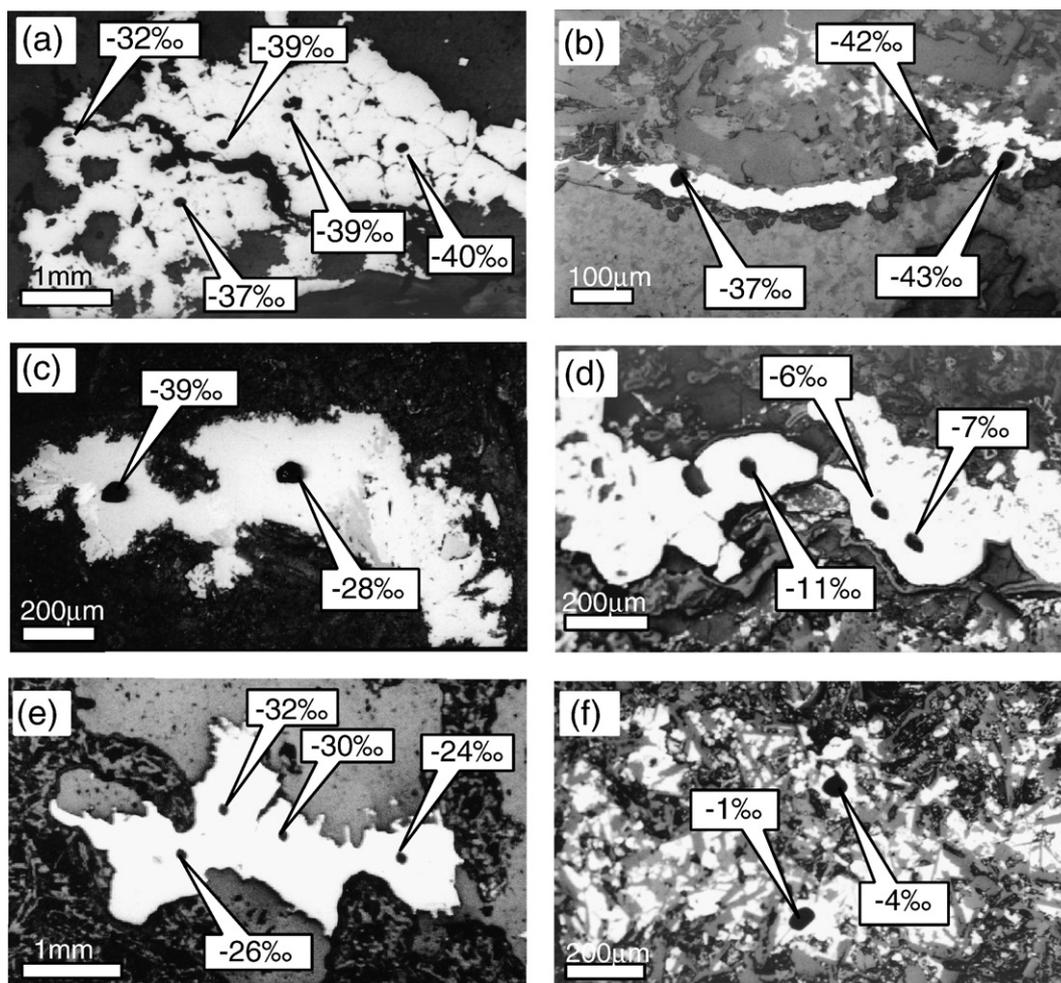


Fig. 3. Photomicrograph of pyrite and marcasite analyzed by ion microprobe with corresponding $\delta^{34}\text{S}$ values. (a) 801C-43R1,29/v; large polycrystalline aggregate of marcasite in 2-cm thick carbonate vein; (b) 801C-6R5,75; pyrite lining carbonate-rich vein; (c) sample 801C-9R1,32; marcasite enrichment in alteration halo; (d) 801C-17R1,100; pyrite in thin vein associated with saponite; (e) 801C-23R1,45; pyrite enrichment in basalt associated with vesicles filled with carbonate; (f) 801C-27R1,50; pyrite-rich patch within microdolerite with titanomagnetite needles intergrowth.

lower than 0.02% to values up to 1.28%. Based on electron microprobe analyses of fresh volcanic glass recovered through the 801C tholeiitic section, primary magmatic S contents are estimated, on average, to be 0.21 ± 0.06 wt.% (Fisk and Kelley, 2002). Since magma degassing at the seafloor leads to loss of, on average, one third of the sulfur in the melt (Moore and Fabbi, 1971), S concentration of the fresh crystalline 801C basalt section is estimated between 0.17 and 0.12 wt.%. Bulk rock analysis of altered basalts at ODP Site 801 (Table 1) reveals that some intervals may display S-enrichment relative to fresh basalts (S up to 1.30%, sample 801C-37R5,30) and negative $\delta^{34}\text{S}$ values (-12.9%). These discrete intervals are best explained by a net addition of secondary sulfide having negative $\delta^{34}\text{S}$. It should be also noted that S-depleted altered basalt, such as sample (801C-15R4,69) may also display minimal S-isotope fractionation, suggesting that sulfide oxidation may proceed without significant S-isotope fractionation.

An important question to address is whether these low and highly variable $\delta^{34}\text{S}$ values and S-enrichment through the basaltic oceanic crust section at ODP Site 801 result from the downward diffusion (or advection) of H_2S from overlying sediment section or result from *in-situ* S-isotope fractionation. Sediments at Site 801 are mostly oxidized pelagic sediments, composed of chert, porcellanite and volcanoclastic turbidites with very little organic carbon (Alt and Burdett, 1992). As a consequence, sulfate reduction is limited throughout the overlying sediment section at ODP Site 801, as demonstrated by porewater sulfate concentrations above 16 mM and the lack of detectable level of dissolved sulfide in porewaters (Alt and Burdett, 1992). In addition, the thick chert and porcellanite Units at 801 provide a low-permeability barrier to vertical diffusion between upper sediments and deeper volcanoclastic turbidites. These layers would have prevented diffusion of H_2S and nutrients into the basement from any organic rich sediments deposited in the high-productivity equatorial upwelling zone at about 90–80 Ma (Alt and Burdett, 1992).

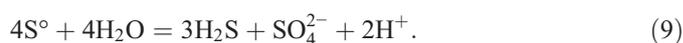
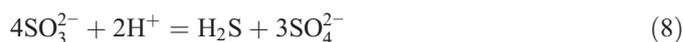
The fact that sedimentary pyrite at ODP Site 801 yields less negative $\delta^{34}\text{S}$ values (between -14 and -21% , Alt and Burdett, 1992) than for secondary pyrite in the underlying altered basement, together with the lack of a systematic downhole trend in $\delta^{34}\text{S}$ values along the volcanic section (Fig. 2) suggests an *in-situ* sulfate reduction origin for secondary sulfide in the volcanic basement at Site 801. In fact, the large heterogeneity of $\delta^{34}\text{S}$ values for secondary pyrite within individual samples (e.g. sample 801C-17R1,100; Table 2) is better explained by *in-situ* S-isotope fractionation within basement rather than sedimentary origin. Low $\delta^{34}\text{S}$ values of pyrite and marcasite in open space (veins) between -35 and -45% are thus consistent with open-system bacterial sulfate reduction under unlimited sulfate supply. In contrast, higher $\delta^{34}\text{S}$ values up to 0% could reflect either closed-system bacterial sulfate reduction or mixing between biogenic and igneous (i.e. unfractionated) sulfides.

It remains unclear, however, whether these highly negative $\delta^{34}\text{S}$ values down to -45% are generated by (1) abiotic fractionation during sulfide partial oxidation and reprecipitation, as suggested previously by Andrews (1979); (2) single-step bacterial sulfate reduction, as suggested from deep marine sediments

porewater studies (Wortmann et al., 2001); (3) bacterial disproportionation of intermediate S species, as commonly proposed for sedimentary sulfides (Canfield and Thamdrup, 1994). Comparisons between $\delta^{34}\text{S}$ values and S concentrations of altered basalts as well as multiple S-isotope systematics may help in solving these issues as described below.

4.2. Mechanisms of S loss and uptake during seafloor weathering

Andrews (1979) proposed that the partial oxidation of magmatic sulfides at low temperature could account for depletions in S as well as for the observed negative S-isotopic compositions. Because the partial oxidation of sulfide under conditions of limited oxygen supply could lead to the formation of unstable S species of intermediate oxidation state, i.e. sulfite SO_3^{2-} , thiosulfate $\text{S}_2\text{O}_3^{2-}$ and elemental S^0 (Zhang and Millero, 1993), the following disproportionation reactions may occur:



In principle, equilibrium fractionation of S isotopes between the oxidized and reduced species in reactions (7), (8) and (9) could lead to enrichment of ^{34}S in sulfate and a corresponding depletion of ^{34}S in sulfide (Ohmoto and Lasaga, 1982). However, the major drawback of this hypothesis is that it requires isotopic exchange between sulfate and sulfonate–sulfur of thiosulfate or sulfide–sulfur before pyrite precipitation. This is highly unlikely, considering the very slow rate, on the order of 10^6 yr, of equilibrium isotopic exchange between sulfide and sulfate at temperature <100 °C (Sakai and Dickson, 1978; Ohmoto and Lasaga, 1982). It has been also shown that the intramolecular isotope exchange of thiosulfate is sufficiently fast to produce isotopically light pyrite even at low temperature, mostly because the sulfonate S of thiosulfate is strongly enriched in ^{34}S relative to the sulfane S (Uyama et al., 1985; Chu et al., 2004). However, the disproportionation of thiosulfate (reaction 7) has been shown to proceed at very slow rates for temperatures below 120 °C (Uyama et al., 1985). In addition, recent studies (Bak and Cypionka, 1987; Jorgensen, 1990; Canfield and Thamdrup, 1994; Cypionka et al., 1998; Habicht et al., 1998) have demonstrated that the disproportionation reactions of thiosulfate, sulfite and elemental S in nature are more likely biologically catalyzed processes rather than inorganic reactions at low temperatures (i.e. <100 °C).

Because $\delta^{34}\text{S}$ values and S concentration of altered basalts may be controlled by the relative importance of the formation of SO_4^{2-} through complete oxidation (i.e., without isotope fractionation) and, potentially through partial oxidation (i.e., disproportionation) of intermediate S species, it is possible to predict theoretically the relationship between $\delta^{34}\text{S}$ values and S concentrations of altered basalts.

The distillation equation linking the fraction F of S loss during partial sulfide oxidation and the S-isotope ratios of the residual S pool ($\delta^{34}\text{S}_\beta$) is:

$$\delta^{34}\text{S}_\beta = (1000 + \delta^{34}\text{S}_0) * F^{(\alpha-1)} - 1000 \quad (10)$$

where $\delta^{34}\text{S}_0$ is the initial S-isotopic composition of basalt, α the fractionation factor between intermediate S species and sulfate generated by the reactions of S-disproportionation (7), (8) or (9). Examples of relationships between S-isotope composition and S concentration are presented in Fig. 4 for the case of complete S oxidation (i.e. no S-isotope fractionation) and partial oxidation reactions (curves (d) and (c) of Fig. 4, respectively).

We are not aware of experimental investigation of S-isotope fractionation during chemical (i.e. abiotic) disproportionation of intermediate S species which are relevant to low-temperature (i.e. <100 °C) conditions. Hence, partial S oxidation pathways are calculated using Eq. (10) in the case of microbial disproportionation reactions where ^{34}S enrichment in sulfate is 13‰. Smaller fractionation factors α near 1.004 can result from microbial disproportionation of thiosulfates ($\alpha=11$) and sulfite ($\alpha=1.009$) (Habicht et al., 1998) whereas the disproportionation of elemental S will result in larger fractionation factors ($\alpha=1.013$) (Canfield and Thamdrup, 1994). Smaller fractionation factors or a combination of complete S oxidation and disproportionation will produce S vs. $\delta^{34}\text{S}$ relationships lying between model curves (c) and (d) in Fig. 4. Hence, altered basalts with low S concentrations and $\delta^{34}\text{S}$ values are consistent with – but do not necessarily prove – S-isotope fractionation during partial S oxidation reactions. In contrast, altered basalts with negative $\delta^{34}\text{S}$ values but higher S concentrations (i.e. lying

on the right side of model curve (c) in Fig. 4) require a net addition of sulfides with low $\delta^{34}\text{S}$ values, which likely derived from the bacterial reduction of seawater sulfate.

In order to evaluate the effect of the addition of sulfide derived from the bacterial reduction of seawater sulfate with low $\delta^{34}\text{S}$ values, we calculated the theoretical mixing (*mix*) between basaltic S (*bas*) and biogenic S (*bio*) using the relation:

$$\delta^{34}\text{S}_{\text{mix}} = (\text{S}_{\text{bio}}\delta^{34}\text{S}_{\text{bio}} + \text{S}_{\text{bas}}\delta^{34}\text{S}_{\text{bas}}) / \text{S}_{\text{mix}} \quad (11)$$

where $\delta^{34}\text{S}_{\text{bio}}$ is calculated using the difference between $\delta^{34}\text{S}$ of Jurassic seawater ($\delta^{34}\text{S} \sim 15\text{‰}$, Claypool et al., 1980) and the fractionation factor during bacterial sulfate reduction. As presented in Fig. 4, all basalt samples (except one sample at 871 m depth) require a fractionation factor $\alpha_{\text{SO}_4\text{-H}_2\text{S}}$ larger than ~ 1.025 (curve (a), Fig. 4) in order to produce the observed $\delta^{34}\text{S}$ vs. S concentration relationships. The addition of S with highly negative $\delta^{34}\text{S}$ values are further confirmed by ion-microprobe analysis of individual pyrite showing the occurrence of $\delta^{34}\text{S}$ values down to -45‰ .

4.3. Timing of S loss and uptake during low-temperature alteration

Based on the scattered relationship between S concentration and $\delta^{34}\text{S}$ values seen in bulk rock (Fig. 4), it is evident that altered basalts at ODP 801 are affected by a combination of S-depletion during sulfide oxidation and secondary S-enrichment due to bacterial sulfate reduction. In most cases, basalt groundmass is affected by S loss due to oxidative seafloor weathering whereas saponite or calcite-rich veins may have secondary pyrite enrichment reflecting more reducing conditions. The timing of such S loss and enrichment is presently unclear but may represent various stages of alteration processes. Alt and Teagle (2003) defined the following multi-stage alteration sequence, which is similar to that described by Talbi and Honnorez (2003). Alteration started in places of high fluid/rock ratio, forming celadonite-rich and Fe-oxyhydroxide alteration halos along fractures. Alteration proceeded away from fractures and into the host rock where lower fluid/rock ratios and more reducing conditions favored the production of smectite and secondary pyrite. As redox conditions changed with time, the formation of phases characteristic of reducing conditions can be observed in previously oxidized rocks. Eventually the entire system became reducing, as demonstrated by the presence of late-stage veins of smectite, calcite, and pyrite. Calcite typically forms the latest minerals that cross-cut all others (Alt and Teagle, 1999) which is consistent with a long duration of alteration (> 50 Ma) as suggested by heat flow data and isotopic ages of secondary phases from the oceanic crust (Staudigel, 2003). Hence, precipitation of secondary pyrite in veins at Site 801 may continue for protracted periods, possibly up to 50 Ma after crust formation of ridge axis. This hypothesis is also consistent with a recent study of Re and Os concentrations and Os isotopic ratios in altered basalt at ODP Site 801 (Reisberg et al., in press) which suggest significant Re uptake during low-temperature alteration. Model ages of Re addition

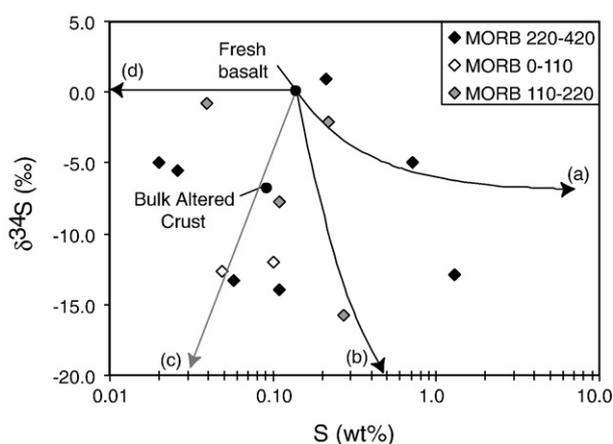


Fig. 4. Plot of S concentration vs. S-isotope composition of whole altered basalts at Site 801 (diamonds). The SUPER composite, representative of the bulk altered crust at Site 801 and fresh basalt are plotted for comparison. Arrows represent schematic trends. Curves (a) and (b) represent mixing lines between fresh basalt and secondary sulfides formed through dissimilatory sulfate reduction with fractionation factors of 1.025 and 1.045 respectively. Curve (c) represents possible evolutions of S concentration and $\delta^{34}\text{S}$ values during partial oxidation of igneous sulfides proceeding through disproportionation reactions and following a Rayleigh-type fractionation process (fractionation factor between forming SO_4^{2-} and intermediate S species is taken at 1.013 after Canfield and Thamdrup (1994)). Curve (d) represents the trend for primary sulfide dissolution (i.e. quantitative leaching).

for altered basalts range from 78 to 160 Ma, which likely represent the average ages of long-lived processes rather than specific events. Since secondary pyrite may have accommodated an important part of the input Re (Reisberg et al., in press), these relatively young model ages suggest that secondary pyrite precipitation may continue for tens of millions of years after crust formation.

Microbial communities that colonize the basaltic surface layer at mid-oceanic ridges may become buried below several hundred meters during seafloor spreading and ageing of the oceanic crust. The microbial community may either die during burial or persist to generate deep biosphere in the ocean crust. The highly negative and heterogeneous $\delta^{34}\text{S}$ values of late-stage pyrite found at a depth of up to 834 mbsf (i.e. 340 m into the basement) demonstrate that there is active S-based metabolism during aging of the altered ocean crust at ODP Site 801.

4.4. ^{34}S – ^{33}S – ^{32}S isotope biosignatures in secondary sulfides in oceanic basement

Multiple sulfur-isotope systems provide unique constraints that are not attainable by conventional $\delta^{34}\text{S}$ analyses alone (Farquhar et al., 2003; Johnston et al., 2005; Ono et al., 2006). The isotope composition of primordial sulfur (e.g. primary sulfide in basalt) is defined at $\Delta^{33}\text{S}=0\text{‰}$ (Fig. 5). Analyses of modern seafloor hydrothermal sulfide minerals and vent fluid H_2S show a slight enrichment of ^{33}S ($<0.03\text{‰}$) which are interpreted to reflect local isotope exchange between seawater sulfate and vent sulfide at temperatures $>300\text{ °C}$ occurring near or at the seafloor (Ono et al., 2007). In contrast, biogenic sulfide data (Ono et al., 2007) plot above the equilibrium mass-dependent fractionation line between SO_4^{2-} and H_2S ($^{33}\alpha \approx ^{34}\alpha^{0.515}$, Fig. 5), consistent with experimental studies showing that microbial sulfate reduction follows a slightly different mass-dependent law ($^{33}\alpha \approx ^{34}\alpha^{0.512}$, (Farquhar et al., 2003; Johnston et al., 2005).

Results of multiple sulfur-isotope analyses at ODP Site 801 are presented in Fig. 5 and define a unique domain in $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ relationships which is strikingly different from natural hydrothermal and sedimentary biogenic pyrite measured in previous studies (Ono et al., 2006; Ono et al., 2007). These data show at least two generations of secondary pyrite in altered basalt. One is depleted in ^{34}S with $\delta^{34}\text{S}$ ranging from -34.5 to -41.5‰ , and plots on the equilibrium mass-fractionation line with respect to seawater sulfate, suggesting that these sulfides are derived from reduction of seawater sulfate through near-equilibrium processes. The apparent equilibrium isotope fractionation factor α between sulfate and sulfide ranges from 1.056 to 1.062 which corresponds to an equilibration temperature of $\sim 60\text{ °C}$, consistent with the estimated temperature of basalt alteration (Alt and Teagle, 2003). In Fig. 5, the equilibrium fractionation line is calculated based on equilibrium S-isotope fractionation between H_2S and present day seawater sulfate (Ono et al., 2007). Since the $\delta^{34}\text{S}$ of seawater sulfate has varied in the past, increasing from the present day value of 21‰ to about 23‰ in the Miocene, then decreasing to about 15‰ in the lower Cretaceous (Claypool et al., 1980), $\Delta^{33}\text{S}$ values of sea-

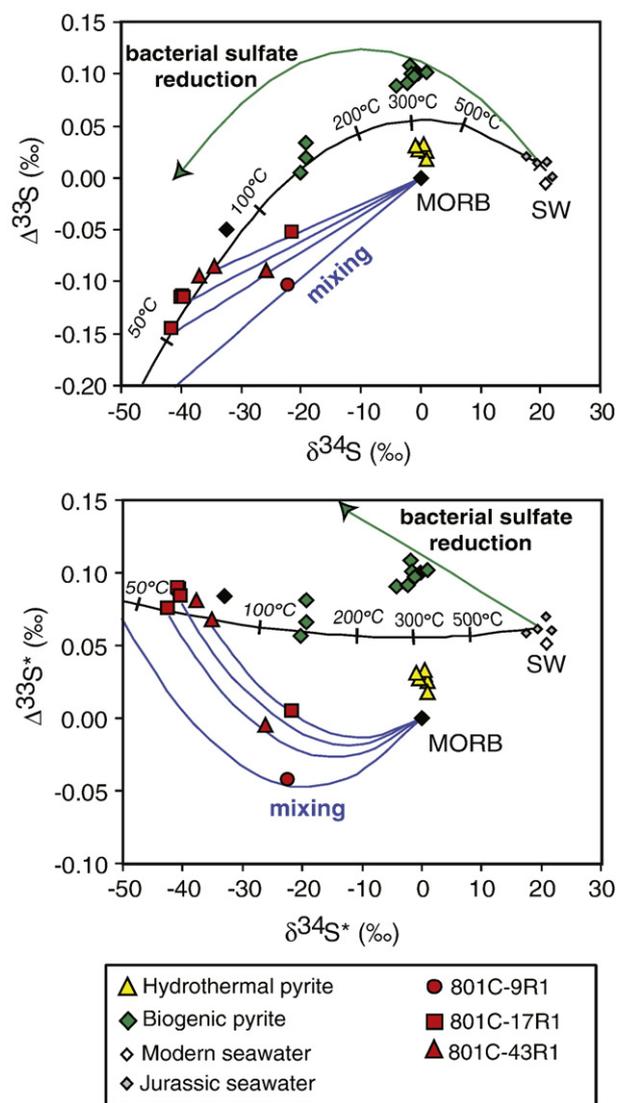


Fig. 5. $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}^*$ vs. $\Delta^{33}\text{S}^*$ compositions of secondary sulfides from Site 801 compared with sedimentary biogenic sulfides (Ono et al., 2006) and hydrothermal pyrite from mid-ocean ridges (Ono et al., 2007). MORB = Mid-ocean ridge basalt, estimated from the analysis of Canyon Diablo Troilite (CDT) which is representative of primordial sulfur in fresh mid-ocean ridge basalt (Ono et al., 2007). SW = Modern to Jurassic seawater determined by the analysis of carbonate-associated sulfate (Ono and Lyons, unpub results) and modern marine sulfate (Ono et al., 2007). Various examples of mixing lines between igneous S and secondary sulfides from Site 801 are plotted. The isotope composition of H_2S in isotope equilibrium with seawater SO_4^{2-} (SW) as a function of temperature is described by the solid black line (after Ono et al., 2007). The isotope composition of H_2S produced by bacterial sulfate reduction using fractionation lines experimentally determined by Farquhar et al. (2003) is also shown for comparison.

water sulfate would have been also different for the past. Multiple S-isotope analysis of carbonate-associated sulfate of Jurassic age (184–176 Ma) (Ono and Lyons, unpub results), however, yields $\Delta^{33}\text{S}$ values between 0.001 and 0.02‰, which are not significantly different from that of modern seawater (Fig. 5).

Another set of sulfides are characterized by intermediate $\delta^{34}\text{S}$ values ranging from -21.4 to -25.8‰ and plot below the equilibrium mass-fractionation line. In order to evaluate the

relationships between these two groups of data, we calculated various mixing lines in $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ coordinates (Fig. 5) between secondary pyrite and magmatic sulfides. The results suggest that pyrite with $\delta^{34}\text{S}$ values ranging from -21.4 to -25.8% are best explained by mixing of primary basaltic sulfide with sulfides that are isotopically equilibrated with seawater sulfate and having $\delta^{34}\text{S}$ values $< -34.5\%$. In one case, it appears that the addition of secondary pyrite with $\delta^{34}\text{S}$ as low as -50% is required for sample 801C-9R1 but such extremely depleted $\delta^{34}\text{S}$ values have not been found using *in-situ* techniques.

The most striking feature of the multiple sulfur-isotope systematics at ODP Site 801 is the demonstration of near-equilibrium isotope exchange between pyrite and seawater sulfate at temperature below $100\text{ }^\circ\text{C}$. Extrapolating the rate law obtained for high-temperature experiments to $70\text{ }^\circ\text{C}$, the timescale for 90% isotope exchange between SO_4^{2-} and H_2S , is on the order of 10^7 yr (Ohmoto and Lasaga, 1982; Sakai, 1983). Considering that pyrite formed relatively rapidly in altered basalts due to the abundance of reactive Fe for pyrite formation in altered basalt (e.g. Fe-oxyhydroxides along veins and alteration halos), it is likely that the H_2S residence time is shorter than the timescale of isotope exchange between H_2S and SO_4^{2-} . Once pyrite formed, the rate of heterogeneous isotope exchange between seawater SO_4^{2-} and pyrite can be considered negligible and pyrite would preserve its initial $\delta^{34}\text{S}$ value. Hence, such large isotope fractionation factors in pyrite reflect more likely biologically catalyzed processes (i.e. enzyme-catalyzed) rather than inorganic reactions.

It is important to note that questions remain about the magnitude of isotope fractionation during microbial sulfate reduction. Culture studies have shown a maximum fractionation factor of 45% (e.g. Canfield, 2002) although fractionations as low as 2% and as large as 72% have been also observed in natural samples (Chambers and Trudinger, 1979; Detmers et al., 2001; Wortmann et al., 2001). As proposed previously for sedimentary sulfides (Canfield and Thamdrup, 1994), bacterial disproportionation of intermediate S species is thought to be required to explain sulfide having $\delta^{34}\text{S}$ values lower than -45% with respect to sulfate (Canfield and Teske, 1996).

Culture based studies by Johnston et al. (2005) and Farquhar et al. (2003) have determined $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ relationships for sulfur compounds associated with dissimilatory sulfate reduction, elemental sulfur disproportionation and sulfite disproportionation. These studies showed that sulfide produced by sulfate reduction follows a trajectory along the biological sulfate reduction line ($^{33}\alpha \approx ^{34}\alpha^{0.512}$) as presented in Fig. 5. These studies also showed that sulfite disproportionation follows a similar relationship ($^{33}\alpha \approx ^{34}\alpha^{0.512}$) when isotope ratios of sulfide are compared with those of reactant (e.g. sulfite). According to Table 2 of Johnston et al. (2005), the mass-dependent exponent $^{33}\theta$ values during sulfite disproportionation range from 0.5103 to 0.5107 for *D. thiozymogenes* and 0.512 for *D. sulfodismutans* when $^{33}\theta$ values are calculated between substrate and product pairs (i.e., sulfite and sulfide) and not between two products (i.e., sulfate and sulfide). These $^{33}\theta$ values are within the range for sulfate reducers ($^{33}\theta$ between 0.5077 and 0.5125) considering sulfate–sulfide pairs (Farquhar et al., 2003; Johnston et al., 2005, 2007). Thus, additional isotope effect associated with dispropor-

tionation of intermediate sulfur species would still follow the biological fractionation line defined by sulfate reducers. Using available experimental studies, it is therefore difficult to explain our data from 801C that show equilibrium with seawater sulfate using available experimental studies. Different environmental factors and growth conditions may result in different multiple sulfur-isotope relationships between natural systems and culture experiments. In particular, pure culture experiments, such as those performed by Johnston et al. (2005) are optimized for a maximum growth with organic substrate in excess. In contrast, natural sulfate-reducing bacteria populations may frequently experience organic substrate-limitation in the environment and generally represent a higher diversity of populations which are not investigated in pure culture fractionation studies.

Considering the putative very low metabolic activity of the deep bacterial biosphere (Parkes et al., 1994; D'Hondt et al., 2002), it is likely that bacterial sulfur metabolisms in altered basement proceeds at a very low rate. Hence, we tentatively interpret the equilibrium S-isotope fractionation between seawater sulfate and secondary pyrite at 801 as the result of bacterial sulfate reduction proceeding at very slow rate with significant back-oxidation of sulfide due to bacterial disproportionation or abiotic reactions. Such a feature may be expected for S metabolism that is limited by nutrient and energy availabilities, consistent with endolithic communities in altered oceanic crust.

4.5. S-isotope budget and implication for the significance of the deep biosphere in volcanic basement

Based on the analysis of the SUPER composite, the bulk altered tholeiitic section recovered in Hole 801C yields an average S concentration of 0.09% , which corresponds to a net loss of ca. $30\text{--}40\%$ of basaltic S during seafloor weathering (considering that S concentration of the fresh crystalline 801C basalt section is between 0.17 and 0.12 wt.%). This confirms previous studies showing that the upper 300 m of the oceanic crust have undergone a net depletion in S due to primary sulfide oxidation (Andrews, 1979; Alt, 1995). However, S-isotope composition of the SUPER composite yields negative $\delta^{34}\text{S}$ values of -6.8% , suggesting significant S gain due to bacterial sulfate reduction that only partially offsets the S loss during seafloor weathering.

Using mass balance considerations between end-member biogenic S with minimum $\delta^{34}\text{S}$ values at around -40% and igneous sulfides ($\delta^{34}\text{S}=0\%$), we calculate that, on average, a minimum of ca. 17% of pyrite-S in altered basalts at Site 801 is derived from bacterial reduction of seawater sulfate. This translates into a minimum of ca. $5\text{ }\mu\text{mol/g}$ of seawater sulfate that is reduced and added to the crust. Using an upper crustal section of 440 m of 165 Ma-old altered crust with an average density of 2.8 g/cm^3 , we calculate a minimum global flux of bacterially reduced sulfate in the upper basaltic crust of ca. $4 \times 10^{-9}\text{ mol cm}^{-2}\text{ yr}^{-1}$. Recent estimates of subsurface microbial activity in marine sediments suggest a global sulfate flux of 2.8×10^{-9} to $13 \times 10^{-9}\text{ mol cm}^{-2}\text{ yr}^{-1}$ for sulfate-rich open-ocean sites (D'Hondt et al., 2002). Hence, our results suggest that bacterial sulfate reduction within the basaltic crust may be

comparable to that in deep-seated heterotrophic systems but is still at least two to three orders of magnitude lower than at ocean-margin sites.

An important aspect of this study is the question of the energy source available to sustain microbial metabolism in basaltic basement. Previous studies suggested that autotrophic organisms such as Fe-oxidizers may be present in the youngest basalts formed at mid-oceanic ridges, whereas older basalts seem to be dominated by heterotrophic organisms (Thorseth et al., 2001). In addition to the potential C-sources available from primary biomass production, supplemental sources of organic C may exist when advective or diffusive exchange takes place between sediment porewaters and basalt aquifers. Although the sediments at Site 801 are mostly oxidized pelagic sediments, with low organic carbon content (Alt and Burdett, 1992), it is possible that a significant source of nutrient and electron donors such as CH₄ and NH₄⁺ may be transported from the overlying sediment across the sediment/basement interface (D'Hondt et al., 2004) without significant H₂S production in the sediments. Production of small quantities of H₂ during seawater/basalt interactions may also support significant autotrophic sulfate reducer communities (Bach and Edwards, 2003) such as those suggested to be active during seafloor serpentinization at low temperatures (Alt and Shanks, 1998). Although the nature of electron donors (H₂ or organic matter) in basaltic ridge flank systems is uncertain, our results show they provide an important fuel for microbial sulfate reduction.

We note that that no additional source of energy is needed to sustain a population of S-disproportionating bacteria because only CO₂ serves as a carbon source (Bak and Cypionka, 1987; Cypionka et al., 1998). Bacteria able to disproportionate chemo-lithotrophically inorganic compounds appear to be widespread in anoxic sediments (Thamdrup et al., 1993) and they could be also present in basaltic environments. Because several strains of sulfate-reducing bacteria can also develop S-disproportionation-based metabolism (Cypionka et al., 1998), microbial communities in the basaltic crust could potentially adapt to changing C-sources and sulfate availability.

5. Conclusions

Previous studies have reported ubiquitous fractionation of sulfur isotopes in altered volcanic rocks but interpretations based on abiotic fractionation between intermediate sulfur species formed during basalt alteration have been preferred. In this paper, we revisited the use of S isotopes as biosignatures in altered oceanic crust at ODP Site 801. *In-situ* ion-probe $\delta^{34}\text{S}$ analyses were used to enable fine-scale assessment of isotopic variations in secondary sulfides and revealed highly negative ($\delta^{34}\text{S}$ down to -45‰) and heterogeneous $\delta^{34}\text{S}$ values found at a depth of 834 m below seafloor (i.e. 340 m into the basement). These results constitute among the clearest evidence for widespread microbial activity in basaltic ocean crust. Bulk rock S concentrations ranging from 0.02% up to 1.28% and $\delta^{34}\text{S}$ values ranging from 0.9‰ to -16‰ are consistent with loss of magmatic primary mono-sulfide and addition of secondary sulfide via microbial sulfate reduction. High-precision multiple

S-isotope (^{32}S , ^{33}S , ^{34}S) analyses show that secondary sulfides exhibit mass-dependent equilibrium fractionation relative to seawater sulfate, consistent with sulfate reduction at low temperature, below 70 °C. The relationship between $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values suggests that bacterial sulfate reduction proceeds at very low metabolic rates. Finally, the determination of the S-isotope composition of bulk altered oceanic crust demonstrates that S-based metabolic activity of subsurface life in oceanic basalt is widespread, and can affect the global S budget in oceanic crust.

Although it is possible that secondary pyrite at Site 801 may form during protracted periods, probably up to 50 Ma after crust formation of ridge axis, additional work is required to better constraint the timing of microbial activity. Microbial communities that colonize the basaltic surface layer at mid-oceanic ridges may become buried below several hundred meters during seafloor spreading and aging of the oceanic crust, but could also enter the basement during fluid exchange with overlying sediments as the crust is buried. Identifying and culturing these widespread deep-endolithic microorganisms in igneous oceanic basement may provide a unique opportunity to test the metabolic limit of microbial life, its relationship with the subsurface biosphere in sediments and its role in affecting chemical exchange between the ocean and lithosphere.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.01.010.

References

- Alt, J.C., 1995. Sulfur isotopic profile through the oceanic crust: sulfur mobility and seawater–crustal sulfur exchange during hydrothermal alteration. *Geology* 23, 585–588.
- Alt, J.C., Burdett, J.W., 1992. Sulfur in Pacific deep-sea sediments (Leg 129) and implications for cycling of sediment in subduction zones. In: Larson, R.L., Lancelot, Y. (Eds.), *Proc. ODP, Sci. Res.*, vol. 129. Ocean Drilling Program, College Station, TX, pp. 283–294.
- Alt, J.C., Shanks, W.C., 1998. Sulfur in serpentinized oceanic peridotites: serpentinization processes and microbial sulfate reduction. *J. Geophys. Res.* 103, 9917–9929.

- Alt, J.C., Teagle, D.A.H., 1999. The uptake of carbon during alteration of ocean crust. *Geochim. Cosmochim. Acta* 63, 1527–1535.
- Alt, J.C., Teagle, D.A.H., 2003. Hydrothermal alteration of upper oceanic crust formed at a fast-spreading ridge: mineral, chemical, and isotopic evidence from ODP Site 801. *Chem. Geol.* 201, 191–211.
- Alt, J.C., Davidson, G.J., Teagle, D.A.H., Karson, J.A., 2003. Isotopic composition of gypsum in the Macquarie Island ophiolite: implications for the sulfur cycle and the subsurface biosphere in oceanic crust. *Geology* 31, 549–552.
- Andrews, A.J., 1979. On the effect of low-temperature seawater interaction on the distribution of sulfur in oceanic crust, layer 2. *Earth Planet. Sci. Lett.* 46, 68–80.
- Bach, W., Edwards, K.J., 2003. Iron and sulfide oxidation within the basaltic ocean crust: Implications for chemolithoautotrophic microbial biomass production. *Geochim. Cosmochim. Acta* 67, 3871–3887.
- Bak, F., Cypionka, H., 1987. A novel type of energy metabolism involving fermentation of inorganic compounds. *Nature* 326, 891–892.
- Canfield, D.E., 2002. Biogeochemistry of sulfur isotopes. In: Valley, J.W., Cole, D.R. (Eds.), *Stable Isotope Geochemistry*: Mineralogical Society of America. *Reviews in Mineralogy*, pp. 607–633.
- Canfield, D.E., Teske, A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature* 382, 127–132.
- Canfield, D.E., Thamdrup, B., 1994. The production of ^{34}S depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* 266, 1973–1975.
- Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.* 54, 149–155.
- Chambers, L.A., Trudinger, P.A., 1979. Microbiological fractionation of stable sulfur isotopes: a review and critique. *Geomicrobiol. J.* 1, 249–293.
- Chaussidon, M., Demange, J.C., 1988. Instrumental mass fractionation in ion microprobe studies of sulphur isotopic ratios. In: Benninghoven, A., Huber, A.M., Werner, H.W. (Eds.), *Secondary Ion Mass Spectrometry VI*. John Wiley Sons, New York, pp. 937–940.
- Chu, X., Ohmoto, H., Cole, D.R., 2004. Kinetics of sulfur isotope exchange between aqueous sulfide and thiosulfate involving intra- and intermolecular reactions at hydrothermal conditions. *Chem. Geol.* 211, 217–235.
- Claypool, G.C., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations. *Chem. Geol.* 28, 199–260.
- Coplen, T.B., Krouse, H.R., 1998. Sulphur isotope data consistency improved. *Nature* 392, 32.
- Cypionka, H., Smock, A., Böttcher, M.E., 1998. A combined pathway of sulfur compound disproportionation in *Desulfovibrio desulfuricans*. *FEMS Microbiol. Lett* 166, 181–186.
- D'Hondt, S., Rutherford, S., Spivack, A., 2002. Metabolic activity of subsurface life in deep-sea sediments. *Science* 295, 2067–2070.
- D'Hondt, S., Jorgensen, B.B., Miller, D.J., et al., 2004. Distributions of microbial activities in deep seafloor sediments. *Science* 306, 2216–2221.
- Detmers, J., Bruchert, V., Habicht, K.S., Kuever, J., 2001. Diversity of sulfur isotope fractionation by sulfate-reducing prokaryotes. *Appl. Environ. Microbiol.* 67, 888–894.
- Farquhar, J., et al., 2003. Multiple sulphur isotopic interpretations of biosynthetic pathways; implications for biological signatures in the sulphur isotope record. *Geobiology* 1, 27–36.
- Field, C.W., Dymond, J.R., Heath, G.R., Corliss, J.B., Dasch, E.J., 1976. Sulfur isotope reconnaissance of epigenetic pyrite in ocean-floor basalts, Leg 34 and elsewhere. *Initial Reports of the DSDP*, vol. 34, pp. 381–384.
- Fisk, M., Kelley, K., 2002. Probing the Pacific's oldest MORB glass: mantle chemistry and melting conditions during the birth of the Pacific Plate. *Earth Planet. Sci. Lett.* 202, 741–752.
- Fisk, M.R., Giovannoni, S.J., Thorseth, I.H., 1998. Alteration of oceanic volcanic glass: textural evidence of microbial activity. *Science* 281, 978–980.
- Furnes, H., Muehlenbachs, K., Torsvik, T., Thorseth, I.H., Tumyr, O., 2001. Microbial fractionation of carbon isotopes in altered basaltic glass from the Atlantic Ocean, Lau Basin and Costa Rica Rift. *Chem. Geol.* 173, 313–330.
- Gao, X., Thiemens, M.H., 1991. Systematic study of sulfur isotopic composition in iron meteorites and the occurrence of excess ^{33}S and ^{36}S . *Geochim. Cosmochim. Acta* 55, 2671–2679.
- Govindaraju, K., Mevelle, G., 1987. Fully automated dissolution and separation methods for inductively coupled plasma-atomic emission spectrometry rock analysis. Application to the determination of rare earth elements. *J. Anal. At. Spectrom.* 2, 615–621.
- Habicht, K.S., Canfield, D.E., Rethmeier, J., 1998. Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite. *Geochim. Cosmochim. Acta* 62, 2585–2595.
- Hu, G.X., Rumble, D., Wang, P.L., 2003. An ultraviolet laser microprobe for the insitu analysis of multisulfur isotopes and its use in measuring Archean sulfur isotope mass-independent anomalies. *Geochim. Cosmochim. Acta* 67, 3101–3118.
- Hulston, J.R., Thode, H.G., 1965. Variations in the S^{33} , S^{34} , and S^{36} contents of meteorites and their relation to chemical and nuclear effects. *J. Geophys. Res.* 70, 3475–3484.
- Johnston, D.T., et al., 2005. Multiple sulfur isotope fractionations in biological systems: a case study with sulfate reducers and sulfur disproportionators. *Am. J. Sci.* 305, 645–660.
- Johnston, D.T., Farquhar, J., Canfield, D.E., 2007. Sulfur isotope insights into microbial sulfate reduction: when microbes meet models. *Geochim. Cosmochim. Acta* 71, 3929–3947.
- Jorgensen, B.B., 1990. A thiosulfate shunt in the sulfur cycle of marine sediments. *Science* 249, 152–154.
- Kelley, K.A., Plank, T., Ludden, J., Staudigel, H., 2003. Composition of altered oceanic crust at ODP Sites 801 and 1149. *Geochem. Geophys. Geosyst.* 4. doi:10.1029/2002GC000435.
- Koppers, A.A.P., Staudigel, H., Duncan, R.A., 2003. High-resolution $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the oldest oceanic basement basalts in the western Pacific basin. *Geochem. Geophys. Geosyst.* 4. doi:10.1029/2003GC000574.
- Krouse, H.R., Brown, H.M., Farquharson, R.B., 1977. Sulphur isotope compositions of sulphides and sulphates, DSDP Leg 37. *Can. J. Earth Sci.* 14, 787–793.
- Larson, R.L., Lancelot, Y., ShipboardScientificParty, 1992. *Proc. ODP, Sci. Results*, vol. 129. CollegeStation, TX.
- Miller, M.F., 2002. Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system; an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* 66, 1881–1889.
- Moore, J.G., Fabbri, B.P., 1971. An estimate of the juvenile sulfur content of basalt. *Contrib. Mineral. Petrol.* 41, 105–118.
- Ohmoto, H., Lasaga, A.C., 1982. Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochim. Cosmochim. Acta* 46, 1727–1745.
- Ono, S., Wing, B.A., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent fractionation of quadruple sulfur isotope system as a new tracer of sulfur biogeochemical cycles. *Geochim. Cosmochim. Acta* 70, 2238–2252.
- Ono, S., Shanks III, W.C., Rouxel, O.J., Rumble, D., 2007. Multiple-sulfur isotope constraints on the seawater sulfate contribution in modern seafloor hydrothermal sulfide. *Geochim. Cosmochim. Acta* 71, 1170–1182.
- Parkes, R.J., et al., 1994. Deep bacterial biosphere in Pacific Ocean sediments. *Nature* 371, 410–413.
- Plank, T., Ludden, J.N., Escutia, C., et al., 2000. *Proc. ODP, Init Repts.*, vol. 185. College Station (TX).
- Pockalny, R.A., Larson, R.L., 2003. Implications for crustal accretion at fast spreading ridges from observations in Jurassic oceanic crust in the western Pacific. *Geochem. Geophys. Geosyst.* 4. doi:10.1029/2001GC000274.
- Pringle, M., 1992. Radiometric ages of basaltic basement recovered at Sites 800, 801, and 802, Leg 129, western Pacific Ocean. In: Y.L., R.L., Larson, Fisher, A., Winterer, E.L. (Eds.), *Proc. Ocean Drill. Program, Sci. Results*, vol. 129. Ocean Drilling Program, Texas A&M University, College Station, pp. 389–404.
- Puchelt, H., Prichard, H.M., Berner, Z., Maynard, J., 1996. Sulfide mineralogy, sulfur content, and sulfur isotope composition of mafic and ultramafic rocks from Leg 147. *Proceedings of the Ocean Drilling Program, Scientific Results*, vol. 147. Ocean Drilling Program, College Station, TX, pp. 91–101.
- Reisberg, L., Rouxel, O., Ludden, J., Staudigel, H., Zimmermann, C., in press. Re-Os results from ODP Site 801: evidence for extensive Re uptake during alteration of oceanic crust. *Chem. Geol.* doi:10.1016/j.chemgeo.2007.07.013.

- Revillon, S., Barr, S.R., Brewer, T.S., Harvey, P.K., Tarney, J., 2002. An alternative approach using integrated gamma-ray and geochemical data to estimate the inputs to subduction zones from ODP Leg 185, Site 801. *Geochem. Geophys. Geosyst.* 3. doi:10.1029/2002GC000344.
- Rice, C.A., Tuttle, M.L., Reynolds, R.L., 1993. The analysis of forms of sulfur in ancient sediments and sedimentary rocks: comments and cautions. *Chem. Geol.* 107, 83–95.
- Sakai, H., 1983. Sulfur isotope exchange rate between sulfate and sulfide and its application. *Geothermics* 12, 111–117.
- Sakai, H., Dickson, F.W., 1978. Experimental determination of the rate and equilibrium fractionation factors of sulfur isotope exchange between sulfate and sulfide in slightly acid solutions at 300 °C and 1000 bars. *Earth Planet. Sci. Lett.* 30, 151–161.
- Staudigel, H., 2003. Hydrothermal alteration processes. In: Holland, H., Turekian, K. (Eds.), *Treatise of Geochemistry*, pp. 511–537.
- Staudigel, H., Hart, S.R., 1983. Alteration of basaltic glasses: mechanisms and significance for the oceanic crust–seawater budget. *Geochim. Cosmochim. Acta* 47, 337–350.
- Talbi, E.H., Honnorez, J., 2003. Low-temperature alteration of Mesozoic oceanic crust, ODP Leg 185. *Geochem. Geophys. Geosyst.* 4. doi:10.1029/2002GC000405.
- Thamdrup, B., Finster, K., Hansen, W., Bak, F., 1993. Bacterial disproportionation of elemental sulfur coupled to chemical reduction of iron and manganese. *Appl. Environ. Microbiol.* 59, 101–108.
- Thorseth, I.H., Furnes, H., Heldal, M., 1992. The importance of microbiological activity in the alteration of natural basaltic glass. *Geochim. Cosmochim. Acta* 56, 845–850.
- Thorseth, I.H., Torsvik, T., Torsvik, V., Daae, F.L., Pedersen, R.B., 2001. Diversity of life in ocean floor basalt. *Earth Planet. Sci. Lett.* 194, 31–37.
- Uyama, F., Chiba, H., Kusakabe, M., Sakai, H., 1985. Sulfur isotope exchange reactions in the aqueous system: thiosulfate–sulfide–sulfate at hydrothermal temperature. *Geochem. J.* 19, 301–315.
- Wortmann, U.G., Bernasconi, S.M., Bottcher, M.E., 2001. Hypersulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology* 29, 647–650.
- Young, E.D., Galy, A., Nagahara, H., 2002. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* 66, 1095–1104.
- Zhang, J.-Z., Millero, F.J., 1993. The products from the oxidation of H₂S in seawater. *Geochim. Cosmochim. Acta* 57, 1705–1718.