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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 ^{34}S relative to igneous sulfides. Although these ^{34}S 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 (^{32}S, ^{33}S, ^{34}S) 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 $\delta^{34}S$ values, between −45‰ and 1‰, whereas bulk rock $\delta^{34}S$ analyses yield a more restricted range of −15.8 to 0.9‰. These low and variable $\delta^{34}S$ 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 ($^{32}S/^{33}S/^{34}S$) analyses suggest that secondary sulfides exhibit mass-dependent equilibrium fractionation relative to seawater sulfate in both $\delta^{33}S$ and $\delta^{34}S$ 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.

Keywords: sulfur isotopes; seafloor weathering; deep biosphere; oceanic crust; sulfur cycle

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 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

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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 $\delta^{34}S$ values generally range from basaltic values at 0‰ to highly negative values down to −50‰. Although these negative $\delta^{34}S$ 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, $S_2O_3^{2-}$) 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 $\delta^{34}S$ values (26.2 to 29‰) of preserved gypsum in exposed ophiolitic oceanic crust have been interpreted 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 $\delta^{34}S$ 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 $\delta^{34}S$ analyses were undertaken to document isotopic heterogeneity and textural relationship for secondary sulfides in altered rocks and veins. Second, analyses of multiple S isotopes ($^{32}S/^{33}S/^{34}S$) for selected secondary sulfides in the altered basalts were used to constrain multiple sulfur-isotope relationships between primordial sulfur and seawater sulfate. Analysis of $\delta^{33}S$ combined with standard $\delta^{34}S$ 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.

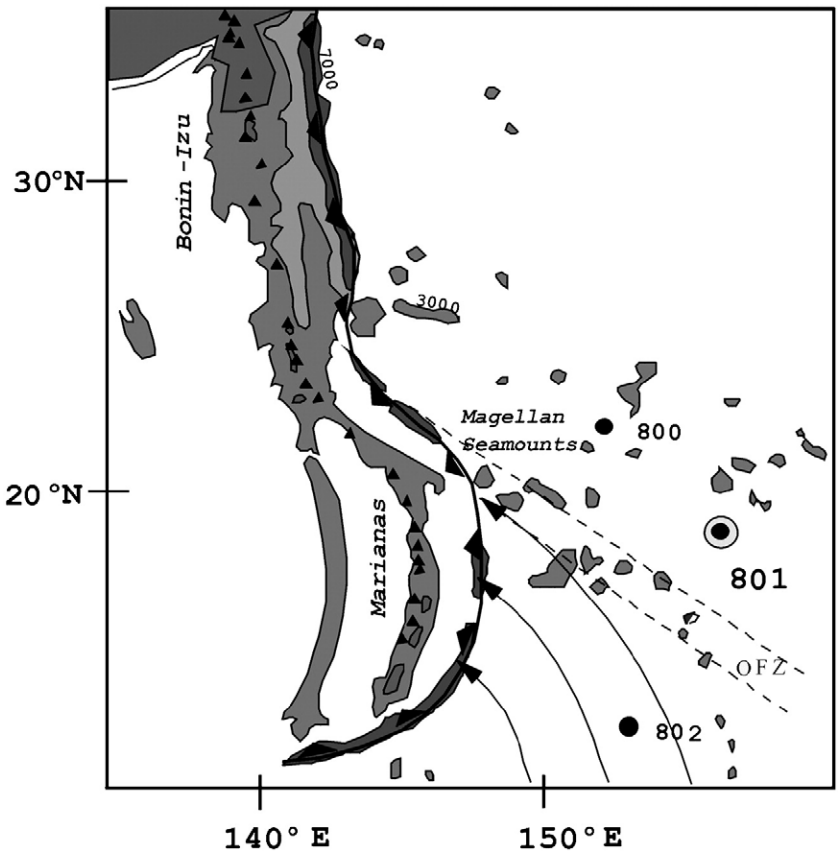

Fig. 1. Map of the West Pacific (Izu and Mariana arcs) and location of ODP Hole 801C drilled during Leg 129 and 185. Modified after Plank et al. (2000).