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Recycled Archean sulfur in the mantle wedge of the Mariana Forearc and microbial sulfate reduction within an extremely alkaline serpentine seamount

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ABSTRACT

The identification of microbial activity under extreme conditions is important to define potential boundaries of the habitable and uninhabitable zones of terrestrial and extraterrestrial living forms. The subseafloor regimes of serpentinite seamounts in the Mariana Forearc are among the most extreme environments for life on earth owing to the widespread presence of highly alkaline fluids with pH values greater than 12. The potential activity of sulfate-reducing microorganisms has been suggested within the South Chamorro serpentinite seamounts on the basis of depletion of sulfate and enrichment of dissolved sulfide in pore water. However, the vertical distribution of sulfate-reducing microorganisms and the origin of sulfate are still uncertain. To address these issues, we analyzed quadruple sulfur isotopes of sulfide minerals and pore water sulfate in the upper 56 m of sedimentary sequences at the summit of the S. Chamorro Seamount and those of dissolved sulfate in upwelling fluids collected as deep as 202 mbsf (meters below the seafloor) in a cased hole near the summit of the same seamount. The depth profiles of the concentrations and the δ^{34}S and Δ^{33}S′ values of sulfide minerals and pore water sulfate indicate microbial sulfate reduction as deep as 30 mbsf. Further, apparent isotopic fractionations ($^{34}\varepsilon$) and exponents of mass dependent relationships ($^{33}\lambda$) during sulfate reduction are estimated to be 62 ± 14‰ and 0.512 ± 0.002, respectively. The upwelling fluids show both the chlorine depletion relative to seawater and the negative δ^{15}N values of ammonia (−4‰). Although these signatures point to dehydration of the subducting oceanic plate, the negative Δ^{33}S′ values of sulfate (−0.16‰ to −0.26‰ with analytical errors of ±0.01‰) are unlikely to originate from surrounding modern crusts. Instead, sulfate in the upwelling fluid likely possess non-mass-dependent (NMD) sulfur. Because NMD sulfur was produced primarily in the Archean atmosphere, our results suggest that the presence of recycled Archean crust that could be incorporated into the upper mantle through subduction of Archean oceanic crusts or from the NMD-bearing OIB seamounts located in the southern margin of the Pacific Plate.

1. Introduction

Serpentinite mud volcanoes in non-accretionary forearcs at convergent margins provide a unique opportunity to study geochemical cycling in subduction zones, mantle wedge composition, and microbial activity in extremely alkaline environments associated with serpentinization (Fryer, 2012). Far below the forearc, the mantle wedge is partially converted into serpentinite during reactions with water derived from the subducting slab. Molecular hydrogen is a major potential product of serpentinization (Neal and Stanger, 1983). In addition, methane can be produced from serpentinization via reactions of molecular hydrogen with carbon dioxide originating from slab decarbonation (e.g., Mottl et al., 2004). These volatile compounds are entrained in aqueous fluids with clasts of subduct-

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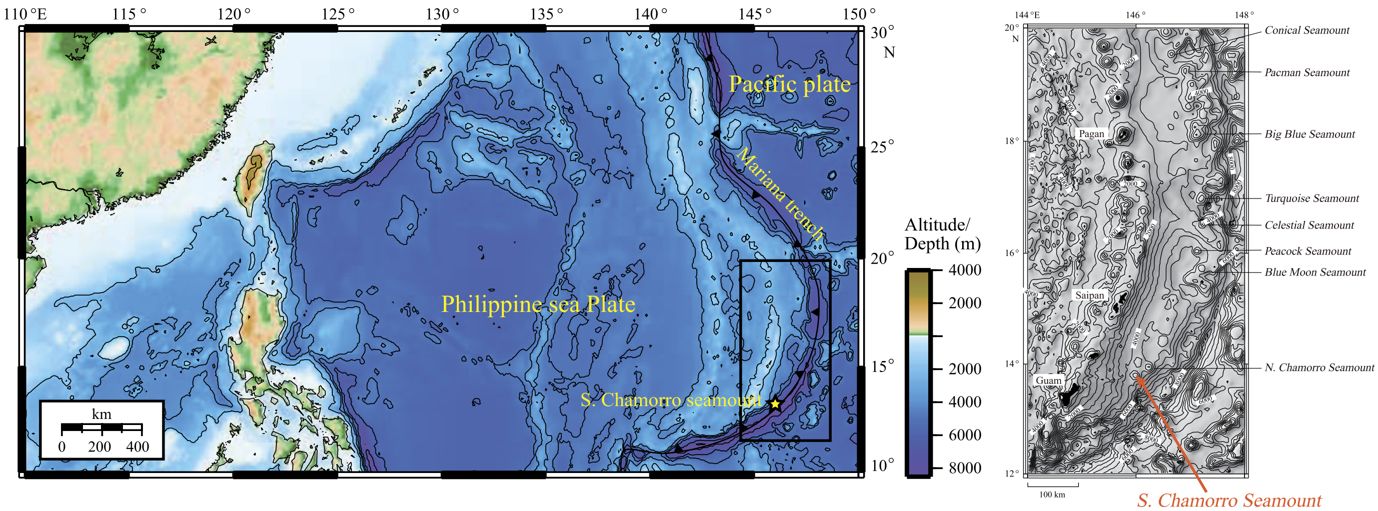

Fig. 1. Location map of the S. Chamorro Seamount (modified from Shipboard Scientific Party, 2002). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

ing basalts and partially serpentinized mantle rocks and ascend to the seafloor along tectonic faults developed beneath serpentine mud volcanoes. Molecular hydrogen, carbon dioxide, and methane in the ascending fluids can be substrates for microbial energy metabolisms such as methanogenesis and dissimilatory reduction of seawater sulfate. Therefore, cold seep systems in serpentinite mud volcanoes may sustain unique chemolithotrophic microbial communities where the highly alkaline nature of ascending fluids (e.g., pH $>$ 12) inhibits the biological activities of normal oceanic microbial communities that are entrained from ambient seawater.

Subseafloor chemolithotrophic microbial communities associated with modern serpentinite-hosted cold seep systems have recently been identified. Mottl et al. (2003) revealed potential functions of sulfate reducers on the basis of pore water chemistry in the relatively shallow zones of core samples obtained from the S. Chamorro Seamount, even though the fluid pH values were greater than 12. Depletion of sulfate concentration and enrichment of dissolved sulfide, together with the presence of lipids in core samples, suggest the occurrence of microbial biomass and activity at a depth down to ∼20 mbsf in the S. Chamorro Seamount. In addition, it has been demonstrated, using domain-specific lipid biomarkers, that the bacterial population is present only near the surface, whereas the archaeal population occurs at depths down to ∼20 mbsf, indicating that some of the archaeal components may be responsible for subseafloor sulfate reduction under highly alkaline conditions. However, the vertical distribution of sulfate-reducing microorganisms and the origin of sulfate within the seamount are still uncertain. Therefore, in this study, we analyze quadruple sulfur isotopes of the sulfide minerals and dissolved sulfate within serpentine muds recovered at the summit of the S. Chamorro Seamount during Ocean Drilling Program (ODP) Leg 195 (Shipboard Scientific Party, 2002). To obtain geochemical information of the subducted slab and mantle wedge beneath the Mariana Forearc, we characterize the sulfur and nitrogen isotope compositions of dissolved sulfur species and ammonia in the upwelling fluids collected at depths of 0–202 mbsf via a cased borehole at the summit of the S. Chamorro Seamount.

2. Geological setting

The Mariana Forearc is a non-accretionary forearc in which most or all of the sediment delivered to the trench via the downgoing plate is subducted (Uyeda, 1982). This forearc extends over a distance of more than 3000 km in the western Pacific and hosts more than 15 serpentinite mud volcanoes (Fryer and Mottl, 1992; Fryer et al., 1999). These serpentinite mud volcanoes are located 30–100 km behind the trench axis, which has formed via subduction of the northwestward Pacific Plate beneath the Philippine Plate since 40 Ma (Fig. 1). Regional seafloor mapping and multichannel seismic surveys demonstrate the interrelationship between faulting and mud volcanism in the outer half of the forearc (e.g., Fryer et al., 1999; Oakley et al., 2008). These serpentinite mud volcanoes are interpreted to have been formed as follows (Fryer, 2012). Volatiles, primarily H_2O, are released from the subducting slab (e.g., sediment and altered basalt) via both compaction and dehydration. The released water reacts with mantle-wedge peridotite, converting depleted harzburgite into serpentinite. Because the density of serpentinite mud is lower than that of ambient harzburgite, serpentinite mud ascends along tectonic faults. Subsequently, accumulated serpentinite mud forms large serpentinite mud seamounts (up to 50 km in diameter and 2 km high) on the seafloor in the Mariana Forearc (Fig. 2(A)). The serpentinite seamounts consist primarily of clay- and silt-sized particles of chrysotile and lizardite with brucite, local antigorite and aragonite, minor to accessory magnetite, talc, and clay (Shipboard Scientific Party, 2002). The temperature of serpentinization in the mantle wedge is estimated to be 300–375 °C from the oxygen isotope fractionation between the serpentine and magnetite from the Conical Seamount, the farthest serpentinite mud volcano from the trench axis (90 km) (Alt and Shanks, 2006). This seamount also contains blueschist facies metabasites, and the P–T conditions to form their mineral assemblages indicate that their basaltic protoliths were derived from 15–20 km below the seafloor (Maekawa et al., 1993).

Pore fluids upwelling through the serpentinite mud volcanoes show lower chlorinities than seawater (Shipboard Scientific Party, 2002; Mottl et al., 2004). These fluids are therefore interpreted as originating from the dehydration of the subducting slab because the dehydration of accretionary sediments is unlikely to occur in a non-accretionary forearc setting. Further, these fluids exhibit systematic variations in their concentrations of alkali elements, alkali earth elements, boron, rare earth elements, and alkalinity with the distance of the host mud volcanoes from the trench axis, which reflects the thermal evolution of the downgoing plate during subduction (Mottl et al., 2004; Hulme et al., 2010).

The S. Chamorro Seamount is the southeasternmost serpentinite mud volcano located in the middle of the Mariana Forearc at 13°47′N 146°00′E at a water depth of 2910 m (Fig. 1). The distance between the S. Chamorro Seamount and the trench is 85 km. The