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Microbial sulfate reduction plays an important role at the initial stage of subseafloor sulfide mineralization

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INTRODUCTION

Seafloor hydrothermal deposits form when hydrothermal fluid mixes with ambient seawater, and constituent sulfide minerals are usually interpreted to precipitate abiogenically. Recent research drilling at Izena Hole and Iheya North Knoll in the middle Okinawa Trough (East China Sea), combined with secondary ion mass spectrometry determinations of $\delta^{34}$S in pyrite grains, provides compelling evidence that the initial stage of subseafloor sulfide mineralization is closely associated with microbial sulfate reduction. During the sulfide maturation process, pyrite textures progress from frambooidal to colloform to euhedral. Pyrite $\delta^{34}$S has highly negative values (as low as $-38.9\%$) in frambooidal pyrite, which systematically increase toward positive values in colloform and euhedral pyrite. Sulfur isotope fractionation between seawater sulfate ($+21.2\%$) and frambooidal pyrite ($-38.9\%$) is as great as $-60\%$, which can be attained only by microbial sulfate reduction in an open system. Because frambooidal pyrite is commonly replaced by chalcopyrite, galena, and sphalerite, frambooidal pyrite appears to function as the starting material (nucleus) of other sulfide minerals. We conclude that frambooidal pyrite, containing microbiobally reduced sulfur, plays an important role at the initial stage of subseafloor sulfide mineralization.

GEOLOGICAL SETTING AND SAMPLES

The Okinawa Trough is a back-arc basin west of the Ryukyu arc in the East China Sea that extends $>1200$ km from the Japanese mainland to Taiwan (Fig. 1A). Owing to its slow extension rate of $3.7 \pm 0.6$ cm/yr (Kotake, 2000) and its geomorphological features (Arai et al., 2017), the Okinawa Trough is considered to be at the nascent stage of back-arc basin formation. The basin is divided into northern, middle, and southern segments by the Tokara Strait and Kerama Gap (Fig. 1A).

Our samples are drill cores from Izena Hole and cores and chimneys from Iheya North Knoll in the middle Okinawa Trough (Fig. 1A). Izena Hole (Fig. 1B) has two hydrothermal sites: the JADE site on the northeastern caldera slope (Halbach et al., 1989; Ishibashi et al., 2015) and the Hakurei site on the southern caldera floor (Ishibashi et al., 2015; Totsuka et al., 2019; Morozumi et al., 2020)
beneath the sediment (Figs. S1 and S2 and Tables S1–S3 in the Supplemental Material) (Nozaki et al., 2018; Totsuka et al., 2019). At Iheya North Knoll, cores were drilled during IODP Expedition 331 at the Original site at Hole C0016B on the eastern flank of North Big Chimney mound (Figs. S1 and S3; Tables S1–S3) (Takai et al., 2011; Yeats et al., 2017). Young and infant chimney deposits at Holes C0016A and C0016B formed after the drilling operation at artificial hydrothermal vents (i.e., drill holes releasing hydrothermal fluid). Samples from these chimneys, which allow secular changes of mineral precipitation (chimney formation) and hydrothermal fluid geochemistry to be observed and in situ experiments to be conducted (Takai et al., 2011; Kawagucci et al., 2013), were collected 5, 11, and 18 months after the IODP Expedition 331 drilling during JAMSTEC research cruises KY11-02 Leg 3 (R/V Kaiyo), NT11-16 (R/V Natsushima), and NT12-06 (R/V Natsushima), respectively. Their petrographic and geochemical details are given by Nozaki et al. (2016).

Under the microscope, pyrite grains from the Hakurei site exhibit various textures (Fig. 2). In pumice fragments and in a sulfidic vein in the hanging wall above the subsurface sulfide body, most pyrite has a framboidal texture and is accompanied by pyrrhotite pseudomorphs replaced by pyrite and marcasite (Fig. 2A). The framboidal pyrite is commonly overgrown by colloform and euhedral pyrites associated with sulfide maturation (Figs. 2B and 2C). This progression from framboidal to colloform and euhedral textures has also been reported in hydrothermal precipitates of chimney mound (Figs. S1 and S3; Tables S1–S3). Histograms of the δ34S data, classified by pyrite texture, are shown in Figure 4. In the drill cores from the Hakurei site, δ34S of framboidal pyrite ranged widely from −38.9‰ to −7.1‰ (average ± 1SD: −17.3‰ ± 10.2‰; n = 42) except in five analyses of highly recrystallized material. The colloform pyrite had a higher δ34S range, from −13.6‰ to −3.0‰ (−7.4‰ ± 2.5‰; n = 29); similarly, δ34S of euhedral pyrite ranged from −13.4‰ to −3.8‰ (−6.8‰ ± 2.7‰; n = 19), with one outlier. Recrystallized framboidal pyrite that consisted of several amalgamated grains (infilled framboidal pyrite; Wei et al., 2016) had δ34S of −10‰ (Fig. 3B), similar to δ34S of colloform and euhedral pyrites, whereas framboidal pyrite retaining its initial texture (normal framboidal pyrite; Wei et al., 2016) in the hanging-wall pumice fragments and sulfidic vein had the lowest δ34S of −35‰ (Fig. 3A; Fig. S5). Similarly, in drill cores from the Original site, framboidal pyrite had lower δ34S than euhedral pyrite (Figs. 3C and 4; Fig. S4). Unlike in the drill cores, however, pyrites in chimneys at this site had a narrow δ34S range around 0‰, irrespective of their texture (Figs. 3D and 4; Fig. S7).

The SIMS measurements yielded a total of 182 δ34S values, representative examples of which are shown in Figure 3 (all measurement sites and data are shown in Figs. S4–S7 and listed in Tables S1–S3). Histograms of the δ34S data, classified by pyrite texture, are shown in Figure 4. In the drill cores from the Hakurei site, δ34S of framboidal pyrite ranged widely from −38.9‰ to −7.1‰ (average ± 1SD: −17.3‰ ± 10.2‰; n = 42) except in five analyses of highly recrystallized material. The colloform pyrite had a higher δ34S range, from −13.6‰ to −3.0‰ (−7.4‰ ± 2.5‰; n = 29); similarly, δ34S of euhedral pyrite ranged from −13.4‰ to −3.8‰ (−6.8‰ ± 2.7‰; n = 19), with one outlier. Recrystallized framboidal pyrite that consisted of several amalgamated grains (infilled framboidal pyrite; Wei et al., 2016) had δ34S of −10‰ (Fig. 3B), similar to δ34S of colloform and euhedral pyrites, whereas framboidal pyrite retaining its initial texture (normal framboidal pyrite; Wei et al., 2016) in the hanging-wall pumice fragments and sulfidic vein had the lowest δ34S of −35‰ (Fig. 3A; Fig. S5). Similarly, in drill cores from the Original site, framboidal pyrite had lower δ34S than euhedral pyrite (Figs. 3C and 4; Fig. S4). Unlike in the drill cores, however, pyrites in chimneys at this site had a narrow δ34S range around 0‰, irrespective of their texture (Figs. 3D and 4; Fig. S7).

Given the δ34S value of +21.2‰ in bottom-seawater sulfate at Iheya North Knoll (Aoyama et al., 2014), the sulfur isotope fractionation between seawater sulfate and framboidal pyrite was as great as −60‰, assuming the same δ34S in seawater sulfate at Iheya North Knoll and Izena Hole. This fractionation factor is close

### RESULTS AND DISCUSSION

In situ δ34S analysis was performed by SIMS (CAMECA IMS1280-HR) at the Kochi Institute for Core Sample Research, JAMSTEC (Nankoku, Japan). A primary 133Cs+ ion beam with an intensity of 100 pA and total impact energy of 20 kV was focused to 2–3 μm in diameter at the sample surface. A gold coat ~30 nm thick was applied to the sample surface, and a normal-incidence electron gun was used for charge compensation. Secondary ions of two sulfur isotopes were accelerated at 10 kV and detected simultaneously by two Faraday cup (FC) detectors with 1014 Ω amplifiers (L1 for 34S and optically axial FC2 for 32S). The entrance slit width was set at 61 μm. The exit slit widths were set at 500 and 243 μm for L1 and FC2, corresponding to a mass-resolving power of ~2200 and ~5000, respectively.

Each analysis consisted of 30 s for pre-sputtering, 50 s for centering of secondary ions in the field aperture, and 40 s for measurement (20 cycles with 2 s integration time). The typical intensity of 32S was ~7 × 1014 counts per second (csp) for pyrite analyses. Each group of nine to 21 sample analyses was bracketed by ten to 12 analyses of pyrite standard UWPy-1 (Ushikubo et al., 2014). Instrumental mass bias and analytical error were determined from average values and two standard deviations (SD) of the bracketing standard analyses. All data were normalized to the Vienna Canyon Diablo troilite (VCDT) standard. Typical uncertainty of δ34S was ±0.4‰ (2SD). Detailed analytical and data reduction procedures were given by Ushikubo et al. (2014).
to the largest values recorded in VMS deposits (–73‰ [Lode et al., 2017], –71‰ [Slack et al., 2019], –66‰ [Velasco-Acebes et al., 2019]). Three dominant sulfur sources for pyrite in SMS deposits have been considered: (1) magmatic sulfur in footwall rocks leached by hydrothermal fluid through water-rock interaction \((\delta^{34}\text{S} = 0\%e \pm 3\%e)\); Campbell and Larson, 1998; Shanks, 2001), (2) thermochemical (abiotic) sulfate reduction of anhydrite and/or gypsum and seawater sulfate by Fe\(^{2+}\)-bearing minerals or organic carbon, and (3) microbial sulfate reduction of seawater sulfate. A solely magmatic sulfur source to explain the highly negative \(\delta^{34}\text{S}\) of seawater sulfate. Euhedral pyrite in drill cores and seawater sulfate, with microbially reduced sulfate reduction of anhydrite and/or gypsum. An alternative process is single-step microbial sulfate reduction in an open system without sulfur disproportionation and reoxidation (Sim et al., 2011).

That framboidal pyrite is commonly replaced by other sulfide minerals such as chalcopyrite and galena (Fig. 2D) as well as sphalerite (Piercey, 2015) indicates that framboidal pyrite provides component material for other sulfide minerals. Our evidence suggests that framboidal pyrite incorporating S derived from microbial sulfate reduction serves as a nucleus for subsequent mineral growth at the initial stage of subseafloor sulfide mineralization. Colloform pyrite with \(\delta^{34}\text{S} = 7\%e\) is overgrown on framboidal pyrite as a result of overprinting by hydrothermal mineralization. We consider the S in colloform pyrite to be a mixture of magmatic S from rocks, as well as S from abiotic sulfate reduction of anhydrite and/or gypsum and seawater sulfate, with microbially reduced seawater sulfate. Euhedral pyrite in drill cores and chimneys has \(\delta^{34}\text{S}\) of \(0\%e\)–\(3\%e\), explained by further overprinting by hydrothermal mineralization (and possibly additional S input through abiotic reduction). The interstitial water geochemistry of drill cores from the Hakurei site shows positive peaks of alkalinity and NH\(_3\), H\(_2\)S, and CH\(_4\) concentrations at 5–10 m above the subseafloor sulfide body, indicating that vigorous microbial sulfate reduction is taking place within the hanging-wall (pumiceous) sediment. Active subseafloor microbial sulfate reduction has also been confirmed by a multiple sulfur isotope study at the Original site (Aoyama et al., 2014) as well as at the Palinuro and Panarea hydrothermal fields in the Tyrrhenian Sea (Peters et al., 2011). The maximum fractionation in \(\delta^{34}\text{S}\) between framboidal pyrite and seawater sulfate (–60‰) together with \(\delta^{34}\text{S}\) evolution through the sulfide maturation process, observed in SMS and in VMS deposits on land (Lode et al., 2017; Slack et al., 2019; Velasco-Acebes et al., 2019), suggest that microbial activity is essential forSMS and VMS deposit formation and that microbial sulfate reduction plays an important role at the initial stage of mineralization beneath the seafloor sediments.

CONCLUSIONS

Microscopic evidence and \(\delta^{34}\text{S}\) values in pyrite from Izena Hole and Ihey North Knoll indicate that pyrite progresses through framboidal, colloform, and euhedral textures accompanied by changes in \(\delta^{34}\text{S}\) to higher values. Because
\( \delta^{34}S \) in framboidal pyrite as negative as \(-38.9\%\) (or \(-60\%\) with respect to seawater sulfate) could not have been produced by magmatic sulfur or abiotic sulfate reduction, the framboidal pyrite must be derived from seawater sulfate through microbial reduction in an open system. The ubiquity and abundance of framboidal pyrite with strongly negative \( \delta^{34}S \) at the initial stage of sulfide mineralization in both SMS and VMS deposits can thus be explained by microbial sulfate reduction, and its widespread replacement by other sulfide minerals indicates that framboidal pyrite serves as a nucleus for subsequent mineral growth.

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Figure 4. Histograms of $\delta^{34}$S in pyrite textural categories. Pink bars in framboidal and euhedral pyrite of Izena Hole represent highly recrystallized framboidal pyrite values and outlier value, respectively.

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