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Sulfur isotope variability in biogenic pyrite: Reflections of heterogeneous bacterial colonization?

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ABSTRACT

The top 20 cm of sediments at active cold seeps in Monterey Bay, coastal California, contain framboidal pyrite that occurs as infillings and pseudomorphs of the chambers of the tests of foraminifera and rarely as irregularly shaped grains. Sulfur isotope compositions obtained with the ion microprobe show depletions in ^{34}S ($\delta^{34}S = -41$ to -5‰, CDT), and large variations both within and among these pyrite grains. Intergranular differences in $\delta^{34}S$ values in the same sediment are as large as 35‰, and intragranular zoning reaches 15‰. Zoning is regular in some grains, with systematic isotope changes from core to rim or from one foraminiferal chamber to another, but irregular in others. The regular zoning is consistent with an increase in ^{34}S through time. Backscattered-electron imaging reveals three types of pyrite: isolated framboids in a porous aggregation (''PF-pyrite''), agglomerated framboids with cementing interstitial pyrite (''F+I-pyrite''), and recrystallized pyrite with isolated relicts of framboids (''RF-pyrite''). In individual grains, RF-pyrite cores grade into F+I-pyrite toward grain rims, and F+I-pyrite grades into PF-pyrite at the grain edges. These textures are consistent with a paragenetic sequence whereby framboids first agglomerate (PF-pyrite), then cement (F+I-pyrite), and finally recrystallize (RF-pyrite). The $\delta^{34}S$ values of RF-pyrite are generally lower than that of F+I-pyrite; if the paragenetic sequence is correct, then this trend parallels the regular core-rim isotopic zoning observed in some grains. The implied increase in $\delta^{34}S$ with time is consistent with Rayleigh fractionation of sulfur in a closed system. Bacteria are intimately involved in the production of pyrite from our samples, and heterogeneous colonization by bacteria provides a simple explanation for the sulfur isotope heterogeneity among and within grains: The foraminifera provide open space for colonization and local nutrients for bacterial growth, whereas the cell walls of the bacteria may provide a local nucleation site for sulfides. If so, then initial colonization is reflected in lower $\delta^{34}S$ values, whereas later bacterial emigration to other foraminifera chambers is indicated by higher $\delta^{34}S$ values.