

Using Calcium Isotopes to Constrain the Fate of Calcium in Hydrothermal Systems

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The balance of calcium in hydrothermal systems remains enigmatic. In theory, calcium from seawater enters the oceanic crust and mixes with calcium contained in basalt. Within the hydrothermal system, calcium may precipitate in carbonate and anhydrite veins or in altered basalt, or it may circulate through vents and return to the ocean. These processes do not seem to be in isotopic balance with respect to the calcium isotopic composition of the known endmembers. The two main sources of calcium in these systems are seawater and basalt, which have $\delta^{44}\text{Ca}$ of 0.80‰ and -0.15‰, respectively (reported relative to Bulk Silicate Earth - BSE)^{1,2}. However, all known sinks for calcium in these systems are disproportionately enriched in ⁴⁰Ca. Measured calcium carbonate veins (-0.9‰ to 0.09‰), gypsum veins (-0.6‰ to -0.3‰), and hydrothermal fluids (-0.2‰) are all light (isotopically depleted).³ This suggests that within the hydrothermal system, a heavy (isotopically enriched) sink must exist whose isotopic composition has not been measured previously.

Alteration halos in basalt that form around veins constitute one possibility for this heavy calcium sink.⁴ Modeling of the calcium isotopic mass balance in hydrothermal systems suggests that if this altered basalt is the missing sink that balances the hydrothermal calcium isotopic budget, its $\delta^{44}\text{Ca}$ must range between 1-4‰. The range is large because other variables within the hydrothermal system, such as the amount of calcium leached from basalt, the partitioning of calcium between vein minerals and altered basalt, and the isotopic composition of these veins, are poorly constrained. We will report the calcium isotopic composition of calcite veins and altered basalts from the Mid-Atlantic Ridge, East Pacific Rise, and Izu-Bonin-Mariana Arc. These measurements will contribute to our understanding of calcium cycling and carbonate vein formation in hydrothermal systems and demonstrate whether altered basalts are a major sink for seawater calcium.

[1] Fantle and Tipper (2014) *Earth Science Rev.* **129**, 148-177 [2] Skulan, et al., (1997) *GCA* **61**, 2505-2510 [3] Amini *et al.* (2008) *GCA* **72**, 4107-4122 [4] Alt and Teagle (2003), *Chemical Geology* **201**, 191-211