Calcium isotope tracers of authigenic carbonate formation in marine sediments

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The removal of carbon from the surface of the planet is a critical component of the long-term carbon cycle; this removal is through the deposition and subsequent burial of carbon-minerals in the ocean. However, what is deposited at the sediment-water interface is not representative of what is ultimately buried because marine sediments are a dynamic chemical and microbial reactor. The subsurface oxidation of organic carbon into dissolved inorganic carbon occurs mainly due to microbial sulfate reduction in anoxic sediments. This microbial sulfate reduction generates subsurface alkalinity, and in theory leads to to the formation of authigenic carbonate. Modern studies pinpointing the important microbial processes for authigenic carbonate formation are key for our extrapolation of the importance of authigenic carbonate in the geological record.

Calcium isotopes in carbonate minerals are enriched in the lighter, ^{40}Ca isotope relative to the fluid in which they precipitate. As such, subsurface authigenic carbonate precipitation should result in an increase in the ^{44}Ca isotope in the remaining sedimentary pore fluid[1]. This is aided by the fact that aqueous calcium isotopes in organic-rich and carbonate-poor sediments remain out of isotopic equilibrium with carbonate minerals likely due to passivation of the mineral surface[2]. In theory, this means that high-resolution pore water studies should be able to isolate the depths of authigenic carbonate formation and the microbially mediated processes driving this formation. We present calcium isotope data from high-resolution porefluids and bulk carbonate from deep-ocean sediments where different microbially mediated processes dominate the subsurface; Site 1081 where microbial sulfate reduction is coupled only to anaerobic methane oxidation, and Site U1385 where microbial sulfate reduction is coupled both to organiclastic sulfate reduction and anaerobic methane oxidation. The calcium isotope data along with the interstitial water data suggests that microbial activity facilitates carbonate precipitation in the upper part of the sediment in these sites.

[1] Teichert *et al*. (2009) *Earth Planet. Sci. Lett.* **279**, 373–382.
[2] Turchyn & DePaolo (2011) *Geochim. Cosmochim. Acta* **75**, 7081–7098.