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Calcium isotopic fractionation in microbially mediated gypsum precipitates

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Abstract

Gypsum ($CaSO_4{\cdot}2H_2O$) precipitation experiments were carried out at low pH in the presence of the sulfur oxidizing bacterium *Acidithiobacillus thiooxidans*. The observed Ca isotopic fractionation (expressed as $\Delta^{44/40}Ca_{s\text{-}f} = \delta^{44/40}Ca_{solid} - \delta^{44/40}Ca_{fluid}$) at the end of each experimental time period (~50 to 60 days) was −1.41‰ to −1.09‰ in the biotic experiments, −1.09‰ in the killed control, and −1.01‰ to −0.88‰ in the abiotic controls. As there were no strong differences in the solution chemistry and the rate at which gypsum precipitated in the biotic and abiotic controls, we deduce a biological Ca isotope effect on the order of −0.3‰. The isotope effect correlates with a difference in crystal aspect ratios between the biotic experiments (8.05 ± 3.99) and abiotic controls (31.9 ± 8.40). We hypothesize that soluble and/or insoluble organic compounds selectively inhibit crystal growth at specific crystal faces, and that the growth inhibition affects the fractionation factor associated with gypsum precipitation. The experimental results help explain Ca isotopic variability in gypsum sampled from a sulfidic cave system, in which gypsum crystals exhibiting a diversity of morphologies (microcrystalline to cm-scale needles) have a broad range of $\delta^{44/40}Ca$ values (~1.2–0.4‰) relative to the limestone wall ($\delta^{44/40}Ca = 1.3‰$). In light of the laboratory experiments, the variation in Ca isotope values in the caves can be interpreted as a consequence of gypsum precipitation in the presence of microbial organic matter and subsequent isotopic re-equilibration with the Ca source.

1. INTRODUCTION

Over the past twenty years, calcium (Ca) isotopes have been increasingly utilized as proxies at a variety of spatial scales to inform such matters as paleo sea surface temperatures and variability in Ca cycling over a range of time scales (e.g., De La Rocha and DePaolo, 2000; DePaolo, 2004; Langer et al., 2007; Farkas et al., 2007a,b; Ewing et al., 2008; Page et al., 2008; Cenki-Tok et al., 2009; Fantle, 2010; Heuser and Eisenhauer, 2010). Notably, in both experimental and natural systems, Ca has been shown to fractionate isotopically to a significant extent during mineral precipitation. This effect has been documented during experimental gypsum, calcite, and aragonite precipitation (Gussone et al., 2003, 2005, 2007; Lemarchand et al., 2004; Tang et al., 2008, 2011; Gussone et al., 2011; Reynard et al., 2011; Harouaka et al., 2014). Calcium isotope fractionation during mineral precipitation is believed to be kinetically controlled, and related to aqueous ion-mineral surface interactions (Fantle and DePaolo, 2007; DePaolo, 2011; Nielsen et al., 2012).

A wealth of evidence suggests that organic molecules affect the nucleation, precipitation kinetics, and morphology of Ca-rich minerals such as gypsum and calcite (e.g., Barcelona et al., 1976; Barcelona and Atwood, 1978, 1979; Cody and Cody, 1989, 1991; Cody, 1991; DeOliveira and Laursen, 1997; Hamdona and Hadad, 2008). In nature, small quantities of organic molecules are

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produced abiotically (e.g., Shock, 1990), but often occur in higher abundances as a result of microbial or other biological activity (e.g., Riding and Awramik, 2000). Given the known links between microorganisms and mineral precipitation kinetics, and the relationship between the Ca isotopic composition and the precipitation kinetics of minerals, it seems both reasonable and useful to quantify Ca isotopic fractionation associated with mineral precipitation in the presence of microbes.

Microbial activity may impact the Ca isotopic composition of minerals either directly or indirectly (Fig. 1). For example, Ca plays an important role in cellular function, such that both eukaryotic and prokaryotic cells actively pump Ca^{2+} in order to maintain low intracellular Ca^{2+} concentrations ($\sim 10^{-4}$ mM; Norris et al., 1991; Yates and Robins, 1999; Collins, 2006). Active pumping may isotopically fractionate Ca, analogous to isotopic effects observed in terrestrial ecosystems associated with plant uptake of Ca^{2+} (Skulan et al., 1997; Skulan and DePaolo, 1999; Page et al., 2008; Cenki-Tok et al., 2009; Holmden and Bélanger, 2010; Cobert et al., 2011; Farkaš et al., 2011; Schmitt et al., 2012).

Assuming that Ca isotopic effects are impacted by precipitation rate, microbial activity can also influence solution chemistry via the production of anions (e.g., SO_4^{2-} associated with sulfur oxidation), which can increase the saturation state and, hence, the precipitation rate of minerals that contain the anion of interest in their structure (e.g., $CaSO_4{\cdot}2H_2O$). On the other hand, microbial production of dissolved organic molecules can reduce the activity of Ca^{2+} in aqueous solution via the formation of organometallic complexes, thereby decreasing saturation state and lowering precipitation rate. Lastly, microbes may sequester Ca in the process of producing extracellular polymeric substances (EPS), in which Ca is an important structural component (e.g., Sutherland, 2001; Braissant et al., 2007; Uroz et al., 2009). Assuming EPS formation isotopically fractionates Ca, the production of biofilm could isotopically distill aqueous Ca, given a sufficient flux into the biofilm. The isotopically distilled Ca source is then reflected in the isotopic composition of contemporaneously formed minerals.

The current study investigates the Ca isotopic composition of microbially-mediated gypsum precipitates grown in the laboratory under controlled conditions, and compares the results to previously-conducted abiotic precipitation experiments. The study is motivated by the observation of significant variability in the Ca isotopic composition of gypsum collected from the sulfidic Frasassi cave system, a Mars analogue site in northern Italy (Galdenzi and Maruoka, 2003; Galdenzi, 2012; Macalady et al., 2007; Jones et al., 2008, 2011). At Frasassi, gypsum replacement crusts form via the oxidation of H_2S gas to H_2SO_4, which corrodes the limestone walls. Speleogenesis occurs in the presence of the sulfur oxidizing bacterium *Acidithiobacillus thiooxidans*, which actively drives the oxidation of H_2S (Macalady et al., 2007; Jones et al., 2008, 2011, 2015).

Accordingly, we precipitated gypsum in multiple laboratory cultures using a Ca-rich medium inoculated with *A. thiooxidans* strain GB30-2C, which oxidizes S^0 to sulfuric acid (H_2SO_4). The magnitude of Ca isotopic fractionation between the final gypsum precipitates and the final fluid ($\Delta^{44/40}Ca = \delta^{44/40}Ca_{solid} - \delta^{44/40}Ca_{fluid}$) was larger in the biotic experiments than in the abiotic controls by ~0.3‰. The isotopic variability between biotic and control experiments was independent of solution chemistry, saturation state, and precipitation rate, yet correlated with crystal aspect ratio. This correlation suggests that the observed isotope effect may be related to surface selective interactions of organic matter with specific crystal faces. The

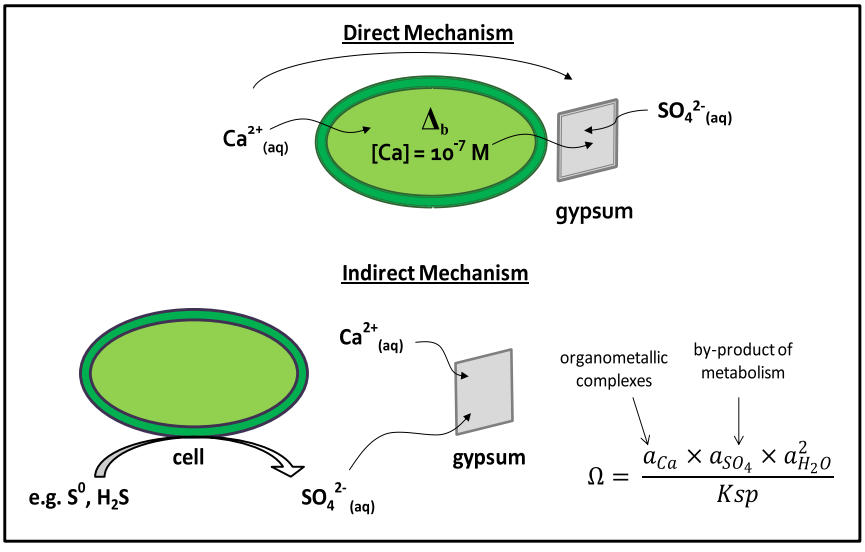

Fig. 1. Schematic of the direct and indirect pathways by which microbes could affect the Ca isotopic composition of gypsum. The pumping of Ca out of the cell is an example of a "direct" mechanism that may induce a biotic isotopic fractionation effect (Δ_b), which may be captured in precipitating gypsum. Changing solution chemistry (specifically mineral saturation state) due to microbial activity is an example of an indirect mechanism. An indirect mechanism can alter the kinetics of gypsum precipitation and the Ca isotopic fractionation factor associated with precipitation, and, hence, the $\delta^{44}Ca$ of the mineral.