

Relating the concentration and isotopic composition of carbonate associated sulfate to parent solutions

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Carbonate associated sulfate (CAS) is structurally bound sulfate found in carbonate minerals of biological and chemical origin. Modern biogenic carbonates taken from sites around the world host CAS, which displays sulfur isotope ratios similar to modern seawater ($\delta^{34}\text{S} = 21\text{‰}$ CDT) [1,2], suggesting that CAS may faithfully record the $\delta^{34}\text{S}$ of the seawater from which the carbonates precipitated. As such, CAS has proven valuable in providing near-continuous proxy records of seawater sulfate, $\delta^{34}\text{S}$, especially during periods in which no sulfate evaporites have been preserved [e.g., 1,3,4]. However, despite this evidence, and the wide use of CAS as a proxy of seawater sulfate, the reliability of the pre-diagenetic isotopic record in CAS has not been verified experimentally. Whether chemical precipitation alone might fractionate the isotopes of sulfur, thereby complicating the interpretation of CAS records, is still unknown.

We experimentally related the concentration and isotopic composition of sulfate within chemically precipitated calcium carbonate to those of aqueous sulfate in the carbonates' parent solution. We dissolved sulfate-free calcium carbonate in stirred solutions containing between 100 μM and 40 mM sulfate by raising the partial pressure of CO_2 ($p\text{CO}_2$) in a sealed glovebox, thereby decreasing the solutions' pH. We reprecipitated the calcium carbonate under near-equilibrium conditions by allowing the CO_2 to diffusively exchange with the air outside the glovebox through a small opening. Aqueous sulfate and CAS concentrations were measured by ion chromatography, and sulfur isotope ratios were measured by high-resolution, multi-collector ICPMS [5].

The results of this study are central for the validation and calibration of CAS, a widely used method for reconstructing the history of sulfur isotope ratios in seawater sulfate.

[1] Kampschulte *et al* (2001), *Chem. Geol.* **175**, 149-173 [2] Burdett *et al* (1898) *Earth Planet. Sci. Lett.* **94**, 189-198 [3] Jamieson *et al.* (2012), *Nature Geosci.* **6**, 61-64 [4] Hurtgen *et al* (2004), *GSA Special Paper* **379** [5] Paris *et al* (2013) *Chem. Geol.* **345**, 50-61