Sulfate in biogenic carbonates: A simple yet complicated story

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Stable isotopes are a powerful tool to reconstruct the chemical composition of the ocean through Earth's history. Over the last years, we made significant progress in reassessing one of the most precious archives to explore S isotopes ($\delta^{34}S$) of seawater sulfate, which track aspects of redox and carbon cycle changes: Carbonate Associated Sulfate, trace sulfate incorporated into the mineral lattice of calcite or aragonite. The $\delta^{34}S$ of CAS reflects that of seawater to the first order but, though different organisms have distinct $\delta^{34}S$. The better constrain the source of this "vital effect", we present new data from organisms that synthesize either low-Mg calcite, high-Mg calcite or aragonite. We measured $\delta^{34}S$ by MC-ICPMS and CAS content from coccolithophores and, benthic foraminifera, cultured at different sulfate concentrations as well as field-collected brachiopods, echinoderms and mollusks. Data are comapred with $\delta^{7}Li$ [1] and Mg/Ca, when available.

The fractionation between CAS and sulfate from the growth media is comprised between -1.5‰ and +1‰ for most biogenic carbonates, and is as large as -7‰ in coccoliths. Such CAS-sulfate fractionations are equal to or lower than the equilibrium fractionation proposed from synthetic carbonates (+1 to +3‰). However, The combined $\delta^{34}S$, CAS content,, $\delta^{7}Li$ and Mg/Ca results suggest that CAS content and $\delta^{34}S$ reflect a combination of inorganic and organic processes. Our data provide new insights into biomineralization pathways and have the potential to inform aspects of sulfur cycling in a given organism. They also confirm that the mixture of different biogenic carbonates can generate unpredictible value, especially for pelagic sediments and should be avoided to explore Phanerozoic seawater $\delta^{34}S$.

[1] Dellinger et al., 2018, GCA