

Mapping the micron-scale spatial distribution and speciation of sulfur in Ordovician carbonates

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Isotopic measurements of sulfate and sulfide phases preserved in carbonates document secular changes in the sulfur cycle and the redox evolution of Earth's surface over geologic time. However, as the isotopic record of ancient oceanic conditions becomes better resolved, reports of coeval but discordant geochemical/isotopic proxies are becoming increasingly common. As a bulk-rock proxy, ³⁴S signals can consist of multiple origins of sulfate and sulfide within carbonate minerals. Deciphering whether changes in $\delta^{34}\text{S}$ derive from the relative contribution of secular change versus from variation in the origin of the components of bulk rock is critical in order to extract meaningful information about depositional and diagenetic environments.

We used X-ray spectromicroscopy to map the distribution of primary and secondary S-bearing sedimentary phases at the micron-scale in a well-characterized suite of Ordovician-aged (~444 million years ago) carbonate strata from Anticosti Island, Quebec. The high-resolution maps of sulfate variability showed major differences between clasts and cement, as well as subtle variation in sulfate concentrations between fossil clades. We can distinguish the sulfate content of different stages of calcite cement, helping to constrain the diagenetic history and relate specific cements with the chemistry of the waters from which they formed. In conjunction with secondary ion mass spectrometry (SIMS) $\delta^{34}\text{S}$ measurements, this new analytical approach can distinguish isotopic signatures between primary and diagenetic phases, enhancing our ability to interpret $\delta^{34}\text{S}$ isotopic signatures and reconstruct biogeochemical sulfur cycling over Earth history.