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Insights into past ocean proxies from micron-scale mapping of sulfur species in carbonates

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ABSTRACT

Geological reconstructions of global ocean chemistry and atmospheric oxygen concentrations over Earth history commonly rely on the abundance and stable isotopic composition ($\delta^{34}S$) of sulfur-bearing compounds. Carbonate-associated sulfate (CAS), sulfate bound within a calcium carbonate mineral matrix, is among the most commonly interrogated sulfur mineral phases. However, recent work has revealed variability in $\delta^{34}S_{CAS}$ values that cannot be explained by evolution of the marine sulfate reservoir,

challenging the common interpretation that CAS is inherently a high-fidelity record of seawater sulfate. To investigate the source of this inconsistency, we used X-ray spectromicroscopy to map the micron-scale distribution of S-bearing sedimentary phases in Ordovician-aged (ca. 444 Ma) shallow marine carbonates from Anticosti Island, Québec, Canada. Clear differences in the abundance of CAS are observed between cements and fossils, suggesting that variance in bulk-rock data could be a consequence of component mixing and that coupled synchrotron-petrographic screening can identify the carbonate components that are most likely to retain primary CAS. Furthermore, we observe multiple, distinct moieties of sulfate (both inorganic and organic). Differences in these moieties among fossil clades could provide new insights into biomineralization mechanisms in extinct organisms.

INTRODUCTION

Stable isotope ratios of carbon- and sulfur-bearing phases in sedimentary rocks retain an extensive record of environmental change throughout Earth history (Garrels and Lerman, 1981; Berner, 2006). Carbonate-associated sulfate (CAS), sulfate trapped within a calcium carbonate mineral matrix at typical concentrations of ~100–10,000 ppm, is one such phase (Burdett et al., 1989). The stable isotope ratio of sulfur in CAS ($\delta^{34}S_{CAS}$) is usually interpreted as a primary record of the stable isotopic composition of sulfate sulfur in contemporaneous seawater sulfate (Fike and Grotzinger, 2008; Gill et al., 2011). However, reports of coeval but discordant $\delta^{34}S_{CAS}$ are common (Fike and Grotzinger, 2008; Ries et al., 2009). Furthermore, $\delta^{34}S_{CAS}$ data from individual locations show more variability than could plausibly be attributed to a primary marine signal (Jones and Fike, 2013; Fike et al., 2015). Higher-resolution analyses of individual carbonate components

(e.g., micrite, spar) and fossils (e.g., brachiopods, bryozoa, crinoids) reveal even larger degrees of isotopic variability in CAS at smaller spatial scales (Present et al., 2015). This variability challenges our assumption that bulk-carbonate CAS uniformly derives from seawater.

To assess the role of compositional heterogeneity in driving the observed variability in $\delta^{34}S_{CAS}$, it is critical to understand how sulfate and sulfide phases are associated with diverse carbonate components. Carbonate petrography can reveal the mixture of fossil fragments, micrite, and various cements that compose the rock, along with detrital siliciclastic material and other authigenic minerals. Furthermore, petrographic textures usually can be used to distinguish the nature and relative timing of primary (early) diagenetic marine components from later diagenetic cements. Because the amount of these components varies among samples, differences in the abundance of CAS or other S-bearing phases among carbonate components could drive the bulk $\delta^{34}S$ variability in the rock record. We used X-ray spectromicroscopy to produce micron-scale maps of the distribution of sulfur phases in an Ordovician-aged (ca. 444 Ma) oncoid grainstone from Anticosti Island, Québec, Canada (Jones et al., 2011; see Fig. DR1 in the GSA Data Repository[1]). The sample is from a stratigraphic section that spans the Hirnantian glaciation and mass extinction, and that records scattered bulk-rock $\delta^{34}S_{CAS}$ values (18‰–32‰; Jones and Fike, 2013). Here we identified and mapped sulfide (e.g., pyrite), inorganic sulfate (canonical "CAS"), and novel organosulfate phases, and determined their petrographic association with various carbonate components.

SULFUR SPECIATION IN ORDOVICIAN CARBONATES

Sulfur K-edge X-ray absorption near-edge structure (XANES) measurements produce distinguishable absorbance spectra from the analysis of samples containing sulfate, sulfide, or both (Fig. 1A). These spectra are sensitive to an array of sulfur species if present, and uniquely enable the identification of multiple forms of inorganic and organic sulfate; both are present in the sampled Ordovician carbonates (Fig. 1B). This technique generates maps of the distribution and abundance of CAS within complex sedimentary carbonates, leading to a better understanding of how this proxy is incorporated, and subsequently altered, in geologic samples. Furthermore, mapping of the spatial distribution of inorganic and organic phases of sulfate that together compose CAS provides new insights into the biomineralization mechanisms of extinct clades of organisms.

The spatial distribution of sulfur species varies across different carbonate components (Figs. 2A–2C). Sulfide occurs predominantly as finely disseminated grains of pyrite within micrite, and in variable abundance in skeletal and non-skeletal (e.g., oncoid, intraclast) grains (see the Data Repository). Sulfide is absent from equant spar cements. This variability in sulfide content suggests that micrite and grains are differentially sensitive to sulfide oxidation, which is important because sulfide oxidation prior to and during traditional bulk-rock CAS extraction is likely a major source of variation in measured $\delta^{34}S_{CAS}$ (Wotte et al., 2012).

Sulfate concentration strongly correlates with carbonate component: micrite, skeletal and non-skeletal grains, and cement have very different CAS concentrations (Fig. 2C). Micrite has a uniform texture but could have had several origins by analogy with recent lime mud: (1) carbonate mud precipitated from supersaturated seawater; (2) mud

derived from the breakdown of calcareous algae; (3) detrital carbonate mud; (4) mucilaginous microbial ooze; or (5) in situ recrystallization by endolithic algae. Sulfate concentrations differ among various micritic components in our sample. We defined regions of interest (ROIs) within the sample based on petrographic analysis and used the ROIs to compare concentrations of sulfate among sample components (Figs. 2B and 4). Within each ROI, we measured several hundred to several thousand sulfate concentrations, in 5 × 5 μm pixels. Pairwise comparisons of the mean sulfate concentrations between ROIs within each sector showed that nearly all could be distinguished ($p < 0.05$, adjusted for multiple comparisons; see the Data Repository). The mean sulfate concentration and its standard error for several components included micrite adjacent to a recrystallized gastropod shell (~64.1 ± 0.3 ppm; ROI 5), micritic coatings around remnant skeletal components (~39.9 ± 0.8 ppm and 70.1 ± 2.1 ppm; ROIs 8 and 9) and non-skeletal fragments (~82.0 ± 0.9 ppm; ROI 2), and the fine-grained detrital material within the gastropod shell (~30.9 ± 0.3 ppm and 68.0 ± 0.9 ppm; ROIs 6 and 7; see the Data Repository). Quantifying spatial variability within sulfate in these different forms of micrite is critical because it is commonly targeted in studies of ancient sedimentary rocks as a homogeneous component assumed to passively record ocean biogeochemical signals (Kaufman et al., 1991; Saltzman et al., 1998; Kump et al., 1999). Skeletal and non-skeletal grains also show variable sulfate concentrations (190.0 ± 2.0 ppm and 44.4 ± 0.4 ppm; ROIs 4 and 1), while the surrounding cement contains variable but extremely low sulfate content (near detection limit; ROI 3). This variability in sulfate concentration is reproduced between grains, micrite, and cement across a thin section. An additional mapped sector in the same thin

section records sulfate concentrations for skeletal grains (50.8 ± 1.1 ppm; ROI 19), non-skeletal grains (198.6 ± 1.2; ROI 16), micritic coatings (105.5 ± 1.1 ppm; ROI 17), and cement (5.2 ± 0.3 ppm; ROI 10; Figures 3A–3C and 4).

Distinct Sulfate Moieties

Detailed examination of the XANES spectra around the sulfate white line (referring to the first sharp rise in a X-ray absorption spectroscopy (XAS) spectrum, and corresponds to transitions of electrons to unfilled bound states) in these components reveals three distinct sulfate moieties within a single region (Figs. 2D and 3D). At the highest energy (2482.7 eV), there is an inorganic sulfate phase, such as is typically seen in abiotic calcite and which is likely canonical CAS. At a slightly lower energy (2482.5 eV), there is another inorganic sulfate component; the downshift of this phase (hereafter referred to as “distorted”) reflects a likely distortion of the carbonate lattice relative to that of calcite, akin to that found in aragonite (Fernández-Díaz et al., 2010) (see the Data Repository). At ~2481.4 eV, there is a third organosulfate moiety, a sulfate ester requiring active biological synthesis (Tamenori et al., 2014). Each of these three sulfate moieties has a different origin, potentially representing distinct biological and/or biogeochemical processes during deposition, lithification, and subsequent alteration (i.e., diagenesis). Information about these individual components is lost during traditional CAS acid extraction. Standard CAS protocols extract the organosulfate component, which undergoes hydrolysis in acidic conditions—a process that can also give rise to a sulfur isotopic fractionation (Burlingham et al., 2003). Thus, complex micron-scale speciation of sulfate within and between individual samples may also contribute to the unexpectedly large scatter usually observed in bulk $\delta^{34}S_{CAS}$ data (Fike et al., 2015).

DISCUSSION

The sulfur speciation maps produced in this study help constrain the relative timing and geochemical conditions associated with cementation and early diagenetic events (Figs. 2B and 3B). For example, the center of the gastropod in Figure 2B contains syndepositional detrital material with variable but low sulfate concentrations (micrite ~30.9 ± 0.3 ppm, detrital grain ~68.0 ± 0.9 ppm; ROIs 6 and 7). Adjacent grains with micritized coatings have higher, inorganic sulfate concentrations (~82.0 ± 0.9 ppm; ROI 2); this is likely associated with calcitization (Fernández-Díaz et al., 2010). The increase in sulfate at the grain rims suggests that micritization and neomorphism occurred in the presence of sulfate-rich fluids (seawater or pore waters in open communication with it), which could reflect increased sulfate uptake in the smaller micrite grains and/or increased substitution of sulfate in the calcite matrix (Fig. 2C). These non-skeletal grains record higher concentrations of organosulfate and a distorted inorganic sulfate moiety caused by different carbonate lattice conditions, similar to aragonite (Figs. 2D and 3D; Fernández-Díaz et al., 2010). However, metastable aragonite reverts to calcite on a 10^7 yr time scale (the oldest known record of intact aragonite is found in Pennsylvanian mollusks; Balthasar et al., 2011), so this distorted component is not expected to be within aragonite per se but rather a calcite with similar lattice spacing for the incorporation of sulfate (see the Data Repository). The originally aragonitic shell of the adjacent gastropod subsequently dissolved and was replaced by later calcite cement with very low sulfate concentrations (near detection limit; Fig. 2B, ROI 3).

Diagenetic effects can be deciphered by careful investigation of variations in major and trace element concentration. For example, Sr and Mn are good indicators for

diagenetic alteration: Sr is abundant in seawater and carbonates that precipitate from it, decreasing in abundance with progressive diagenetic recrystallization; Mn is found in only trace quantities in oxic seawater and primary marine carbonates, however it is abundant in anoxic fluids, and its abundance can increase in carbonates diagenetically altered in the presence of later anoxic fluids. Complementary synchrotron micron-scale trace element analyses can provide information about the environmental histories of individual petrographic components (e.g., Figs. 2E and 2F). For example, the abundance of Fe and Mn in the cement replacing the gastropod shell indicates that the cements formed in association with anoxic fluids in which these metals are soluble (Figs. 2E, 2F, 3E, and 3F).

The identification of organosulfate components was unexpected and may provide insights into biomineralization mechanisms of extinct clades of organisms. Organosulfate could represent a chemical fossil of calcification potentially mediated by organosulfate-bearing polysaccharides (Cuif et al., 2008; Trong Nguyen et al., 2014). Sulfate concentrations are highest in the cellular framework of a dasyclad alga, which shows contributions from inorganic and organic sulfate (Figs. DR2A–DR2E). This fossilized organosulfate is inferred to derive from sulfate-bearing polysaccharides, rather than inorganic lattice-substituted sulfate (Gorzelak et al., 2013). In modern coral skeletons, X-ray fluorescence mapping has shown that sulfate is associated with organic fibers related to the sites of calcification (Cuif et al., 2003). Specifically, banding patterns of sulfate have been imaged in fibrous parts of coral septa, evincing a biochemical zonation that corresponds to the step-by-step growth of fibers. These sulfate bands can be diagnostic among extant coral clades, with more distinct banding recorded in *Montastraea* than in

Lophelia, and weaker signals observed in *Favia* (Cuif et al., 2003). Our results demonstrate the ability to distinguish inorganic from organic moieties of sulfate in a variety of carbonate grains (Figs. 2 and 3) and fossil algae (Fig. DR2), and we speculate that organosulfate templates were involved in the precipitation of calcitic and aragonitic biocrystals of mollusk shells or coral skeletons.

SUMMARY

Variation in CAS among various carbonate components—not all of which record a primary signal—presents a major challenge to using $\delta^{34}S_{CAS}$ records from bulk carbonates to understand the evolution of Earth's atmosphere and oceans. A basic assumption of the CAS proxy is that it is evenly distributed within sedimentary carbonates, reflecting a homogenous source from the ocean. However, primary CAS reflects the ambient sulfate pool from which the carbonate component precipitated, whether it be seawater or pore water. Thus, early marine cements forming in pore fluids can have a primary CAS signature that may be reflective of marine conditions, whereas marine fossils that recrystallized in chemically evolved pore fluids may incorporate nonmarine CAS. The data presented here show that CAS abundances vary among fossils, muds, and cement components, and that at least three distinct sulfate moieties are preserved (Figs. 2 and 3; Fig. DR2), all of which contribute variably to the bulk chemistry of the sample (see the Data Repository; Figs. DR4–DR6). The $\delta^{34}S$ of sulfate among the various carbonate components and classes of sulfate moieties cannot be assumed to be identical to each other or to all uniformly record coeval seawater sulfate; given the diversity in their provenance, the $\delta^{34}S$ of distinct sulfate components could be quite different (Present et al., 2015). Bulk-rock $\delta^{34}S_{CAS}$ will reflect the weighted mixing

of the $\delta^{34}S_{CAS}$ of these carbonate components and moieties of sulfate, each with their own variable composition and diagenetic histories. Stratigraphically varying mixtures of distinct sulfate-bearing components, rather than any change in the marine sulfate reservoir itself, could contribute to the scattered bulk-rock $\delta^{34}S_{CAS}$ data spanning the Late Ordovician Hirnantian glaciation and mass extinction records (Jones and Fike, 2013; Rose et al., 2019).

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FIGURE CAPTIONS

Figure 1. A: X-ray absorption near-edge structure (XANES) measurements across sulfur K-edge resolve sulfate from sulfide and other sulfur phases, as well as enable identification of multiple forms of (inorganic and organic) sulfate. Spectra localities are from a crinoidal grainstone (from Anticosti Island, Québec, Canada; see the Data Repository [see footnote 1]). Inset: Spectra for sulfur phases from the European Synchrotron Radiation Facility (Grenoble, France) ID21 Sulfur XANES Spectra Database (https://www.esrf.eu/home/UsersAndScience/Experiments/XNP/ID21/php.html). R—Raman; DMSO—Dimethyl sulfoxide. B: Inorganic sulfate (2482.7 eV), distorted inorganic sulfate (2482.5 eV), and organosulfate (2481.4 eV) concentrations across the micritized rim of a non-skeletal grain from an Ordovician oncoid grainstone from Anticosti Island, Québec, Canada (see Fig. 3D).

Figure 2. A: Optical image through an oncoid grainstone (from Anticosti Island, Québec, Canada) featuring replaced gastropod shell (right side of image). B: Schematic diagram and associated legend of optical image shown in A, highlighting the different carbonate components with the localities of spectral analyses. Data summary for the numbered regions of interest (ROIs) can be found in the Data Repository (see footnote 1). C: Corresponding sulfate abundances (2482.7 eV) showing the difference in distribution of carbonate-

associated sulfate (CAS) within grains, between grains, and within calcite cement. D: Maps showing abundance of inorganic sulfate, distorted sulfate, and organosulfate, and a composite of the three moieties across micritized rim of the grain (region outlined with red box in A). E,F: Complementary elemental abundance maps (warm colors indicate increased abundance) for Fe (E) and Mn (F).

Figure 3. A: Optical image through gastropod shell in an oncoid grainstone (from Anticosti Island, Québec, Canada). B: Schematic diagram and legend of the optical image shown in A, highlighting different carbonate components with the localities of spectral analyses. Data summary for the numbered regions of interest (ROIs) can be found in the Data Repository (see footnote 1).
C: Corresponding sulfate abundances (2482.7 eV). D: Maps showing abundance of inorganic sulfate, distorted sulfate, organosulfate, and a composite of these moieties across non-skeletal grain with micritic coating (region outlined with red box in A). E,F: Complementary elemental abundance maps (warm colors indicate increased abundance) for Fe (E) and Si (F).

Figure 4. Notched boxplots for sulfate concentrations in the regions of interest (ROIs) 1–9 (Fig. 2) and ROIs 10–19 (Fig. 3) from fan oncoid grainstone (from Anticosti Island, Québec, Canada). Each column represents data from one ROI. Box encloses 50% of the data (25th to 75th percentile), and whiskers extend 1.5× interquartile range beyond box. Points represent outliers as defined by Tukey's method (method of comparing least squares means for equality; https://www.itl.nist.gov/div898/handbook/prc/section4/prc461.htm). Width of the notch defines the 95% confidence interval of median. nonskel—non-skeletal.

[1]GSA Data Repository item 2019xxx, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.