



Large Carbonate Associated Sulfate isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician strata



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ABSTRACT

Carbonate Associated Sulfate (CAS) is trace sulfate incorporated into carbonate minerals during their precipitation. Its sulfur isotopic composition is often assumed to track that of seawater sulfate and inform global carbon and oxygen budgets through Earth's history. However, many CAS sulfur isotope records based on bulk-rock samples are noisy. To determine the source of bulk-rock CAS variability, we extracted CAS from different internal sedimentary components micro-drilled from well-preserved Late Ordovician and early Silurian-age limestones from Anticosti Island, Quebec, Canada. Mixtures of these components, whose sulfur isotopic compositions vary by nearly 25‰, can explain the bulk-rock CAS range. Large isotopic variability of sedimentary micrite CAS (³⁴S-depleted from seawater by up to 15‰) is consistent with pore fluid sulfide oxidation during early diagenesis. Specimens recrystallized during burial diagenesis have CAS ³⁴S-enriched by up to 9‰ from Hirnantian seawater, consistent with microbial sulfate reduction in a confined aquifer. In contrast to the other variable components, brachiopods with well-preserved secondary-layer fibrous calcite—a phase independently known to be the best-preserved sedimentary component in these strata—have a more homogeneous isotopic composition. These specimens indicate that seawater sulfate remained close to about 25‰ (V-CDT) through Hirnantian (end-Ordovician) events, including glaciation, mass extinction, carbon isotope excursion, and pyrite-sulfur isotope excursion. The textural relationships between our samples and their CAS isotope ratios highlight the role of diagenetic biogeochemical processes in setting the isotopic composition of CAS.

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1. Introduction

The sulfur isotopic composition of Carbonate Associated Sulfate (CAS) is routinely measured as a proxy for the composition of ancient seawater sulfate and informs Earth's surface redox balance (Burdett et al., 1989; Kampschulte and Strauss, 2004). CAS is trace sulfate commonly found in carbonate rocks of all ages (e.g. Burdett et al., 1989; Kah et al., 2004; Kampschulte and Strauss, 2004; Paris et al., 2014a), and generally thought to be incorporated from ambient seawater during precipitation of carbonate phases (Burdett et al., 1989). Because carbonate strata are nearly ubiqu-

itous in the geologic record, and carry abundant geological and geochemical context, CAS has the potential to provide a robust and high-resolution archive of changes in the sulfur cycle (Kampschulte and Strauss, 2004).

Much effort has gone into constructing time-series records of marine sulfate's isotopic composition. Sulfur isotopic compositions are reported in the common $\delta^{34}\text{S}$ notation as part-per-thousand (‰) deviations of ³⁴S/³²S relative to the Vienna Canyon Diablo Troilite (V-CDT) reference standard. Modern oceans constitute a large sulfur reservoir thought to be at steady-state between weathering and volcanic influxes and reduced and oxidized outputs (Bottrell and Newton, 2006; Garrels and Lerman, 1984). Sulfate reduction to sulfide is directly linked to the carbon cycle by microbial metabolisms, and a fraction of this sulfide flux is preserved as pyrite. There can be large kinetic sulfur isotope fractionations associated with microbial sulfate reduction (MSR), so the relative size of the pyrite sink can affect the isotopic composition of seawater (Garrels and Lerman, 1984). Today, this conceptual model

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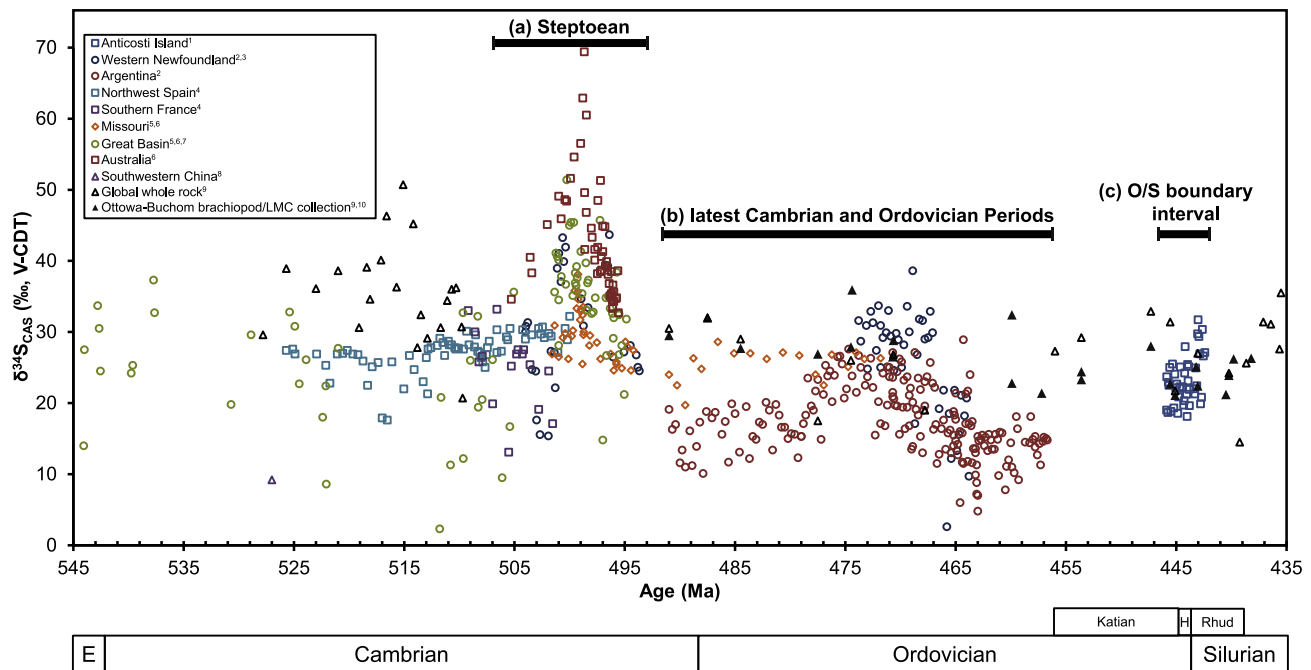


Fig. 1. Compilation of previously reported CAS $\delta^{34}\text{S}$ values from early Paleozoic successions, plotted by sample collection location. Open symbols represent CAS extracted from bulk-rock (commonly micritic) samples, and closed symbols represent CAS extracted from biogenic calcite. See the text for discussion regarding the Steptoean Stage (a), the latest Cambrian and Ordovician periods (b), and the Ordovician–Silurian (O/S) boundary interval (c). E = Ediacaran, H = Hirnantian, LMC = low-magnesium calcite. Data references: ¹Jones and Fike (2013), ²Thompson and Kah (2012), ³Hurtgen et al. (2009), ⁴Wotte et al. (2012b), ⁵Gill et al. (2007), ⁶Gill et al. (2011b), ⁷Loyd et al. (2012b), ⁸Goldberg et al. (2005), ⁹Kampschulte and Strauss (2004), ¹⁰Wu et al. (2014).

leads to an estimated 20 Myr residence time of sulfate in the ocean (Bottrell and Newton, 2006), so longer-term changes in seawater $\delta^{34}\text{S}$ reflect the distribution of oxidized and reduced chemical species on Earth's surface. However, there is a high degree of stratigraphic variability in many CAS $\delta^{34}\text{S}$ records, especially those obtained from bulk-rock samples from early Paleozoic strata (Fig. 1).

Large stratigraphic CAS variability around longer-term trends may be primary, or be a result of secondary processes (Kampschulte and Strauss, 2004). Primary CAS variability would reflect temporal changes in seawater sulfate, or spatial patterns between depositional settings or basins. Secondary processes involve incorporation of sulfate from post-depositional sources. These could include burial or dolomitizing fluids, diagenetically-modified pore fluids, or oxidation of other sulfur-bearing phases in the rock (Gill et al., 2008; Lyons et al., 2004; Marengo et al., 2008b; Rennie and Turchyn, 2014). While secondary processes may mask the interpretation of sulfur isotopes in a global mass balance framework, they do contain additional information about the paleoenvironment and basin history. Finally, sample preparation itself might oxidize sulfur-bearing phases in the rock and result in measurement of a mixture of CAS and newly generated sulfate (Marengo et al., 2008a; Mazumdar et al., 2008; Wotte et al., 2012a).

Previous workers have tried different methods to reduce the contribution of secondary processes. These methods include mathematically smoothing variability (e.g. Kampschulte and Strauss, 2004; Song et al., 2014), selecting the most robust or best-preserved samples (e.g. fossils in Gill et al., 2011a; Kampschulte et al., 2001; Kampschulte and Strauss, 2004; Newton et al., 2011) (filled triangles in Fig. 1), chemically isolating CAS during extraction from other sulfur-bearing phases (Wotte et al., 2012a), and applying independent geochemical indicators of preservation (Gill et al., 2011a; Goldberg et al., 2005).

Other studies have hypothesized that high CAS variability mainly reflects the primary distribution of marine sulfate, especially in Precambrian and early Paleozoic strata (Gill et al., 2011b;

Kah et al., 2004; Loyd et al., 2012b; Thompson and Kah, 2012; Wotte et al., 2012b). The implication is that a small marine sulfate reservoir is necessary to explain observations of rapidly changing (<1 Myr) or spatially heterogeneous isotopic composition. For example, CAS datasets from the late Cambrian Period include a large positive $\delta^{34}\text{S}$ excursion that coincides with the Steptoean Positive Isotopes of Carbon Excursion (SPICE) event, but the magnitude of the excursion varies strongly between localities (interval "a" in Fig. 1) (Gill et al., 2007, 2011b; Hurtgen et al., 2009). Similarly, latest Cambrian through Ordovician CAS records from Argentinian strata show a large range of more than 10‰ over both short and long intervals, and display different trends from North American CAS records of the same age (interval "b" in Fig. 1) (Gill et al., 2007; Thompson and Kah, 2012).

To a certain extent, the ability to choose ideal samples for sulfur isotope analysis has been limited by the amount of sulfate required by traditional gas-source mass spectrometric methods. Typically, millimoles of sulfate, corresponding to tens of grams of Phanerozoic carbonates, are precipitated as barite and combusted (as summarized by Wotte et al., 2012a). Because many geologic successions do not offer texturally homogeneous samples, traditional CAS analysis of such samples may thus integrate many different phases (primary grains, micrite, and cements of different age). A recent multi-collector inductively coupled plasma-source mass spectrometric (MC-ICP-MS) method for sulfur isotopic analysis of aqueous sulfate (Paris et al., 2013) facilitates the analysis of nanomole-level sulfur samples from <10 mg of typical Phanerozoic carbonates.

Interval "c" (Ordovician–Silurian boundary interval) in Fig. 1 shows a CAS record from texturally heterogeneous limestones collected on Anticosti Island, Canada (Jones and Fike, 2013). This record has variability that is nearly half of the magnitude of secular changes over the entire Phanerozoic interval (Kampschulte and Strauss, 2004; Wu et al., 2014) but is interpreted to reflect a constant seawater $\delta^{34}\text{S}$ composition during Late Ordovician time (Jones and Fike, 2013). Near the end of Late Ordovician time there was a major climate change into a glaciated

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