# Large $\delta^{34}S_{CAS}$ variability among sedimentary components in end-Ordovician-age strata

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The sulfur isotopic composition of Carbonate Associated Sulfate ($\delta^{34}S_{CAS}$) is routinely measured as a proxy for the composition of ancient seawater sulfate. However, the variance among geologic samples greatly exceeds analytical precision, resulting in noisy records and raising questions about the accuracy of the proxy. CAS analytical techniques commonly require large samples (>40μmol $SO_4^{2-}$, normally >30g $CaCO_3$), so integration of different components of sedimentary rocks formed at different times (fossils, other grains, matrix, and cements) may explain this scatter.

To test if intra-sample variability explains noise in CAS records, we analyzed 5-10mg samples (20-100nmol $SO_4^{2-}$) of different components from Late Ordovician-age hand samples collected on Anticosti Island, Canada. We observed a $\delta^{34}S_{CAS}$ range up to 21‰ between components in the same sample using a new sulfur isotope MC-ICP-MS analytical technique on aqueous samples [1]. The component with the least variability (up to 2‰) is the secondary fibrous layer of brachiopod fossils, which were independently demonstrated to have little diagenetic alteration [2]. Micritic cement matrix, often chosen for CAS analysis, is 5‰ to 15‰ lighter than contemporaneous brachiopods. Coarsely recrystallized fossils and late cements are enriched up to 6‰ from brachiopods.

We confirmed that brachiopods may provide good archives for seawater $\delta^{34}S$: the measured value of a modern brachiopod (20.52±0.11‰, V-CDT) is very slightly depleted relative to modern seawater (20.97±0.10‰, V-CDT) [1].

With a bulk-rock $\delta^{34}S_{CAS}$ record from Anticosti Island with 8‰ variance, Jones and Fike [3] argued that the $\delta^{34}S$ of seawater sulfate did not fluctuate along with carbon and pyrite-sulfur isotope excursions during the End-Ordovician Mass Extinction. Our analysis of less-variable brachiopods also does not record a $\delta^{34}S_{CAS}$ excursion, and supports their hypothesis.

[1] Paris *et al* (2013) *Chem. Geol.* **345,** 50-61. [2] Finnegan *et al* (2011) *Science* **331,** 903-906. [3] Jones & Fike (2013) *EPSL* **363,** 144-155.