Gypsum sulfur isotopic record of the early Cambrian: implications for the seawater sulfur cycle

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Cambrian marine sulfate $\delta^{34}S$ data have been shown [1] to be consistently higher than both earlier Proterozoic and later Ordovician seawater $\delta^{34}S$. However, Cambrian data are still sparse, sometimes stratigraphically ambiguous, and were acquired from possibly diagenetically-influenced sulfate associated with phosphorites and carbonates. Direct evidence from marine evaporite deposits is rare. In this study, we report sulfur isotope data from Xiaotan section, SW China, where two layers of gypsum with a combined stratigraphic thickness of 15 meters are preserved in the lower Cambrian Shanyicun Formation (upper Cambrian Series 2).

Conventional sulfur isotope ratio measurement of gypsum is performed by IRMS, whereby gypsum is first precipitated as barium sulfate and then converted into sulfur dioxide, which is time-consuming and relatively imprecise, with analytical errors of up to 1-3‰ [2]. In this study, gypsum sulfur was extracted from evaporite rock samples using dionized water at 40ºC. Sulfur isotope ratio measurement was performed using a standard-sample bracketing method on a Neptune Plus MC-ICP-MS at the State Key Laboratory for Mineral Deposits Research, Nanjing University, China. Calcium concentration after dilution was low enough (<0.3 mM) for matrix effects to be insignificant [3]. The analytical reproducibility (2SD) using this approach is below 0.3 ‰.

Results show that the gypsum samples have $\delta^{34}S$ values ranging from 29.7‰ to 32.5‰, averaging 31.3‰ (n=7). Almost identical constraints on seawater $\delta^{34}S$ have been confirmed from evaporites (Siberia) and barites (Canada, Sardinia) of Cambrian age [1, 4]. The consistency of evaporite $\delta^{34}S$ data stands in contrast to the more variable CAS record, and implies some underlying continuity in baseline seawater $\delta^{34}S$ during the Cambrian. A simple box model of the seawater sulfur cycle suggests that seawater sulfate concentrations were relatively high during much of the early Cambrian. However, additional contemporaneous sedimentary sulfide and carbonate-associated sulfur $\delta^{34}S$ works are required to more fully understand the marine sulfur cycle in Cambrian.

[1] Shields *et al*. (2004) *Chem. Geol.* **204**, 163-182. [2] Fry *et al*. (2002) *Rapid Commun. Mass Spectrom*. **16**, 854-858. [3] Liu *et al*., (2016) *Talanta* **151**, 132-140. [4] Strauss et al. (2000) *Precambrian Res*. **175**, 17– 28.