Sulfur-isotope signatures of Paleoproterozoic VMS deposits: Constraints on the composition of ambient sea-water

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$\delta^{34}S$ ratios of metallic sulfide minerals have been reported from eight Pleoproterozoic VMS deposits of the 1.8 Ga old Penokean Volcanic Belt (PVB) in the Lake Superioir Region of the United States. These deposits are: Back Forty, Bend, Eisenbrey, Flambeau, Horseshoe, Lynne, Reef, and Schoolhouse [1]. The average $\delta^{34}S$ values from most of these deposits lie within the mantle-range between -2 and 2‰ (VCDT). Average $\delta^{34}S$ values from Back Forty and Lynne deposits are slightly higher: 2.5 and 2.4‰ respectively [2]. There is no systemaic variation in $\delta^{34}S$ based on the type of sulfide mineral, nature or depth of the host rock, ore-texture or host-rock alteration.

Tight ranges of $\delta^{34}S$ values around 0‰ for most deposits indicate either a strong derivation of S from the mantle source, and/or a near 0‰ value of S in sea-water. Although no significant temporal variation of $\delta^{34}S$ for magmatic sulfur has been found [2], the $\delta^{34}S$ variation for the seawater sulfate reservoir has been uncertain. The high $\delta^{34}S$ value of ~21.0‰ of the modern seawater sulfate is considerably higher than inferred values in Archean and Paleoproterozoic. Oxidative continental weathering started at about 2.3 Ga and the $\delta^{34}S$ values progressively increased through Proterozoic in response to addition of oxidized sulfur.

When $\delta^{34}S$ values from the eight studied VMS deposits are plotted in a geographical map, the countour lines connecting similar $\delta^{34}S$ values tend to orient parallel to the inferred southern margin of the Archean Superior Craton. The $\delta^{34}S$ values increase consistently in a N-NE direction. This could be indicative of high ^{34}S input from the coastalline along the southern margin of the continent and thus, a higher degree of oxidation in shallow levels of the oceanic water. This could imply a Paleoproterozoic ocean water column, stratified with respect to the availability of oxygen.

[1] Moleski, N., Boxleiter, A. and Thakurta, J. (2019) *Minerals*, **9**, 6, doi.org/10.3390/min9010006; [2] Huston, D. L.; Pehrsson, S.; Eglington, B. M.; Zaw, K. (2010) *Economic Geology,* **105**, 571-591.