Multiple Sulfur Isotopic Records of Diagenetic and Hydrothermal Effects on Pyrites in 2.7 Ga Shales

Jianghanyang Li, Long Li, Richard Stern, Gang Yang, Judith Hannah, Holly Stein

Archean supracrustal rocks provide precious opportunities to examine the supporting environments for and the evolution of Earth's early life. As an example, S isotopes have been widely used to infer the energy source and microbial activities in the Archean ocean based on the exotic mass-independent fractionation signatures of different S sources and the mass-dependent isotope fractionations associated with microbial activities. However, all the discovered Archean rocks have undergone green-schist facies or higher-grade metamorphism. The effect of metamorphism (commonly associated with hydrothermal fluids) on the S isotope compositions of Archean rocks has not been quantitatively assessed so far, leaving uncertainties in interpreting the S isotopic data.

Here, we collected high-resolution multi-S isotopic data from diagenetic pyrite nodules and secondary hydrothermally precipitated pyrites in 2.7Ga shales from the Superior Province. The results show that the $\delta^{34}S$ and $\Delta^{33}S$ values of hydrothermal pyrites display a positive relationship and can be explained by a mixing between two end-members with one pointing toward the rim of pyrite nodules and the other with high $\delta^{34}S$ value (>7.7‰) and high $\Delta^{33}S$ value (>4.8‰), which likely corresponds to the signature of hydrothermal fluid. Pyrite nodules, although strongly fractured and infilled by secondary quartz during metamorphism, show strong cross-grain isotopic variations from medium $\delta^{34}S$ values (~1‰) and low $\Delta^{33}S$ values (~-1‰) in the core to negative $\delta^{34}S$ values (-2‰ to -3‰) and relatively high $\Delta^{33}S$ values (~2‰) at the rim. This negative relationship between $\delta^{34}S$ and $\Delta^{33}S$ values not only indicates clearly no hydrothermal overprints on pyrite nodules but also argues against the two commonly referred pathways for pyrite.