Questioning the Biogenicity of Neoproterozoic Superheavy Pyrite

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The Neoproterozoic sulfur isotope ($\delta^{34}S$) record is characterized by anomalous $\delta^{34}S_{pyrite}$ values that are higher than the apparently contemporaneous $\delta^{34}S_{sulfate}$ values. These pyrites are commonly known as "superheavy pyrite", and have been reported globally, including the Cryogenian Datangpo Formation in South China. Notably, all published models assume a biogenic and syndepositional origin for the Datangpo superheavy pyrite (DSP). This assumption hypothesizes that all the pyrites formed by microbial sulfate reduction (MSR) in the water column or during early diagenesis in shallow marine sediment.

To evaluate these models, integrated petrographic and in situ $\delta^{34}S$ analyses were conducted for the DSP using the SEM-SIMS technique at unprecedented spatial resolution (2 μm ion beam diameter). For the first time, a bimodal distribution of $\delta^{34}S$ values are found in this study to be closely coupled with distinct textures of pyrites in the Datangpo Formation. The isotopically light pyrites ($\delta^{34}S$ from 16.6 to 26.7‰) are disseminated and are likely to be early authigenic in origin. In contrast, the DSPs ($\delta^{34}S$ from 56.3 to 71.0‰) are mostly perserved as nodules or veins and petrographically replace rhodochrosite and illite, which we interpret as a late diagenetic product. On a basin scale, the DSPs are associated with ancient faults in South China, suggesting intimate association with external fluids. Based on these lines of sedimentological and geochemical evidence at both basin- and μm-scales, we conclude that the DSP formed via thermochemical sulfate reduction (TSR) after deposition and that previous models that assuming MSR should be reevaluated. Our results suggest that post-depositional TSR can play an influential role in generating high $\delta^{34}S$ values. Consequently, interpretations of high $\delta^{34}S$ values from the ancient geological record should consider the influence of post-depositional processes in generating superheavy pyrite associated with noteworthy biogeochemical events in the Earth's history.