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Questioning the biogenicity of Neoproterozoic superheavy pyrite by SIMS

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Abstract

The Neoproterozoic sulfur isotope ($\delta^{34}S$) record is characterized by anomalously high $\delta^{34}S_{pyrite}$ values. Many $\delta^{34}S_{pyrite}$ values are higher than the contemporaneous $\delta^{34}S_{sulfate}$ (i.e., $\delta^{34}S_{pyrite} > \delta^{34}S_{sulfate}$), showing reversed fractionation. This phenomenon has been reported from the Neoproterozoic post-glacial strata globally and is called "Neoproterozoic superheavy pyrite." The commonly assumed biogenic genesis of superheavy pyrite conflicts with current understanding of the marine sulfur cycle. Various models have been proposed to interpret this phenomenon, including extremely low concentrations of sulfate in seawaters or pore waters, or the existence of a geographically isolated and geochemically stratified ocean. Implicit and fundamental in all these published models is the assumption of a biogenic origin for pyrite genesis, which hypothesizes that the superheavy pyrite is syngenetic (in the water column) or early diagenetic (in shallow marine sediments) in origin and formed via microbial sulfate reduction (MSR). In this study, the Cryogenian Datangpo Formation in South China, which preserves some of the highest $\delta^{34}S_{pyrite}$ values up to +70‰, is studied by secondary ion mass spectrometry (SIMS) at unprecedented spatial resolutions (2 μm). Based on textures and the new sulfur isotope results, we propose that the Datangpo superheavy pyrite formed via thermochemical sulfate reduction (TSR) in hydrothermal fluids during late burial diagenesis and, therefore, lacks a biogeochemical connection to the Neoproterozoic sulfur cycle. Our study demonstrates that SEM-SIMS is an effective approach to assess the genesis of sedimentary pyrite using combined SEM petrography and micrometer-scale $\delta^{34}S$ measurements by SIMS. The possibility that pervasive TSR has overprinted the primary $\delta^{34}S_{pyrite}$ signals during late diagenesis in other localities may necessitate the reappraisal of some of the $\delta^{34}S_{pyrite}$ profiles associated with superheavy pyrite throughout Earth's history.

Keywords: Microbial sulfate reduction (MSR), thermochemical sulfate reduction (TSR), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), sulfur isotopes, framboidal pyrite; Isotopes, Minerals, and Petrology: Honoring John Valley