

Development of superheavy $\delta^{34}\text{S}$ values in Paleozoic pyrite detected by SIMS microanalysis and ion imaging

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In the deep biosphere, microbial sulfate reduction (MSR) is exploited for energy. Here we show that in fractured continental crystalline bedrock in three areas in Sweden, this process produced sulfide that reacted with iron to form pyrite extremely enriched in ^{34}S relative to ^{32}S . Secondary Ion Mass Spectrometry (SIMS)-microanalyses and ion imaging detected an overall $\delta^{34}\text{S}_{\text{pyrite}}$ variability in the fracture systems of 186‰CDT and variation of >140‰ in single pyrite crystals. The lightest $\delta^{34}\text{S}_{\text{pyrite}}$ values suggest a very large fractionation during MSR, with an isotope enrichment of >70‰ from the initial sulfate ($\delta^{34}\text{S}_0$). Fractionation of this magnitude requires slow a MSR rate, a feature we attribute to nutrient and electron-donor shortage as well as initial sulfate abundance. The superheavy $\delta^{34}\text{S}_{\text{pyrite}}$ values were produced by Rayleigh fractionation effects in a diminishing sulfate pool. Large volumes of pyrite with superheavy values of >+100‰ within single fractures, or actually single borehole intercepts, homogeneous superheavy $\delta^{34}\text{S}_{\text{pyrite}}$ values throughout individual crystal growth zones, associated heavy average values up to +75‰ and heavy minimum $\delta^{34}\text{S}_{\text{pyrite}}$ values suggest isolation of significant amounts of isotopically light sulfide in other parts of the fracture system. Large fracture-specific $\delta^{34}\text{S}_{\text{pyrite}}$ variability and overall average $\delta^{34}\text{S}_{\text{pyrite}}$ values lower than the anticipated $\delta^{34}\text{S}_0$ support this hypothesis. The superheavy pyrite found locally in the borehole intercepts thus represents a late stage in a much larger fracture system undergoing Rayleigh fractionation. Micro-scale Rb-Sr dating and U/Th-He dating of co-genetic minerals revealed that most pyrite formed in the Paleozoic era. The $\delta^{13}\text{C}$ values in co-genetic calcite pointed to that the superheavy $\delta^{34}\text{S}_{\text{pyrite}}$ values were related to organotrophic MSR, in contrast to findings from marine sediments where superheavy pyrite has been proposed to be linked to anaerobic oxidation of methane. The findings provide new insights into MSR-related formation of large fractions of ^{34}S -rich pyrite.