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A first glimpse of CAS in deep groundwater fracture systems

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Microbial sulfate reduction is an important process in deep rock-hosted ecosystems. In deep fractures of the Paleozoic bedrock of the Fennoscandian shield (down to 800 meters), pyrite with extreme $\delta^{34}S$ variability, of -54 to 143 ‰ V-CDT exists in paragenesis with calcite [1]. The calcite fracture coatings formed during different episodes from Paleozoic time to 13 Ma ago [2]. The extreme variability and in particular the ^{34}S-enrichment in the pyrite indicates microbial sulfate reduction in a closed-system microenvironment and it suggests a super heavy sulfate source. To date, no sulfate of this kind has been reported. In this study, we aim to decipher this enigmatic source sulfate by analyzing carbonate-associated sulfate (CAS) of calcite in paragenesis with superheavy pyrite. The small size of fracture coating calcite required MC-ICPMS analyses of extracted CAS. Interestingly, the $\delta^{34}S_{CAS}$ values show moderate ^{34}S enrichment, with values between 2.3 and 28.2 ‰. Hence, the $\delta^{34}S_{CAS}$ values are much lower than the bulk $\delta^{34}S_{pyrite}$ values of up to 80 ‰ [1] indicating a decoupled sulfate pool for CAS and pyrite.

Two different types of microbial sulfate reduction may have impacted the $\delta^{34}S_{CAS}$ and the $\delta^{34}S_{PYRITE}$ values. The vast ^{34}S-fractionation in pyrite requires very slow rates of organoclastic sulfate reduction, which rather led to calcite dissolution, because these low rates do not cause enough alkalinity. Therefore, even if calcite formed in the same microenvironment as pyrite, calcite could not precipitate when superheavy pyrite formed. Instead, the calcite shows moderate signs for anoxic methane oxidation coupled to sulfate reduction as reflected by negative $\delta^{13}C$ [2] and moderately enriched $\delta^{34}S$ values.

We propose that the combined limiting conditions for both nutrients and ions, their episodic input into the deep fracture system together with low diffusion rates of the fracture fluids enabled an episodic balance and completion of the microbial processes, which could lead to extreme isotope fractionation of $\delta^{34}S_{PYRITE}$ and only moderate $\delta^{34}S_{CAS}$ values.

[1] Drake, Whitehouse, Heim, et al. (2018), Geobiology 16, 556-574.

[2] Drake, Heim, Roberts, et al. (2017), Earth and Planetary Science Letters 470, 108-118