

The origin of dissolved sulfate in deep fracture water of Witwatersrand Basin, South Africa

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Fracture waters have been trapped in the deep subsurface of Witwatersrand Basin, South Africa for millions of years. Interestingly, microbial communities coupling sulfate reduction and H₂ oxidation as their metabolic pathways have been discovered from some of the most isolated fracture waters. However, the origin of dissolved sulfate, which is the essential substrate to support the sulfate reducer-dominated subsurface ecosystem, was poorly constrained. Here, we employ multiple sulfur isotopes (^{32, 33, 34, 36}S) and oxygen isotopes (^{16, 18}O) to assess potential sulfate sources and secondary processes that could affect the sulfur and oxygen isotope compositions of dissolved sulfate in the fracture waters. The isotope results suggest that Archean sulfides in the wall rocks rather than carbonate associated sulfate (CAS) from overlain Transvaal dolomite are responsible for the sulfate origination. Modeling provides that it only takes less than 0.33 million years to reach oxygen isotope equilibrium between dissolved sulfate and fracture water, which are orders less than the residence time (1-100 million years) of the studied fracture systems. However, the oxygen isotope compositions of the dissolved sulfate from shallow fractures (< 1.4 km) show disequilibrium with that of water, but fall well in the δ¹⁸O range of sulfate produced by oxic weathering of sulfide, indicating that the oxidation of sulfide is relatively recent or even ongoing in these oxic fracture systems. In contrast, the samples from two deep sites (>3 km) show oxygen isotope equilibrium between SO₄ and H₂O, suggesting much slower sulfate production. This may be attributed to the fact that these fracture systems are relative anaerobic and sulfate is produced by less efficient oxidation mechanism, such as radiolytic oxidation.

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