ISOTOPIC INSIGHTS INTO HABITABILITY AND POTENTIAL MICROBIAL ACTIVITY IN THE LONG-ISOLATED DEEP TERRESTRIAL SUBSURFACE. L. Li^{1,2}, B. A. Wing^{3,4}, T. H. Bui⁴, J. M. McDermott², G. F. Slater⁵, S. Wei¹, G. Lacrampe-Couloume², and B. Sherwood Lollar², ¹Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3, ²Department of Earth Sciences, University of Toronto, Toronto, Ontario, Cananda M5S 3B1, ³Department of Geological Sciences, University of Colorado Boulder, Boulder, CO, USA 80309, ⁴Department of Earth and Planetary Sciences and GEOTOP, McGill University, Montreal, Quebec, Canada H3A 0E8, ⁵School of Geography and Earth Sciences, McMaster University, Hamilton, Ontario, Canada L8S 4K1.

The Earth's Precambrian cratons are considered to be terrestrial analogues to Mars due to similarities in geology and age. Recently, ancient waters with noble gas-derived mean residence times of tens of million years (in the Witwatersrand Basin, South Africa^{1,2}) to billions of years (1.1-1.7 billion years at Kidd Creek inthe Canadian Shield³) have been discovered in the fractures of the Precambrian cratons. These ancient fracture waters are generally characterized by high salinity and low reduction potential with abundant reduced gas components (e.g., H₂, CH₄) produced by fluid-rock interation, but with few measurable oxidizing components^{4,5}.

While microbial investigations on the Kidd Creek fracture water are still ongoing, novel microbial ecosystems dominated by sulfate-reducing bacteria coupling H₂ oxidation and sulfate reduction have been discovered inhabiting the 25 million-year-old fracture water at 2.8 km below the surface in the Witwatersrand Basin^{2,6}. The understanding of habitability, in particular the sustainability of energy sources, and possible microbial activities, in these deep subsurface water systems, has important implications for the search for life on extraterrestrial rocky planets.

So far, H₂, the major electron donor inferred to support metabolic reactions of deep subsurface ecosystems, has been found to originate mainly from serpentinization of wall rocks or radiolysis of water^{4,7}. However, the cycling of sufate, the coupled electron acceptor, remain less well known. Here, we use multiple sulfur isotopic techniques to examine dissolved sulfate in the billion-year-old water from 2.4 km below surface at Kidd Creek, in order to infer the source and sustainability of sulfate in the fracture waters and possible microbial activity in this ancient groundwater system.

Our results show that the dissolved sulfate in the fracture waters from Kidd Creek carry a sulfur isotope mass-independent fractionation (S-MIF) signature, which has only been reported in Archean sulfide and sulfate minerals as a result of atmospheric sulfur cycling through the oxygen-free Archean atmosphere^{8,9}. The magnitude of the S-MIF signal of the dissolved sulfate correlates well with the pyrite minerals in the wall rocks¹⁰, which comparise part of the 2.7 Ga Kidd

Creek VMS ore deposit. This finding indicates that the dissolved sulfate in the fracture water at Kidd Creek is derived from oxidation of pyrite in the wall rocks. Given that these fracture waters are strongly reduced and lack substantial abundances of other oxidants (e.g., O₂, Fe^{3+} , NO₃), we suggest that the sulfide oxidation is implemented by oxidizing radicals (e.g., O[•], HO[•] and H_2O_2) produced by radiolysis of water, the same process that produces H_2^{7} . This oxidation process differs from direct radiolysis on sulfide minerals, and is thus termed indirect radiolytic oxidation of pyrite (IROP). Modeling of sulfate production by IROP and free energy calculations suggest that the IROP mechanism can produce sufficient sulfate to sustain approximately 100 to 3,000 cells per litre of fluid (a biomass density consistent with those found in the fracture fluids in the Witwatersrand Basin^{2,6}) over geological time scales.

In addition, we observed orders of magnitude lower abundance and ³⁴S enrichment in the dissolved sulfate, indicating the importance of another process in addition to IROP. Our modeling shows that these shifts are best explained by microbial sulfate reduction, either through a steady-state slow reduction over billions of years or through an episodic fast reduction occurring on a timescale of millions of years.

This analogue study suggests that the deep subsurface fracture water trapped in crystalline rocks can sustain a stable habitable environment over geological time scales. Such geological settings may be considered as potential targets for future Mars missions in addition to paleosedimentary settings.

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