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Novel isotopic techniques to investigate the deep subsurface acetate cycle

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Deep groundwater sequestered in the continental crust represents a vast, under-constrained reservoir of water and carbon. These environments host microbial communities that can be isolated from surficial biogeochemical cycles on timescales from decades to hundreds-of-millions of years [1]. Carbon cycling in subsurface fracture fluids operates on a spectrum from abiotically- to biotically-driven. Organic acids may play an important role across this spectrum, as they can be synthesized by microbial metabolisms or via water-rock interactions, including radiolytic chemistry. They can also accumulate to low-millimolar concentrations in the subsurface [2]. Here, we applied a new Orbitrap-based technique [3] for measuring $d^{13}C$ and $d^{2}H$ of acetate to investigate organic acid turnover in an abiotically dominated site (Kidd Creek Mine, Canada) and a more microbially active site (Birchtree Mine, Canada). We measured $d^{13}C$ values of acetate that were relatively enriched in Kidd Creek fracture fluids (-7 to -9‰) and relatively depleted in Birchtree (-27‰), potentially reflecting different formation mechanisms [2]. However, at both sites, we determined that the hydrogen atoms on acetate's methyl group were in isotopic disequilibrium with ambient water, based on theoretical calculations of the acetate-water equilibrium isotope effect (EIE). Through a series of high-temperature hydrothermal autoclave experiments (100-250°C, 30 MPa), we demonstrated that acetate exchanges hydrogen atoms with water at a temperature-dependent rate. Given Kidd Creek's *in situ* temperature (25°C), its pool of acetate should have fully equilibrated with fracture fluids within 10^6 years. If the calculated EIE is accurate, acetate could be cycling 1000-times faster than the residence time of Kidd Creek's fluids (10^8-10^9 years). Our observations may suggest that radiolytic reactions between host rock and deep groundwater sustain long-term organic acid production. Organic acids are common substrates for microorganisms to assimilate carbon and generate energy. Therefore, a sustainable, low-temperature source of acetate that only requires water-rock interactions represents an auspicious mechanism to support early-life on Earth and microbial life on other celestial bodies.

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