

Oxygen isotope compositions of phosphates in deep fracture fluids in Precambrian rocks

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Saline fracture fluids rich in hydrogen and methane within Precambrian Shield rocks have been shown to provide habitable environments for subsurface microbial life [1]. At Kidd Creek mine, Timmins, Canada, fracture fluids with mean residence times of 1.1-1.7 Ga were discovered at ~2.4 km depth below the surface [2]. In this study, we measured the ¹⁸O/¹⁶O ratio of dissolved phosphate ($\delta^{18}\text{O}_{\text{PO}_4}$) that binds to iron(III)-(hydr)oxides as the fracture fluids discharge and oxidize. Iron(III)-(hydr)oxides are very efficient scavengers of dissolved phosphate, and record its $\delta^{18}\text{O}_{\text{PO}_4}$ value with no measurable fractionation between dissolved phosphate and iron-(hydr)oxide-bound phosphate [3]. At Kidd Creek mine, iron(III)-(hydr)oxide deposits were formed by oxidation as fracture fluids rich in reduced iron come in contact with air on the rock walls and mine floor during 2007-2013.

The measured $\delta^{18}\text{O}_{\text{PO}_4}$ values range from 6.4 to 10.9 ‰ (VSMOW, n=4) and closely match the equilibrium $\delta^{18}\text{O}_{\text{PO}_4}$ values (7.1 to 10.6 ‰) calculated using eq. of [4] with measured fracture fluid $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (-14.3 to -11.6 ‰, [5]) and present-day fracture fluid temperature (22.8 to 27.4 °C, [5], same as mine air temperature). O-isotopic equilibrium takes ca. 10⁴-10⁵ years in abiotic dissolved phosphate-water systems at pH 5-9 and 22-28 °C, however, enzymatic catalysis can drive the system to equilibrium at rates ca. 10⁸ times faster [4]. Given the geologically long residence time of the Kidd Creek fracture fluids and evidence of microbial activity within the mine, we cannot distinguish between equilibrium due to abiotic and/or microbial reactions, however, we propose that iron(III)-(hydr)oxide-bound phosphate is a proxy for dissolved phosphate, and that its $\delta^{18}\text{O}_{\text{PO}_4}$ value is a useful temperature proxy.

[1] Lin *et al.* (2006) *Science* **314**, 479-482. [2] Holland *et al.* (2013) *Nature* **497**, 357-360. [3] Blake *et al.* (2010) *Nature* **464**, 1029-1032. [4] Chang & Blake (2015) *GCA* **150**, 314-329. [5] Li *et al.* (2016) *Nature Commun.* **7**, 13252.