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Iron oxide-bound PO_4 biomineral proxy for environmental temperature and life

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Iron oxides have a strong affinity to bind inorganic phosphate (PO_4). This is particularly true for iron oxides derived from oxidation of Fe^{2+}-rich hydrothermal fluids, which contain several wt% phosphorus (P) typically derived from surrounding seawater. In addition to high P concentration, the O-isotopic composition of PO_4 ($d^{18}O_P$) associated with iron oxides (*e.g.*, sorbed, occluded or co-precipitated) contains information on environmental temperature, especially in the case of iron oxides derived from the oxidation of Fe^{2+} by iron-oxidizing bacteria (FeOB). Furthermore, high amounts of P found in microbial iron oxides are derived from metabolism which carries a $d^{18}O_P$ signature reflective of intracellular cycling/equilibration with ambient water/temperature conditions similar to bioapatite in bones and teeth [1]. Importantly, at relatively low vent temperatures (<150 °C) and over the relatively short timescales of active hydrothermal venting, biological activity (*i.e.*, enzyme-catalyzed PO_4-water O-isotope exchange) is required to imprint ambient temperature onto $d^{18}O_P$, thus providing additional evidence of a biological origin [2]. Microbial iron biominerals such as those formed by the Zetaproteobacterium *Mariprofundus ferrooxydans* –a major contributor to prolific microbial iron oxide mats found at undersea volcanic sites (*e.g.*, Kamaʻehuakanaloa (formerly Loihi) Seamount, 9°N EPR) often form distinct, morphological structures and are typically highly enriched in P (> 6 wt%).

We will present results of morphological, geochemical (SEM, nanoSIMS) and O-isotope(O-18, O-17) analyses of iron oxides from wide-ranging settings including: deep-sea hydrothermal systems, microbial mat deposits, freshly-precipitated iron oxides from pure laboratory cultures and FeOB grown *in situ* at active vent sites, as well as iron oxides precipitated from >1 Ga groundwater. $d^{18}O_P$ values of microbial iron oxides consistently reflected ambient environmental temperatures. Notably, all iron oxides analyzed proved to be excellent repositories for dissolved PO_4 and to contain largely untapped environmental temperature information in the $d^{18}O_P$ proxy. These results further demonstrate $d^{18}O_P$ as a powerful geochemical indicator of the biogenicity of iron oxide minerals, especially in cases where FeOB do not produce tell-tale morphological structures (*e.g.* anoxygenic phototrophic FeOB, several marine FeOB).

[1] Jaisi et al., 2010, GCA, 74,1309-1319.

[2] Chang etal., 2021, EPSL 570: 117071. DOI: 10.1016/.epsl.2021.117071.