Effects of structural phosphate on the microbial reduction of iron oxide and secondary mineralization product formation and reactivity

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The bioreduction of Fe (III) oxides may result in the production of a suite of Fe (II)-bearing secondary mineralization products, including magnetite, siderite, ferrous hydroxy carbonate, vivianite, and green rusts. To better understand the effects of iron oxide structure and composition on the formation of particular secondary mineralization products of Fe (III) oxide bioreduction, we examined the effects of phosphate doping on the bioreduction of lepidocrocite (γ-FeOOH) by the dissimilatory iron-reducing bacterium *Shewanella putrefaciens* CN32 and the reactivity of the secondary mineralization products with U (VI).

Anoxic defined mineral medium containing 75 mM formate and 80 mM Fe (III), in the form of phosphate doped (0 – 0.7 mass % P) lepidocrocite, was inoculated with *S. putrefaciens* CN32. Samples were collected for measurement of Fe (II) and characterization of the secondary mineralization products by X-ray diffractions, scanning electron microscopy, and ^{57}Fe Mössbauer spectroscopy. Aqueous suspensions of secondary mineralization products were spiked with U (VI) and subsequent U speciation was measured by U L_{III}–edge X-ray absorption fine structure spectroscopy (XAFS).

In the absence of structural phosphate, lepidocrocite was rapidly and stoichiometrically reduced to magnetite, which over time was partially transformed to ferrous hydroxy carbonate. Doping with between 0.2 – 0.7 mass % P significantly inhibited the initial reduction of lepidocrocite but ultimately resulted in greater overall Fe (II) production and the formation of carbonate green rust as the dominant secondary mineralization product; doping with 3.0 % P resulted in the formation of green rust and vivianite. In the presence of green rust, U (VI) was completely reduced to nanoparticluate uraninite; however, U (VI) was only partially reduced to U (IV) by magnetite.

Geochemical and isotopic characteristics of the Nuvvuagittuq belt: Implications for Earth's early crust formation

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The first 500 million years of the Earth's history are unrepresented in the rock record. As a result, the nature of the Earth's early crust and the processes responsible for its formation are largely conjecture. However, recent ^{142}Nd studies of the Nuvvuagittuq faux-amphibolites suggest that this greenstone belt formed nearly 4.3 billion years ago, making it the only known remnant of Hadean crust preserved on Earth. Moreover, the faux-amphibolites are mafic in composition and likely were produced directly by melting of the primordial mantle, unlike the granitic sources of Hadean zircons. The faux-amphibolite can be divided into three distinct chemical groups mainly based on the abundance of high field strength and rare earth elements. These groups are stratigraphically superimposed and have compositional analogues in three types of ultramafic sills following the same stratigraphic succession that appears to record an evolution from 'tholeiitic to 'calc-alkaline' magmatism.

A new series of faux-amphibolite were analysed for ^{142}Nd isotopic composition. The new data confirm previously reported deficits in ^{142}Nd. The ^{142}Nd/^{144}Nd ratios for the faux-amphibolite correlate positively with their Sm/Nd ratios producing a slope corresponding to an age of 4276^{+61}_{-104} Ma for all faux-amphibolite. The lowest ^{142}Nd/^{144}Nd ratios were found in the enriched low-Ti faux-amphibolites. Line fitting only these sample corresponds to an age of 4263^{+41}_{-64} Ma. When including the corresponding cogenetic ultramafic sills we obtain a ^{146}Sm-^{142}Nd age of 4310^{+43}_{-61} Ma.

The composition of the faux-amphibolite is consistent with its protolith being Hadean basaltic to andesitic hydrothermally altered volcanic rocks with a geochemical evolution typical of the volcanic successions of many younger Archean greenstone belts. Regardless of the exact tectonic setting, this volcanic succession suggests that the geological processes responsible for the formation and evolution of Archean greenstone belts were active as early as 4.3 Ga.