As(V)-bearing lepidocrocite and green rust reduction by *Shewanella putrefaciens*: Evidence for Fe(II) carbonate hydroxide formation

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Arsenic is a toxic metalloid involved in important health issues due to the contamination of water resources. High arsenic concentrations typically derive from the breakdown of As-bearing Fe-oxides, particularly under anaerobic conditions. A variety of microorganisms influences arsenic mobility using oxidation, reduction, and methylation reactions that strongly control arsenic speciation in the environment. In the present study, *Shewanella putrefaciens* strain ATCC 12099, an iron-respiring bacterium, was incubated under anaerobic conditions with As(V) ions, As(V)-bearing lepidocrocite, or a lepidocrocite without arsenic. Results show that strain ATCC 12099 is capable of reduction of $HAs(V)O_4^{2-}$ to $H_3As(III)O_3$ when the former oxoanion is dissolved in solution (at pH 7.8), or when it is adsorbed onto the surface of lepidocrocite. Cultures in which lepidocrocite was used as the sole electron acceptor led to the formation of biogenic hydroxycarbonate green rust prior to ferrous carbonate hydroxide. In contrast, when the electron acceptor was As(V)-bearing lepidocrocite, XRD analysis revealed ferrous carbonate hydroxide to be the dominant reaction product; no green rust formation was observed in this case. As K-edge XANES spectroscopy indicated that all As(V) (K-edge(max) = 11875eV) was reduced to As(III) (K-edge(max) = 11871.3eV). These results suggest the presence of As(III) either on the surface of ferrous carbonate hydroxide, and/or in another ferrous-solid phase, and they show for the first time bacterial reduction of hydroxycarbonate green rust.

Nd Isotopic Constraints from the 3.8 Ga Nuvvuagittuq Greenstone Belt for the Degree of Depletion of the Early Earth's Mantle

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Rare occurrences of Eoarchean mantle-derived crust provide the only compositional and isotopic constraints on the early crust-mantle differentiation of the Earth. There is currently considerable debate about the implications of the Nd isotopic compositions of such early Archean mantle-derived rocks. The relatively high positive initial εNd values obtained on Eoarchean rocks (Nulliak Assemblage, Labrador, Canada; Amîtsok Gneisses, Akilia and Isua supracrustal assemblages, SW Greenland) are interpreted to indicate derivation from a mantle source already strongly depleted in the Eoarchean, implying that significant volumes of continental crust had formed early in the Earth's evolution. Here we present the Nd isotope data of the newly discovered ca. 3.8 Ga Nuvvuagittuq greenstone belt (Northern Québec, Canada), and discuss their implications for early mantle depletion.

The Nuvvuagittuq greenstone belt contains numerous ultramafic and gabbroic sills. Most of the gabbro and ultramafic samples display positive $\varepsilon Nd_{(3.8Ga)}$, values ranging from -1.8 to +3.9, with an average of $+1.3 \pm 0.2$ in 29 samples. The few samples that yield $\varepsilon Nd_{(3.8Ga)}$ values > +3 (up to +3.9) suggest that they may have been derived from a mantle source that had already experienced an extensive trace element depletion well before 3.8 Ga, equivalent to that seen in the present-day MORB source. Such a degree of depletion of the early Archean mantle, however, is not supported by the flat to slightly LREE-depleted profiles of the gabbros. Furthermore, whole rock analyses for a series of samples from an ultramafic sill and a second series of samples from a gabbroic sill fall along ~3.8 Ga isochrons with initial εNd values of +1.3 and +2 respectively, values which are similar to the mean of all the individual sample values. This suggests that the few higher $\varepsilon Nd_{(3.8Ga)}$ values are either anomalous or indicate heterogeneity of the mantle source of Nuvvuagittuq's rocks. Nevertheless, the Nd isotopic compositions of these mantle-derived rocks suggest that the degree of depletion of the mantle recorded in the Nuvvuagittuq greenstone belt is not as extreme as that indicated by the Nd isotopic compositions of the 3.8 Ga SW Greenland rocks.