

ARSENIC BIOREMEDIATION BY BIOGENIC IRON OXIDES AND SULFIDES

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Millions of people globally are exposed to groundwaters that exceed the World Health Organization (WHO) safe guideline value of 10 ppb (or 0.13 μM) for arsenic in groundwater [1-3]. In this study we used microcosms containing sediment from an aquifer in Cambodia with naturally elevated levels of arsenic (As) in the associated groundwater to evaluate the effectiveness of microbially-mediated production of iron minerals for *in situ* As remediation. The microcosms were initially incubated without amendments to allow the microbial release of As, and other geogenic chemicals from the sediments into the aqueous phase. Following this period, either nitrate, or a mixture of sulfate and lactate were then added to stimulate biological Fe(II) oxidation and sulfate reduction, respectively.

Without treatment, soluble As concentrations in the microcosms reached 3.9 (± 0.9) μM at the end of the 143 day experiment. However, As levels had decreased to 0.01 and 0.41 (± 0.13) μM in the nitrate, and in the sulfate with lactate treated microcosms, respectively by the end of the experiment. Analyses using a range of biogeochemical and mineralogical tools, indicated that sorption onto freshly formed hydrous ferric oxide (HFO) and ferrous iron monosulfide (FeS) are the likely mechanisms for As removal in the respective treatments. Incorporation of the experimental results into a one-dimensional transport-reaction model suggests that, under conditions representative of the Cambodian aquifer, the *in situ* precipitation of HFO would be effective in bringing groundwaters into compliance with the World Health Organization (WHO) safe water limit for As, although soluble Mn release accompanying biogenic HFO generation presents a potential health concern. In contrast, production of biogenic iron sulfide minerals would not remediate the groundwater As concentration below the recommended WHO limit.

[1] Smedley & Kinniburgh (2002) *Applied Geochemistry*, **17**, 517-568. [2] Ravenscroft P, Brammer H, Richards K (2009) *Arsenic Pollution: A Global Synthesis*. [3] Polya et al. (2005) *Mineralogical Magazine*, **69**, 807-823.

Geochemical and isotopic characteristics of Earth's early mafic crust: a comparison between Nuvvuagittuq and Isua greenstone belt metavolcanic rocks

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Investigation of Earth's primitive crust largely has focused on felsic rocks because they are the most likely host rocks of zircons, providing robust geochronological constraints. However, these felsic rocks cannot be directly produced from melting of the mantle but instead originate by melting of an older mafic precursor. Despite the scarcity of preserved early mafic crusts, the Isua and Nuvvuagittuq greenstone belts are dominated by basaltic metavolcanic rocks. The Isua greenstone belt includes geochemically distinct subterranean rocks dominated by tholeiites and boninite-like rocks (Garbenschiefer) interpreted to have been produced in an arc setting. Similarly, the Nuvvuagittuq belt is mainly composed of a succession of tholeiitic, boninitic and calc-alkaline rocks (Ujaraaluk unit) also sharing geochemical characteristics with suprasubduction related rocks. Both greenstone belts comprise rocks with ¹⁴²Nd anomalies compared to modern terrestrial Nd. Because ¹⁴²Nd anomalies can only be produced while ¹⁴⁶Sm decay was active, i.e. before 4 Ga, both suites of rocks acquired their ¹⁴²Nd isotopic composition in the Hadean. The Isua metavolcanic rocks were formed between 3.7-3.8 Ga. Therefore, their elevated ¹⁴²Nd isotopic composition is consistent with their Eoarchean derivation from an incompatible-element depleted Hadean mantle source. Consequently, they show no correlation between their ¹⁴²Nd/¹⁴⁴Nd and Sm/Nd ratios. However, the Nuvvuagittuq mafic rocks display a positive correlation between their ¹⁴²Nd/¹⁴⁴Nd and Sm/Nd ratios consistent with them being formed in the Hadean, between 4.3 and 4.4 Ga, from a "normal" depleted mantle. The Nuvvuagittuq rocks with the strongest arc-like signature have larger ¹⁴²Nd anomalies compared to the tholeiitic rocks. However, most Isua mafic rocks analyzed so far for their ¹⁴²Nd isotopic composition are tholeiites. Here we present a ^{146,147}Sm-^{142,143}Nd isotopic study of the Garbenschiefer which has the strongest arc-like signature in the Isua greenstone belt, allowing comparisons between the different groups of Isua mafic rocks. The studied set of Garbenschiefer rocks covers a relatively wide range of ¹⁴⁷Sm/¹⁴⁴Nd ratios (0.1650-0.2610) and preliminary analyses suggest that they also yield ¹⁴²Nd anomalies. The Isua and Nuvvuagittuq greenstone belts represent the oldest preserved mantle-derived suites of rocks and despite the fact that they were most likely formed ~500 million years apart, they share striking geochemical similarities. A geochemical and isotopic comparison between these greenstone belts will allow us to better understand the evolution of Earth's early crust through time and the geological processes responsible for its formation.