Biogeochemical arsenic cycling linked to iron and sulfur redox cycles in Paleoarchean marine sediments

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Arsenic (As) is thought to be abundant and important to microbial life in the Archean, yet little evidence of its journey through ancient sedimentary environments is preserved in the rock record [1-4]. Arsenic was observed in shallow marine sediments from a 3.26 Ga outcrop in the Fig Tree Group of the Barberton Greenstone Belt. Outcrop and cm-scale patterns show As was introduced and mineralized early. Handheld XRF measurements show the highest [As] in ferruginous cherts and Fe-rich pebbles in an overlying fan-delta conglomerate. These cherts and conglomerates were connected by shallow vents now preserved as black chert dikes, providing an avenue for fluid recycling between the very reduced subsurface and the more oxidized sediment-water interface, enabling redox sensitive As, Fe, and S to accumulate. Patterns of Fe, As, and S in pebbles were examined using μ-XRF, Raman, and As K-edge XANES. Arsenic is preserved as arsenopyrite (FeAsS) and spatially associated with hematite (Fe_2O_3) in pebbles that underwent a post-depositional or early diagenetic reduction step. Arsenic lines pre-erosional surfaces, laminations, and early veins within pebbles. These observations are best explained by the introduction of As during deposition or very early diagenesis, before silicification. We propose that As was introduced as As(III) or As(V) by adsorption to amorphous Fe-oxide phases during sedimentation. Following deposition partial microbial reduction of Fe(III), SO_4^{2-}, and As(V) led to early mineralization as microcrystalline FeAsS, a process known to occur in modern reducing and arsenic-contaminated aquifer sediments [5]. We conclude that early As mineralization is essential to its preservation in Archean environments. These results indicate that a complete biogeochemical As redox cycle was active in the Archean ocean, having major implications for Archean microbial activity and evolution.

[1] Duval *et al.* (2008) *BMC Evol. Biol* **8**, 1-13. [2] Kulp *et al.* (2008) *Science* **321**, 967-970. [3] Lebrun *et al.* (2003) *Mol. Biol. Evol* **20**, 686-693. [4] Oremland *et al.* (2009) *Geomicrobiol. J* **26**, 522-536. [5] Saalfield & Bostick (2009) *ES&T* **43**, 8787-8793.