

Characterization of nanoparticulate arsenic in waters draining abandoned gold mine tailings

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Waters draining abandoned gold mine sites often contain elevated concentrations of As, however, relatively few studies have attempted to distinguish between colloidal As and truly dissolved As. This distinction is important since it impacts the mobility, bioavailability, and toxicity of As. We collected surface waters draining abandoned gold mine tailings in Nova Scotia, Canada and sequentially filtered them through standard 450 nm pore size filters followed by stirred cell ultrafiltration through 10 nm polycarbonate membranes. Arsenic concentrations in the <450 nm fraction, traditionally termed "dissolved", ranged from 0.2 – 1.6 mg/L. Colloids, operationally defined here as suspended solids of 10 to 450 nm diameter, accounted for 5 – 56% of this As. SEM inspection of the 10 nm filters indicated that Fe and Ca were commonly associated with As-bearing nanoparticles. This was corroborated by synchrotron-based μ XRF mapping which revealed that As was closely correlated with Fe, and to a lesser extent Ca. Multiple μ XANES analyses indicated that arsenate was the dominant form of nanoparticulate As, with minor amounts of arsenite. These analyses showed no evidence for As-bearing sulfides, implying that arsenopyrite, the original mineralogical host of As prior to mining, was not a significant contributor to colloidal As. Synchrotron-based μ XRD examination was hampered by the limited sample mass collected on the filter; however, akaganeite was found to be associated with As hotspots identified by μ XRF mapping. Taken together, these preliminary data suggest the primary nanoparticulate vectors of As are secondary mineral assemblages such as hydrous (Ca-)Fe arsenates and Fe oxyhydroxides, previously shown to be major As-rich phases within the near-surface, weathered tailings at these historical gold mine sites [1].

[1] Walker *et al.* (2009) *Can. Mineral.* **47**, 533-556.

Cadmium isotopic composition in cultured marine phytoplankton

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Cadmium (Cd) has been used as a marine paleo-nutrient proxy [1] despite its complex and poorly understood biogeochemical cycling in the oceans. The past five years have seen an increasing interest in the stable isotopic composition of Cd in the marine environment as this information has the potential to be used as a tracer for the physical and biological controls of Cd cycling in the oceans and its use as a micronutrient. It has also been suggested that Cd isotopes themselves may be a reliable paleoproxy for primary productivity [2].

Both iron (Fe) and zinc (Zn) have been shown to influence the uptake of Cd in both cultured and natural phytoplankton populations [3]. Phytoplankton utilize Cd in the place of Zn for the enzyme carbonic anhydrase (CA) with some species expressing a Cd-specific CA enzyme when grown under Zn-limiting conditions [4].

Using multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with double spiking techniques, significant 0.1%-level isotopic fractionation of Cd in seawater has been demonstrated and attributed to biological uptake [5]. Using these techniques, we examined the Cd isotopic fractionation associated with biological uptake in cultured marine phytoplankton under varying Fe and Zn-limiting conditions.

These experiments confirm that there is an isotopic fractionation associated with biological uptake of Cd, leaving the residual medium isotopically heavy. Fractionation factors calculated, assuming a Rayleigh distillation model, for these cultures demonstrate that Zn-limitation is influential in the resulting Cd isotopic compositions.

The importance of Zn bioavailability on Cd isotopic composition implies that the biogeochemical cycling of Cd in the oceans is complex, which calls into question the potential application of Cd stable isotopes as a paleonutrient proxy.

[1] Elderfield and Rickaby (2000) *Nature* **405**, 305-310. [2] Abouchami *et al.* (2011) *EPSL* In Press. [3] Frew *et al.* (2001) *Deep-Sea Res. Part II* **48**, 2467-2481. [4] Lane *et al.* (2005) *Nature* **435**, 42-42. [5] Ripperger *et al.* (2007) *EPSL* **261**, 670-684.