

Mineralogical and geochemical processes occurring in sulfide-rich tailings after 60 years of subaqueous storage

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The oxidation of sulfide minerals in subaerial tailings deposits generates acid and releases sulfate and metals to pore water. Subaqueous disposal of tailings is a common method for limiting sulfide-mineral oxidation. Numerous short-term studies have demonstrated that shallow water covers are effective at limiting oxygen diffusion to submerged tailings; however, long-term studies are lacking. The former Sherritt-Gordon Zn-Cu mine, located in Sherridon, Manitoba, Canada, deposited sulfide-rich tailings into Fox Lake during 1951. The tailings formed a number of small exposed islands with the majority of material submerged underwater, extending outward into the Lake. Exposed tailings were visually oxidized and submerged tailings commonly were overlain by naturally-established vegetation. Surface water, porewater and core samples were collected in 2001 and 2009 to examine long-term biogeochemistry of land-deposited tailings and the submerged tailings under approximately 1 m of water.

Mineralogical examination of the land-deposited tailings showed a well-defined, ochreous oxidation zone that extended from surface to about 40 cm depth. The interval from 40 to 60 cm was a transitional or intermediate zone of much weaker oxidation, and at depths >60 cm sulfide minerals in the tailings were not altered. In contrast to the thickness of the oxidation zone in the land-based tailings, the equivalent zone in the submerged tailings extended <6 cm below the water-solids interface. Porewater collected from the land-based tailings was characterized by low pH, depleted alkalinity and elevated concentrations of dissolved sulfate and metals. Microbial communities within these tailings were dominated by neutrophilic sulfur oxidizing bacteria. Conversely, the natural colonization of vegetation over the subaqueous tailings resulted in the development of strong reducing conditions evident from circumneutral pH conditions, low concentrations of dissolved sulfate and metals, H₂S production and strong $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{13}\text{S}_{\text{DIC}}$ fractionation indicating microbially-mediated (dissimilatory) sulfate reduction. Within the submerged tailings, secondary marcasite was observed in the relic ochreous zone occurring as coatings on primary minerals. This observation indicates that, following a period of oxidation, metals were subsequently sequestered from solution in this zone. This finding further emphasizes the influence of reducing conditions and microbial activity on metal mobility within mine tailings. Results from this study provide insight for the submergence of sulfide-rich tailings under a shallow water cover as a viable method for long-term storage.

Isotopic fractionation of U(VI) during reduction by sulphide

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Understanding isotopic fractionation of $^{238}\text{U}/^{235}\text{U}$ between soluble U(VI) and insoluble U(IV) is useful in various ways, from understanding the geochemistry of U to its use as a paleoredox proxy [1]. In the environment, deposits of uranium formed by low temperature redox processes (e.g. black shales, roll front deposits) are observed to be isotopically heavy compared to the fluid from which they precipitated by 0.4-1.0‰ (e.g. the $^{238}\text{U}/^{235}\text{U}$ of the Black Sea sediments is consistently heavier than the overlying water column) [1,2,3]. This idea is consistent with theoretical calculations which predict that U⁴⁺ should be heavier than UO₂²⁺ by 1.3‰, primarily due to nuclear volume effects [4,5]. Despite the prevalence of this effect in nature, it has been surprisingly difficult to produce isotopically-heavy reduced U phases experimentally. Two independent studies have shown that the reduction of U(VI) using zero-valent Zn and Fe produces no isotopic fractionation [2,6]. In experiments with two different cultures of U-reducing bacteria, researchers found that the reduced phase was isotopically light by 0.31-0.34‰, opposite of observations in the environment.

Motivated by this discrepancy and reasoning that sulfide is a common and abundant reductant in environmental settings, we set up experiments to measure isotopic fractionation during abiotic U reduction by sulfide. We reduced a 4 ppm U(VI)-CO₃ solution in the presence of 2.1 mM sulfide and 4.11 mM bicarbonate, maintained at a pH of 6.8 using a TRIS/HCO₃ buffer under a UHP He atmosphere [7]. At regular time intervals, the solution containing the soluble U(VI) and a suspended insoluble precipitate, presumably U(IV) in the form of uraninite [7], was sampled using a syringe and rapidly separated using syringe filtration.

Our initial results are well-described by a Rayleigh model and indicate that the reduced uranium phase is lighter than the solution by 0.189±0.097‰ ($\alpha = 0.999811\pm 0.000097$, 2σ). This effect is opposite that observed in nature but similar to results observed for U-reducing bacterial cultures. Since all laboratory experiments so far produce moderately light or unfractionated reduced U, it is possible that isotopic equilibration of U(VI)⇌U(IV) is not achieved on laboratory timescales. Alternatively, the chemical details of the lab experiments may differ from natural systems and theoretical models in some key respect. For example, U speciation may have a large effect, or other reactions, such as U adsorption, could occur.

[1] Weyer *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 345-359, 1370-1375 [2] Stirling *et al.* (2007) *Earth Planet. Sci. Lett.* **264**, 208-225. [3] Romaniello *et al.* (2009) *AGU Fall meeting 2009*, abstract # V54C-06. [4] Bigeleisen (1996) *J. Am. Chem. Soc.* **118**, 3676-3680. [5] Abe *et al.* (2008) *J. Chem. Phys.* **129**, 164309. [6] Rademacher *et al.* (2007) *Environ. Sci. Technol.* **41**, 5927-5933 [7] Hua *et al.* (2006) *Environ. Sci. Technol.* **40**, 4666-4671