

## Bioweathering of chrysotile asbestos

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The serpentine mineral, chrysotile, is the most common asbestiform mineral at asbestos-contaminated sites. Similar in mechanism to other asbestos minerals, its toxicity is related to the presence of iron, which induces oxidative stress, and the fiber's shape, which can lead to piercing of lung alveoli and induces inflammation.

Previous research has developed the idea that fungi endemic to serpentine substrates (*Fusarium oxysporum* and *Verticillium leptobactrum*) can remove atoms of key elements from asbestos particles, rendering them less toxic [1]. In this study, we investigate natural mechanisms of removal of impurity elements (Fe) and structural cations (Mg, Si) from the chrysotile asbestos fibers. We ran greenhouse experiments using heavy metal accumulating plant species, *Brassica juncea*, *Helianthus annuus*, and *Thlaspi caerulescens*. We also planted the native serpentine grassland species, *Sorghastrum nutans*, whose roots form mutualist relationships with arbuscular mycorrhizal fungi (AMF). We also evaluated the use of fungal exudates to remove iron from asbestiform chrysotile through cultured fungal experiments for different species of *Fusarium*.

We analyzed the iron content of plant tissue, fungal tissue, and iron in solution in fungal growth media and organic acid solutions over time via ICP-OES. We imaged the chrysotile fibers and fungi mycelium using an ESEM to determine the change in mineral structure and aspect ratio over time, and we assessed the change in mineral composition of untreated and treated asbestos samples via XRD. Preliminary data demonstrate that *Brassica juncea* was able to remove an average of 300ppm Fe per gram of plant tissue from the surface of chrysotile asbestos, and there was no difference in plant biomass when compared to plants grown with the addition of fertilizer containing iron. Preliminary results from the fungi treatments show that fungi take up iron but do not liberate the iron into the broth solution.

[1] Daghino, S. *et al.* 2006. ES&T 40: 5793-5798.

## Cd isotope fractionation during sorption to Mn oxide at low and high ionic strength

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Two potential applications of Cd isotopes motivate this study:

First, some diatoms have evolved to use Cd instead of Zn in their carbonic anhydrase enzyme [1]. Because these diatoms strongly fractionate Cd isotopes [2], marine sediments may preserve isotopic records of Cd utilization and diatom productivity in the past. A recent study [3] indicated that ferromanganese crusts in particular might preserve a straightforward record of global deepwater Cd isotopes.

Second, for freshwater or groundwater contaminated with Cd, sorption to Mn oxyhydroxide particles can be the dominant process retarding mobility of this toxic heavy metal (except in sulfide-rich conditions). If sorption drives a distinctive isotope effect, then determining the extent to which sorption reactions are attenuating flow of Cd may be possible by tracking Cd isotope signatures in soils or water.

To lay groundwork for these potential applications and to investigate fractionation mechanisms for Cd, we conducted sorption experiments using particles of the Mn oxyhydroxide birnessite, both in pure water and in synthetic seawater. Suspensions of synthetic birnessite particles were doped with Cd and allowed to react for 24 hours (pH adjusted to 8-8.5). Dissolved and sorbed Cd pools were separated by filtration, purified by ion exchange chromatography, and analyzed by MC-ICP-MS.

At low ionic strength we observed a constant offset of +0.15‰ ( $\Delta^{114/112}\text{Cd}$ ) between dissolved and sorbed Cd (sorbed is lighter), regardless of proportion sorbed. This is consistent with reversible sorption driving an equilibrium isotope effect. At high ionic strength, the magnitude of fractionation increased with the proportion of Cd adsorbed, suggesting a kinetic or Rayleigh effect. The difference between low and high ionic strength results is likely driven by solution speciation; *chloro-* complexes dominate Cd speciation in synthetic seawater. We hypothesize that the difference in bonding environment between  $\text{Cd}^{2+}$  and an inner-sphere sorbed complex drives the equilibrium effect at low ionic strength, while fractionation in solution between various *chloro-* complexes becomes important at high ionic strength.

[1] Price & Morel (1990) *Nature* 344, 658. [2] Lacan *et al.* (2006) *Geochim. Cosmochim. Acta.* 70, 5104. [3] Horner *et al.* (2010) *G<sup>3</sup>*, doi:10.1029/2009GC002987.