The biogeochemistry of indium, gallium, and germanium in mine wastes

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Indium, gallium, and germanium have important uses in new families of high efficiency photovoltaic cells, and indium and gallium are used extensively in LEDs. While all of these metals have been in use for the past 30-70 years (indium in ball bearings, germanium and gallium in semiconductors), emerging energy markets are likely to dramatically expand the industrial use of these metals, potentially by orders of magnitude. Despite this increased use, the environmental behavior and toxicity of these metals are poorly understood. However, there is some indication that humans are already having a significant impact on the natural cycling of these metals. Our present study aims to determine the biogeochemical cycling of indium (In), gallium (Ga), and germanium (Ge) associated with mining processes, since our previous studies suggest that mining and smelting processes are currently the largest sources of these metals to the environment. In particular, these metals are byproducts of lead and zinc mining. Their biogeochemistry at mining-impacted sites has a significant impact on the range of their transport, and subsequent human exposure to these metals.

Our study was based at the Tar Creek Superfund Site in Oklahoma, USA, an abandoned lead and zinc mine. We found that Ge is highly elevated in the mine wastes at this site; large particles (>0.5 mm) contain 3-15x crustal concentrations, and small particles (<2.5 um) contain up to 40x crustal concentrations, while Ga and In concentrations were not significantly higher than crustal. Ge also behaves differently than known contaminant metals in this area. For example, over 85% of the Ge in mine wastes from this site is bound in a residual mineral fraction (e.g. silicates) that is not liberated by a hot nitric acid leach. By contrast, Pb, Zn, and Cd are mainly present in a recalcitrant phase. Additionally, simulated gastric fluid extractions release twice as much Ge as a hot nitric acid extraction, indicating that some fraction of the recalcitrant phase is bioaccessible. Again, this contrasts with Pb, Zn, and Cd, and with Ga and In, for which simulated gastric fluid extractions release significantly less than a hot nitric acid leach. Future studies will further explore the cycling of Ga, Ge, and In at the Tar Creek site, including differences in the speciation, mobility, and bioaccessibility of each, in order to more thoroughly understand the behavior and potential impacts of these metals of emerging concern.