The Biogeochemistry of Indium, Gallium, and Germanium in Mine Wastes

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Indium (In), gallium (Ga), and germanium (Ge) are elements critical to new energy technologies, and their use is rapidly increasing. Because they are found as byproducts of lead (Pb) and zinc (Zn) sulfides, mining and smelting appear to be the largest sources of these metals to the environment. Nonetheless, their life cycles are poorly understood, including partitioning and speciation during mining processes and environmental behavior. To understand the cycling of In, Ga, and Ge related to mining, we characterized mine tailings at the Tar Creek Superfund Site in Oklahoma, USA, where historical mining of sphalerite (ZnS) and galena (PbS) has left wastes elevated in Pb, Zn, and cadmium (Cd). Small tailings particles (<2.5 μm) contain higher concentrations of In, Ga, and Ge than large particles (>0.5 mm), similar to Pb, Zn, and Cd. Ge is elevated (3-12 μg/g) in the tailings at this site, whereas Ga (3-11 μg/g) and In (0.1-0.2 μg/g) are not significantly higher than crustal values. Whereas Pb, Zn, and Cd have been shown to be highly labile, sequential extractions suggest that In, Ga, and Ge are less so. In and Ga are released primarily by solutions that target amorphous or crystalline sulfides and Fe- and Mn-oxyhydroxides. In contrast, over 85% of Ge in tailings is bound in a residual fraction not liberated by concentrated nitric acid. Preliminary electron microprobe analyses suggest that Ge is in sphalerite and recalcitrant hemimorphite [$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$]. Concentration and speciation of In, Ga, and Ge impact the potential to recover them from historical mine wastes, and dictate their mobility and bioaccessibility.