Hydrothermal formation of Cu, Ni, and Co arsenide and sulfide minerals: an experimental study of thermochemical arsenite reduction

NICHOLAS C. ALLIN[1] AND CHRISTOPHER H. GAMMONS[2]

Montana Tech, Dept. of Geol. Eng., Butte MT 59701 USA
[1]nallin@mtech.edu; [2]cgammons@mtech.edu

New hydrothermal experiments show for the first time that thermochemical arsenite reduction (TAR) occurs at a much faster rate than thermochemical sulfate reduction (TSR) at temperatures between 150 and 300°C and at SWVP. Elemental Cu, Ni, or Co foils were interacted in sealed silica tubes with acidic solutions containing sulfate, arsenite ($As(OH)_3$), or near equal parts sulfate + arsenite at 50°C intervals between 150-300°C. TAR reactions produced arsenide and poly-arsenide minerals including Cu_3As, Ni_5As_2, and CoAs at all temperatures over time scales of hours to one week. In contrast, TSR reactions produced sulfide minerals including chalcocite (Cu_2S), vaesite (NiS_2), and CoS only at 250 or 300°C. Solutions reacted at 250°C in the presence of metal foils and near equal concentrations (500 mg/L) of arsenite + sulfate quickly (< 12 h) reduced arsenite to arsenide, resulting in complete replacement of the foil surface by a crust of fine-grained metal arsenide. Perched on top of this crust were coarser-grained (up to 50 µm), euhedral crystals of metal sulfide minerals that formed at a later time by the slower TSR reaction.

This study shows that inorganic reductants, such as elemental Cu, Ni, or Co, can drive TAR at temperatures as low as 150°C, while TSR does not occur at measureable rates until T ≥ 250°C. Because both TAR and TSR are thermodynamically favorable, the observed differences are due to kinetics. This agrees with previous field and experimental studies that show that TSR is extremely slow at T < 200°C. In nature, an oxidized, relatively low temperature hydrothermal fluid co-transporting dissolved metals, sulfate, and arsenite will rapidly produce native metals (e.g., Cu, Ag) as well as insoluble arsenide minerals at a reduction front, whereas precipitation of sulfide minerals by TSR will be kinetically inhibited. This helps to explain the abundance of arsenide minerals and scarcity of sulfide minerals in certain types of hydrothermal mineral deposits, including unconformity-type U-Ni deposits, native Cu and Cu-As deposits of the Keweenawan Penisula, Michigan, USA, and veins of the five-element suite (Ni-Co-As-Ag-Bi) of which Cobalt, Ontario, Canada is a well known example.