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Formation of native arsenic in hydrothermal base metal deposits and related supergene U^{6+} enrichment: The Michael vein near Lahr, SW Germany

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Abstract

Native arsenic is an occasional ore mineral in some hydrothermal base metal deposits. Its rarity (compared to pyrite, arsenopyrite, galena, sphalerite, or chalcopyrite, for example) is surprising, as arsenic is a common constituent of upper crustal fluids. Hence, the conditions of formation must be quite special to precipitate native arsenic. An ideal location to investigate the formation of native As and to explore the parameters constraining its crystallization is the Michael vein near Lahr, Schwarzwald, southwest (SW) Germany. Here, galena, sphalerite, and native arsenic are the most abundant ore minerals. The two important ore stages comprise (1) galena-barite and (2) sphalerite-native arsenic-quartz, the latter with a general mineral succession of pyrite → sphalerite ± jordanite-gratonite solid solution → galena → native As. The native arsenic-bearing mineralization formed by cooling of an at least 130 °C hot saline fluid accompanied by a reduction due to the admixing of a sulfide-bearing fluid.

Thermodynamic calculations reveal that for the formation of native arsenic, reduced conditions in combination with very low concentrations of the transition metals Fe, Co, and Ni, as well as low sulfide concentrations, are essential. "Typical" hydrothermal fluids do not fulfill these criteria, as they typically can contain significant amounts of Fe and sulfide. This results in the formation of arsenides, sulfarsenides, or As-bearing sulfides instead of native arsenic. Very minor amounts of pyrite, sulfarsenides, and arsenides record the very low concentrations of Fe, Co, and Ni present in the ore-forming fluid. High concentrations of aqueous Zn and Pb lead to early saturation of sphalerite and galena that promoted native arsenic precipitation by decreasing the availability of sulfide and hence suppressing realgar formation.

Interestingly, native arsenic in the Michael vein acted as a trap for uranium during supergene weathering processes. Infiltrating oxidizing, U^{+VI}-bearing fluids from the host lithologies reacted under ambient conditions with galena and native arsenic, forming a variety of U^{+VI} (±Pb)-bearing arsenates such as hügelite, hallimondite, zeunerite, heinrichite, or novacekite together with U-free minerals like mimetite or anglesite. Some parts of the vein were enriched to U concentrations of up to 1 wt% by this supergene process. Reduced (hypogene) uranium phases like uraninite were never observed.

Keywords: Native arsenic, jordanite-gratonite, hydrothermal, base metal, uranylarsenates, hallimondite