

Dissolution-precipitation vs. solid-state diffusion: Mechanism of mineral transformations in sylvanite, $(\text{AuAg})_2\text{Te}_4$, under hydrothermal conditions

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ABSTRACT

Under hydrothermal conditions, diffusion-driven solid-state reactions can compete with fluid-mediated reaction mechanisms. We have obtained an insight into the complex textures resulting from this competition by studying experimentally the transformation of Au-Ag-telluride sylvanite to Au-Ag alloy under hydrothermal conditions, and exploring the effects of temperature (160–220 °C), pH (2–10), and redox conditions on the sample textures and the reaction kinetics. Sylvanite transformed to Au-Ag alloy over all hydrothermal conditions investigated, but not under dry conditions. The replacement was pseudomorphic, as the Au-Ag alloy preserved the external dimensions of the sylvanite grains. The resulting Au-Ag alloy was porous, consisting of worm-like aggregates with diameters ranging from 200 nm to 1 μm . In addition to Au-Ag alloy, a range of other phases were observed as intermediate products, including petzite (Ag_3AuTe_2), hessite (Ag_2Te), and two compositions of calaverite: an Ag-rich-Te-depleted composition, $(\text{Au}_{0.78}\text{Ag}_{0.22})\text{Te}_{1.74}$, and a normal calaverite, $(\text{Au}_{0.93}\text{Ag}_{0.07})\text{Te}_2$.

The transformation of sylvanite to Au-Ag alloy follows a complex reaction path, with competing reactions proceeding either via interface-coupled dissolution and reprecipitation (ICDR) mechanism or via solid-state exsolution. Initially, sylvanite was replaced by an Au-Ag alloy following an ICDR mechanism, with sylvanite dissolution being the rate-limiting step relative to Au-Ag alloy precipitation. Tellurium was lost to the bulk solution as tellurite or telluride complexes, depending on the redox conditions. Once the concentration of Te in solution reached a critical state, the reaction switched and sylvanite dissolution was coupled to the precipitation of an Ag-rich-Te-depleted calaverite. This Ag-rich-Te-depleted calaverite decomposes via exsolution to calaverite and phase *X* ($\text{Ag}_{3+x}\text{Au}_{1-x}\text{Te}_2$ with $0.1 < x < 0.55$), which in turn breaks down to a mixture of low petzite and low hessite below 120 °C via exsolution. As the reaction continues, the calaverite and phase *X* are all transformed to Au-Ag alloy via ICDR. In the ICDR reactions the Au-Ag alloy precipitated locally near the telluride dissolution site. Such local Au-Ag alloy precipitation is facilitated by fast heterogeneous nucleation onto the sylvanite, calaverite, and petzite surfaces. The dissolution of sylvanite and of the intermediate telluride species, and the overall reaction, are oxidation reactions. The diffusion of oxygen through the porous Au-Ag alloy layer plays an important role in sustaining the reaction.

A similar combination of dissolution-precipitation and solid-state processes may be responsible for the formation of some of the Au and Au-Ag telluride assemblages observed in Nature. These processes may also play a role in the formation of mineral assemblages in Cu-Fe sulfide systems, where the solid-state mobility of Cu^+ ions is relatively high at moderate temperatures. The interplay of different reaction mechanisms results in complex textures, which could easily be misinterpreted in terms of complex geological evolution. At 220 °C, solid-state replacement of sylvanite by Au-Ag alloy is slow (months), but under hydrothermal conditions sylvanite grains $\sim 100 \mu\text{m}$ in size can be fully replaced in as little as 96 h, providing a possible alternative to roasting as a pre-treatment of telluride-rich gold ores.

Keywords: Sylvanite, gold, dissolution-precipitation, exsolution, pseudomorphism, replacement, reaction mechanism, texture