American Mineralogist, Volume 100, pages 1584–1594, 2015

Weathering of galena: Mineralogical processes, hydrogeochemical fluid path modeling, and estimation of the growth rate of pyromorphite

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Abstract

In many natural and anthropogenically affected environments, alteration of galena produces thermodynamically more stable secondary lead phases. These secondary minerals control the mobility of the toxic heavy metal lead in water. These textural, paragenetic, and stability relations have not been investigated in detail in the literature yet. An extensive petrographic study of 41 thin sections of weathered, zoned galena and adjacent country rock from the Schwarzwald mining area, southwest Germany, is presented. The observed textures were evaluated using PHREEQC fluid path modeling and sequences of stable secondary mineral assemblages were predicted.

The most common secondary (supergene) lead minerals of interest here are cerussite, anglesite, and pyromorphite group minerals (PyGM; pyromorphite, mimetite, and vanadinite). These lead phases show a spatially well-ordered zoned texture around the preexisting/relic galena. Cerussite and anglesite commonly occur either as in situ replacement of galena and/or as euhedral crystals in cavities of former, partially dissolved galena. The PyGM are present either as crusts around the margin of the former/relic galena or are common as infiltration products into the host rock/gangue. During progressive weathering anglesite typically disappears first followed by cerussite. Finally, only the highly insoluble PyGM persist as a perimorphose. Hence, a spatially and temporally zoning texture is formed.

Thermodynamic models of various fluid evolution paths using PHREEQC show the influence of temperature, pH, variable P_{CO_2}, phosphorous contents and/or different mineral reactions on the sequence of formation and stability of the secondary lead phases. Already small changes in one or more of these parameters can lead to different mineral assemblages or sequences of secondary lead minerals. Over almost the whole relevant pH range, PyGM are the most stable lead phases, precipitating at very low ion activities explaining their textural position. Whether cerussite or anglesite forms, depends mainly on the pH value of the supergene fluids, which is affected by the quite variable fluid pathways. Furthermore a solubility diagram for a typical near-surface fluid was calculated, showing that anglesite is the most soluble phase, followed by cerussite and PyGM. This again reflects the microscopic observations.

As a further step, the time span for the formation of a natural millimeter-thick pyromorphite crust was evaluated using subsoil phosphorous fluxes from the literature. The calculation indicates that millimeter-thick pyromorphite crusts can be formed in few tens to about hundred years, which is in agreement with observations in the nature.

In this study, a framework for predicting stable secondary lead mineral assemblages and textures by fluid path modeling is given. These models are potentially important for predicting the retention and mobilization of lead in systems around contaminated sites or natural ore deposits.

Keywords: Lead, supergene weathering, phase stabilities, galena, cerussite, anglesite, pyromorphite, reaction path modeling, growth rate