

The hydrothermal Wenzel deposit, South Germany: Implications for the formation of Kongsberg-type silver deposits

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The post-Variscan Kongsberg-type Wenzel deposit near Wolfach, Schwarzwald, Germany, the type locality of the Ag-Sb alloy dyscrasite, was investigated by ore microscopy, electron microprobe analysis, stable isotope and fluid inclusion analysis. Three mineralization stages could be distinguished in the vein. Whereas the first stage is a typical sulfide mineralization including galena and tetrahedrite, the second and third stage show a sulfide-poor association of Ag-Sb alloys with Fe-, Co- and Ni-arsenides and -sulfarsenides in a calcite matrix. The main ore minerals of this stage are allargentum and dyscrasite.

Seven distinct generations of calcite were distinguished. The $\delta^{13}\text{C}$ (V-PDB) and $\delta^{18}\text{O}$ (V-SMOW) values of these generations show a positively correlated trend that evolves from -13.0 to -4.0 ‰ and from 12.3 to 23.6 ‰, respectively.

Fluid inclusion data of stage I fluorite and quartz show homogenization temperatures of 100-180 °C at salinities of 17-26 wt.% NaCl eqv. Fluid inclusions in stage II calcite display similar, but more restricted values of 110-150 °C and 25-28 wt.% NaCl eqv., respectively. The stage III fluid inclusions of calcite show similar homogenization temperatures, but different salinities. Earlier Ag-Sb-alloy bearing calcite of this stage contains inclusions with salinities of 27-30 wt.% NaCl eqv., whereas later ore-free calcite crystals show lower salinities of 3-10 wt.% NaCl eqv. The initial ice melting temperatures of most fluid inclusions range between -45 and -60 °C and are typical of an H_2O -NaCl- CaCl_2 fluid.

Based on all available geochemical data and phase equilibrium constraints in the system Ag-Ca-Na-C-Si-Cl-O-H, we favor a model in which basement-derived near-neutral-pH hydrothermal fluids remobilized older Ag-Sb-bearing mineralizations. Mixing of these fluids with more alkaline formation waters from the Mesozoic cover rocks resulted in the precipitation of the silver alloys in an enrichment zone at P-T conditions of 120-150 °C and approximately 200 bars. A significant pH shift from near-neutral to alkaline is able to explain the abundant association of silver alloys with calcite gangue and the general absence of quartz in the enriched ore zone. This conceptual model can be applied to similar ore deposits world-wide, where rich ores of native silver and silver alloys are hosted by calcite-rich and quartz-poor gangue mineral assemblages.

Interpreting reaction rates at the field scale

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Interpreting reaction rates and associated rate formulations (rate constants, catalytic and inhibitory effects, reaction affinity) at the field typically requires explicit consideration of transport. This is because overall rates may be either locally transport-controlled in the case of heterogeneous systems, or even globally transport-controlled if sufficiently large length scales for reaction are considered. The potential role of physical and chemical heterogeneity has been discussed, but is still not routinely evaluated at the field scale. Heterogeneity may introduce a scale dependence to field-scale rates even in the case where the pore fluids remain far from equilibrium due to either transverse concentration (and therefore rate) gradients, or as a result of longitudinal gradients that develop where the extent of reaction is large. These two effects can be quantified in models of the field-scale system respectively by 1) comparing results from 2D or 3D representations with those from 1D continuum models, and 2) by comparing results from 1D models with those from well-mixed flowthrough reactor models. The analysis indicates that well-mixed reactor models, implicit in the so-called "Inverse Models" to the extent that they are used to determine rate constants, should be used with considerable caution at the field scale.

Another effect associated with the presence of heterogeneities that complicates the interpretation of field-scale rates has to do with the determination of hydrologically accessible reactive surface area. Some regions within the reactive domain may be largely inaccessible because of their low permeability, or mass transfer from the low to high permeability regions (where the bulk of the flow occurs) may be rate-limited. An approach that uses the retardation of a reactive tracer to quantify the hydrologically accessible reactive surface area is presented and is combined with an example involving the weathering of smectite to kaolinite at the Shale Hills site in Pennsylvania, USA.

The complexity of many multicomponent reaction networks presents another significant obstacle to the interpretation of rates at the field scale. Problems are usually manifested when an incomplete data set has been collected at the field scale, in which case potentially important pathways may be neglected altogether. In this regard, combining major and minor element aqueous and solid phase chemical analyses with isotopic analyses offers a powerful approach for delineating all of the important pathways within a field-scale reaction network. Successful examples of such an approach will be provided.