Chapter 5

Experimental Constraints on the Transport and Deposition of Metals in Ore-Forming Hydrothermal Systems

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Abstract

Owing to the polar nature of the water molecule and the ability of metals to form strong aqueous complexes, hydrothermal liquids, vapors and vapor-like fluids are able to transport a large variety of metals of economic interest in concentrations sufficient to form ore deposits. The stability of the complexes depends on the nature of the metal and ligand. In the absence of experimental data, this stability can be predicted qualitatively by the hard/soft acid/base (HSAB) principle, which states that soft metals will form strong complexes with soft ligands and hard metals with hard ligands. Thus, gold will form strong complexes with bisulfide ions but not fluoride ions, whereas the rare earth elements (REEs) will form strong complexes with fluoride ions but not bisulfide ions. Copper, zinc, and, to a lesser extent, silver are transported in nature mainly as chloride species, whereas molybdenum is transported mainly as oxyacid species, gold as bisulfide species, and the REEs as chloride species (despite the fact that they form far stronger complexes with fluoride ions). In vapors and vapor-like supercritical fluids, the partial pressure of H$_2$O is the principal control on metal solubility, which increases with the hydration number of the species and exponentially with pressure. The available experimental data on the speciation of selected base, precious, and critical metals in conjunction with thermodynamic data for the corresponding ore minerals are used to address a number of observations of ore-forming systems. For example, they may help explain why the ore in porphyry Cu-Mo deposits commonly comprises a deep, molybdenite-rich zone and a shallower chalcopyrite or chalcopyrite-bornite–rich zone, both associated with potassic alteration. Our modeling shows that this zoning could be attributed to the different complexation of copper and molybdenum, and could be the result of simple cooling of a single ore fluid. In another example, we evaluate the need for fluid mixing in the genesis of Mississippi Valley-type (MVT) deposits. The titration of H$_2$S into a zinc-bearing brine reveals that the solubility of sphalerite is so low that the concentration of H$_2$S is effectively zero until there is almost no dissolved zinc. Thus, as has been pointed out previously, reduced sulfur and zinc cannot be transported in the same fluid, and mixing of zinc and H$_2$S-bearing solutions is an excellent mechanism for MVT ore deposition. A common assumption, based on the occurrence of fluorite in many REE deposits and the high stability of REE fluoride complexes, is that the REEs are transported dominantly as these complexes. Our modeling shows, however, that this is not the case because HF is a weak acid, thereby limiting the availability of fluoride ions at low pH, and because at higher pH, fluoride ion activity is buffered to low levels by highly insoluble REE-fluoride solid (fluocerite). Instead, it would appear that the REEs are transported dominantly as chloride complexes and deposit in response to decreasing temperature and/or increasing pH. Finally, we show that the solubility of gold as a hydrated chloride species is high enough for hydrothermal vapors and vapor-like fluids to transport economic concentrations of gold in porphyry and high sulfidation epithermal systems. These examples underline the value of using experimental data on metal speciation to determine the solubility of ore minerals in hydrothermal liquids and vapors, and quantitatively evaluate the mechanisms of metallic mineral deposition (cooling, fluid mixing, boiling, and fluid-rock interaction) in ore-forming systems.

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