

The effect of carbon dioxide on metal transport by geological fluids

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Carbon dioxide is the second major component (after water) of most crustal fluids responsible for metal ore deposit formation. Its contents amount up to 10-20 wt% in porphyry Cu-Au-Mo fluids [1] and more than 50 wt% in metamorphic, skarn, orogenic gold, and PGE deposits [2]. In contrast to H₂O-dominated fluids, models of metal transport and deposition by high-temperature and pressure (T-P) CO₂-rich fluids are subjects to debate.

In this contribution, we combined thermodynamic modeling, based on few data available from the literature, with new solubility experiments in H₂O-CO₂-salt-sulfur systems to assess, in a systematic way, the role of CO₂ on the behavior of metals at hydrothermal conditions. Our analysis shows that the presence of CO₂ may have the following impacts on metals transport: a) the presence of CO₂ expands the field of vapor-liquid immiscibility, which causes both changes in metal solubility in the liquid phase (mostly owing to changes in pH), and a redistribution of metals between vapor and liquid; b) CO₂ decreases both water activity and the dielectric constant of the solvent, which in turn affects ion pairing and the activity coefficients of charged species; c) the formation of complexes with C-bearing ligands (CO₃²⁻, HCO₃⁻, CO, COS) may be important for some metals (e.g., Rare Earth Elements, U, Sn, Fe, Ni); and d) at high concentrations (>~50 wt%), CO₂ may also specifically solvate some non-polar complexes (e.g., AuHS(H₂S) [3]) and thus enhance their solubility.

To evaluate the contribution of these factors, we are currently investigating experimentally the solubility of major ore minerals (FeS₂, CuFeS₂, MoS₂, SnO₂, PtS, and Au) in H₂O-KCl-CO₂-H₂S supercritical fluids in the presence of acidity and redox mineral buffers, and as function of CO₂ content. Data obtained in H₂O-dominated experiments allow a revision of the available speciation models for metals in high T-P aqueous fluids. These results will provide the necessary basis for interpreting experimental runs in CO₂-rich fluids, which are in progress.

[1] Kouzmanov & Pokrovski (2012) *Society of Economic Geologists, Inc. Special Publication* **16**, 573-618. [2] Phillips & Evans (2004) *Nature* **429**, 860-863. [3] Pokrovski *et al.* (2008) *Earth & Planet. Sci. Letters* **266**, 345-362.

Using model mineral-organic matter-water interfaces as a step towards determining the fate of pollutants in the environment

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Mineral-organic matter-water interfaces play a valuable role in our ecosystem and are a major role player in determining the bioavailability as well as the fate and transport of anthropogenic contaminants (ACs) in the environment. Anthropogenic contaminants include a vast amount of compounds that are harmful to the environment and its inhabitants. The mineral-organic matter component of the mineral-organic matter-water interface has been found to play a major role in the sorption of ACs in soils and sediments, thus decreasing their presence in other environmental compartments, such as groundwater. This mineral-organic matter component is highly complex, especially in terms of the organic matter constituent, leading to a lack of detailed chemical insight into AC sorption. In order to address this void and gain valuable information that a real soil and sediment samples cannot provide, a simpler more homogeneous mineral-organic matter model system is needed to serve as a model system. To better understand the chemical mechanism of pollutant sorption to the mineral-organic matter component, this project uses a combination of highly adjustable model synthetic mineral-organic matter sorbent systems. The model system consists of silica, a model mineral surface, functionalized with alkyl, aromatic, and O-alkyl groups to echo the natural structure of organic matter. Solid state Nuclear Magnetic Resonance (NMR) as well as a range of other techniques are used for characterization of the model synthetic mineral. Sorption and desorption batch experiment studies are performed using commonly used pesticides as model organic pollutants as an initial step towards understanding the geochemical mechanisms that occur at mineral-water interfaces.