

# The effect of CO<sub>2</sub> on metal transport and fractionation by geological fluids

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Although carbon dioxide is the second major component (after H<sub>2</sub>O) of crustal fluids responsible for ore deposit formation, its effect on transport and precipitation of metals remains largely unknown due to a lack of experimental data and physical-chemical models for CO<sub>2</sub>-rich fluids. Here we combined laboratory experiments and thermodynamic modeling to quantify the role of CO<sub>2</sub> on the solubility of economically important metals (Fe, Cu, Au, Mo, Pt, Sn) under hydrothermal conditions. Solubility measurements of common ores of these metals (FeS<sub>2</sub>, CuFeS<sub>2</sub>, Au, MoS<sub>2</sub>, PtS, SnO<sub>2</sub>) were performed in a homogeneous supercritical fluid (CO<sub>2</sub>-H<sub>2</sub>O-S-KCl, 450°C, 600-700 bar), buffered with iron sulfide-oxide and alkali-aluminosilicate mineral assemblages, using a flexible-cell Coretest reactor.

Our results show that Au, Mo, Pt, Cu do not display clear trends with CO<sub>2</sub>, whereas Fe and Sn increase significantly with increasing CO<sub>2</sub> contents. These data were used to parameterize a model based on the dielectric constant of the H<sub>2</sub>O-CO<sub>2</sub> solvent and metal speciation in aqueous fluids [1]. For example, our predictions show that in a supercritical CO<sub>2</sub>-H<sub>2</sub>O fluid typical of porphyry and orogenic gold deposits, in equilibrium with pyrite and chalcopyrite, the Fe-to-Cu ratio increases by 2 orders of magnitude with an increase of CO<sub>2</sub> content from 0 to 70 wt%. This effect is due to the difference in solvation of the dominant species of Cu (CuCl<sub>2</sub><sup>-</sup>) and Fe (FeCl<sub>2</sub><sup>0</sup>) in the presence of CO<sub>2</sub>. Our results explain the Fe enrichment and Cu impoverishment in metamorphic gold deposits formed by CO<sub>2</sub>-rich fluids. The thermodynamic model described in [2] was experimentally confirmed for AuHS<sup>0</sup> and Au(HS)<sub>2</sub><sup>-</sup>. This study thus demonstrates, for the first time, that the presence of CO<sub>2</sub> in a fluid phase may lead to significant fractionation among metals, an effect that has been ignored so far.

[1] Akinfiev & Zotov (1999) *GCA* **63**, 2025-2041 [2] Pokrovski *et al.* (2014) in Garofalo & Ridley (eds) *Geol Soc London Spec Pub* **402**, 9-70