



The role of carbon dioxide in the transport and fractionation of metals by geological fluids

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Abstract

Although carbon dioxide is one of the major components of crustal fluids responsible for ore deposit formation, its effect on transport and precipitation of metals remains unknown, due to a lack of direct experimental data and physical–chemical models for CO₂-rich fluids. To fill this gap, we combined laboratory experiments and thermodynamic modeling to systematically quantify the role played by CO₂ for the solubility of economically important metals such as Fe, Cu, Zn, Au, Mo, Pt, Sn under hydrothermal conditions. Solubility measurements of common ore minerals of these metals (FeS₂, CuFeS₂, ZnS, Au, MoS₂, PtS, SnO₂) were performed, using a flexible-cell reactor equipped with a rapid sampling device, in a single-phase fluid (CO₂–H₂O–KCl) at 350–450 °C and 600–750 bar, buffered with iron sulfide and oxide and alkali-aluminosilicate mineral assemblages. In addition, another type of experiments was conducted to measure gold solubility in more sulfur-rich supercritical CO₂–H₂O–S–NaOH fluids at 450 °C and 700 bar using a batch reactor that allows fluid quenching. Our results show that the solubilities of Si, Au, Mo, Pt and Cu either decrease (within <1 log unit) or remain constant upon CO₂ increase, whereas those of Fe, Zn and Sn increase significantly (>1 log unit) with CO₂ contents in the fluid increasing from 0 to 50 wt%. These data were interpreted using a simple model that does not require any new adjustable parameters, and is based on the dielectric constant of the H₂O–CO₂ solvent and on the Born solvation parameter for the dominant metal-bearing species in an aqueous fluid. Our predictions using this model suggest that in a supercritical CO₂–H₂O–S–salt fluid typical of metamorphic Au deposits, in equilibrium with pyrite and chalcopyrite, the Cu/Fe ratio decreases by up to 2 orders of magnitude with an increase of CO₂ content from 0 to 70 wt%. This effect is due to the decrease of the fluid dielectric constant in the presence of CO₂, which favors the stability of neutral species (FeCl₂⁰) compared to charged ones (CuCl₂⁻). Our results explain the Fe enrichment and Cu depletion in metamorphic gold deposits formed by CO₂-rich fluids. The transport of gold is unfavorable in the presence of CO₂ only in S-rich (>0.5 wt% S) fluids in which Au forms the negatively charged Au(HS)₂⁻ and Au(HS)S₃⁻ complexes. By contrast, it is only weakly affected in S-poor (<0.1 wt% S) acidic-to-neutral fluids in which the uncharged Au(HS)⁰ complex predominates. Thus, even at very high CO₂ contents (>50 wt% CO₂), the capacity of such fluids to transport gold (up to 100s ppb Au) remains comparable to that of aqueous fluids. These findings are in agreement with analyses of natural fluid inclusions in metamorphic deposits. In more saline oxidizing and S-rich fluids such as those in magmatic porphyry Cu–Au deposits, the

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Fe, Cu, and Au solubilities in the presence of CO₂ decrease by ~1 order of magnitude with CO₂ increasing to 20–30 wt%, following the decrease in the stability of their dominant charged species (FeCl₄²⁻, CuCl₂⁻, Au(HS)₂⁻ and Au(HS)S₃⁻), but stay almost constant at higher CO₂ contents (30–70 wt%) as controlled by the neutral species (FeCl₂⁰, Cu(HS)⁰ and Au(HS)⁰). Such solubility trends suggest a new potential trigger of ore precipitation in porphyry systems by CO₂ pulses from the magmatic chamber, which may operate along with commonly admitted depositional mechanisms such as cooling, vapor-brine immiscibility, and water–rock interaction. The direct effect of CO₂ on the mobility of Pt and Mo, metals that likely form hydrogen sulfide and oxy-hydroxide complexes, respectively, is expected to be weak in most settings. Among the studied elements, Sn is the only one whose solubility may be favored at high CO₂ content (>20 wt%) due to carbonate complexing. This study demonstrates, for the first time, that, contrary to common belief, the presence of CO₂ in a supercritical fluid may lead to enhanced mobility or, on contrary, to massive precipitation of some metals, depending on salinity and sulfur content, and, more generally, to significant fractionations between different metals.

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1. INTRODUCTION

Hydrothermal deposits of base and precious metals on Earth are characterized by the ubiquitous presence of CO₂, which is a major volatile in geological fluids and silicate melts (e.g., Lowenstern, 2001; Manning et al., 2013). Analyses of fluid inclusions show that CO₂ concentrations in aqueous low-salinity fluids that formed intrusion-related and orogenic gold deposits in metamorphic belts reach more than 50 wt% (Boiron et al., 2003; Phillips and Evans, 2004; Garofalo et al., 2014), with some inclusions hosting almost pure CO₂ vapor or liquid phases (e.g., Schmidt Mumm et al., 1997). Carbon dioxide contents in saline fluids from magmatic–hydrothermal porphyry Cu–Mo–Au deposits amount to 10 wt% (~5 mol%) on average, locally attaining 20 wt% (Rusk et al., 2008; Rusk et al., 2011). Carbon dioxide is also universally present in fluids from epithermal and Carlin-type Au deposits, attaining 5–10 wt% in some cases (e.g., Bodnar et al., 1985; Koděra et al., 2005; Catchpole et al., 2011). Carbon dioxide is supplied to hydrothermal systems via fluxing from subduction zones beneath fore-arcs and arcs, including dissolution of C-bearing minerals in fluids, metamorphic reactions, and direct magmatic degassing, with total flux ranging from 14 to 66 Mt C/y (Dasgupta, 2013; Kelemen and Manning, 2015 and references therein). This flux is lower than that of water by only a factor of 5–10, but is higher than that of sulfur and chlorine by a factor of ~10 (Wallace, 2005). It is unclear how CO₂ fluxing may affect the transfers of metals, which are believed to be controlled by water, together with S and Cl, both in magmatic and hydrothermal systems (e.g., Hedenquist and Lowenstern, 1994; Richards, 2011).

Although direct analyses of metal concentrations in CO₂-rich fluid inclusions still remain scarce owing to analytical difficulties and lack of adequate internal standards (e.g., Hanley and Gladney, 2011; Rauchenstein-Martinek et al., 2014), there is growing evidence that the capacity of CO₂-rich fluids to transport some metals at high temperatures (*T*) and pressures (*P*) may be comparable to that of H₂O-dominated solutions. For example, tens to hundreds ppm Cu, Te, Ni, Bi and Pd were analyzed in CO₂-rich fluid inclusions from mafic pegmatites of the Lac des Iles

Complex, Ontario, Canada (Hanley and Gladney, 2011), up to 5 ppm Au and 350 ppm Cu and As were found in CO₂-rich low-salinity fluid inclusions from the Sigma gold deposit, Val d'Or, Canada (Garofalo et al., 2014), and tens to hundreds ppm As in metamorphic vein systems of the Central Alps, formed by CO₂-bearing fluids (Rauchenstein-Martinek et al., 2014). Very high Cu concentrations (0.1–3.4 wt%) were reported in CO₂/CH₄-rich fluid inclusions from the Fenghuangshan orogenic Cu–Fe–Au deposit, China (Lai and Chi, 2007). In spite of such wide occurrence and large abundance of CO₂ and of the observed metal enrichment in CO₂-rich fluids, the true role of CO₂ on metal transport and deposition remains unappreciated.

Carbon dioxide may affect metal behavior in hydrothermal fluids in different ways, both direct and indirect. First, CO₂ may act as a ligand forming carbonate and hydrogen-carbonate complexes with metals, a phenomenon known in low-temperature aqueous solution for some ‘hard’ metals (Ca, Sr, U, Rare Earth elements; Haas et al., 1995 and references therein). However, carbonate complexes at elevated *T–P* have not been unambiguously determined for most economic metals whose speciation is dominated by Cl, HS or OH complexes in saline, sulfur-bearing, and slightly acidic to neutral fluids of magmatic or metamorphic origin (e.g., Seward and Barnes, 1997; Wood and Samson, 1998; Kouzmanov and Pokrovski, 2012; Seward et al., 2014 and references therein). The abundance of carbonate complexes is furthermore limited by very low concentrations of the hydrogencarbonate and carbonate ions in most high *T–P* fluids and vapors, in which molecular CO₂ largely dominates, and by low solubility of major carbonate minerals such as calcite, dolomite or ankerite (e.g., Manning et al., 2013; Seward et al., 2014 and references therein).

Second, other carbonic species, such as CO, are known to form stable complexes with transition metals like Ni and Fe or platinum group elements (PGE) and gold both in gas and solid state (e.g., Dell'Amico et al., 2010). Such species might also form in hydrothermal H₂O–CO₂–HCl vapors as indicated by recent vapor–liquid partitioning experiments (Kokh et al., 2016). However, in general, in most natural fluids this phenomenon would be of limited occurrence owing to the low abundance of CO (e.g., few

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