Combined effect of carbon dioxide and sulfur on vapor–liquid partitioning of metals in hydrothermal systems

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Abstract

Although CO_2 is a ubiquitous volatile in geological fluids typically ranging from a few to more than 50 wt%, its effect on metal vapor–liquid fractionation during fluid boiling and immiscibility phenomena in the Earth's crust remains virtually unknown. Here we conducted first experiments to quantify the influence of CO_2 on the partition of different metals in model water + salt + sulfur + CO_2 systems at 350 °C and CO_2 pressures up to 100 bar, which are typical conditions of formation of many hydrothermal ore deposits. In addition, we performed in situ Raman spectroscopy measurements on these two-phase systems, to determine sulfur and carbon speciation in the liquid and vapor phases. Results show that, in S-free systems and across a CO_2 concentration range of 0–50 wt% in the vapor phase, the absolute vapor–liquid partitioning coefficients of metals ($K_{vap/liq} = C_{vap}/C_{liq}$, where C is the mass concentration of the metal in the corresponding vapor and liquid phase) are in the range 10^{-6}–10^{-5} for Mo; 10^{-4}–10^{-3} for Na, K, Cu, Fe, Zn, Au; 10^{-3}–10^{-2} for Si; and 10^{-4}–10^{-1} for Pt. With increasing CO_2 from 0 to 50 wt%, $K_{vap/liq}$ values decrease for Fe, Cu and Si by less than one order of magnitude, remain constant within errors (±0.2 log unit) for Na, K and Zn, and increase by 0.5 and 2 orders of magnitude, respectively for Au and Pt. The negative effect of CO_2 on the partitioning of some metals is due to weakening of hydration of chloride complexes of some metals (Cu, Fe) in the vapor phase and/or salting-in effects in the liquid phase (Si), whereas both phenomena are negligible for complexes of other metals (Na, K, Zn, Mo). The only exception is Pt (and in a lesser extent Au), which partitions significantly more to the vapor of S-free systems in the presence of CO_2, likely due to formation of volatile carbonyl (CO) complexes. In the S-bearing system, with H_2S content of 0.1–1.0 wt% in the vapor, $K_{vap/liq}$ values of Cu, Fe, Mo, and Au are in the range 0.01–0.1, those of Pt 0.5–2.0, those of alkali metals are similar to the S-free system, and the partitioning of none of the studied metals is influenced by the presence of CO_2 (up to 50 wt% in the vapor). Our data thus confirm the large enhancement of volatility in the presence of reduced sulfur (H_2S) due to formation of sulfide complexes for chalcophile metals such as Au, Pt, Mo and, to a lesser extent, Cu and Fe, as reported in previous studies of CO_2-free water-salt systems. The negligible effect of CO_2 on vapor–liquid partitioning of the studied metals in S-bearing systems is due to the lack of hydration of metal sulfide species making them little sensitive to changes in water activity and solvation power of CO_2–H_2O vapor. Our findings, combined with existing data over a wide range of temperature on vapor–liquid partitioning of metals in H_2O-dominated systems, suggest that CO_2 exerts mostly an indirect impact on metal fractionation, by extending vapor–liquid immiscibility to higher temperatures and pressures or depth compared to a CO_2-free H_2O-S-salt system. The deeper vapor–liquid separation, in particular in S-bearing systems, is expected to cause more significant partitioning of precious metals and molybdenum (Au, Pt, Mo) into the vapor phase while base metals (Fe, Zn, Cu) remain concentrated in the salt-rich (NaCl, KCl) liquid phase. In

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addition, irrespective of the presence of sulfur, an expansion of the immiscibility domain to higher temperature and pressure conditions in the presence of CO_2 will also increase the depth of ore deposition and affect the vertical metal zonation in hydrothermal systems.

1. INTRODUCTION

Fluid boiling and vapor–liquid immiscibility are ubiquitous phenomena occurring during the formation of most magmatic-hydrothermal and metamorphic ore deposits, as well as in active volcanic-geothermal systems on Earth. These phenomena are controlled by the physical–chemical properties of geological fluids containing water, salts and volatiles (e.g., S, C) that allow for the coexistence of the vapor and liquid phases across the wide range of temperatures (T), pressures (P), and fluid compositions of the Earth's crust (e.g., Hedenquist and Lowenstern, 1994; Barnes, 1997; Heinrich, 2007). Fluid immiscibility has two fundamental effects on the fate of metals that are carried by the fluid. First, it is known to induce precipitation of some metals from the liquid phase owing to enhanced metal concentration and changes in the acidity, redox, and ligand content in the residual liquid as a result of the removal of volatile components (H_2S, H_2, HCl, CO_2) into the vapor (e.g., White, 1973; Drummond and Ohmoto, 1985; Spycher and Reed, 1989). Second, it may cause metal redistribution between the two phases, depending on temperature, liquid and vapor density, and sulfur content and leading to enhanced partitioning into the vapor of noble metals such as Au and Pt (e.g., Heinrich et al., 1999; Ulrich et al., 1999; Pokrovski et al., 2005, 2008; Seo and Heinrich, 2013) or, in contrast, to enrichment of the brine phase by base metals and Cu (e.g., Lerchbaumer and Audétat, 2012). The goal of this study is to better understand the role of CO_2, the most common volatile in geological fluids, on metal behavior during immiscibility processes.

Fluid inclusions from a variety of mineralized systems, from magmatic to epithermal, record the ubiquitous presence of CO_2 in fluids, which underwent boiling/unmixing phenomena presumably leading to ore deposition. Compared to water, CO_2 is usually exsolved from magmas at earlier stages of their evolution and/or greater depths (e.g., Audétat and Simon, 2012; references therein). Yet, fluids of magmatic-hydrothermal porphyry Cu–Au–Mo deposits show up to 10–20 wt% CO_2 (Rusk et al., 2008, 2011), and those of epithermal Au–Ag–Cu and Carlin-type Au deposits systematically contain 1–10 wt% CO_2 (e.g., Bodnar et al., 1985; Koděra et al., 2005; Catchpole et al., 2011). Carbon dioxide concentrations in fluids that formed metamorphic Au and skarn Cu–Au deposits, and mafic pegmatite-hosted Cu-PGE deposits often attain 40–50 wt% and, locally, more than 95 wt% CO_2 in vapor as inferred from fluid inclusions that often contain a CO_2 liquid phase (at ambient conditions) and CO_2–H_2O clathrates (on cooling) (Schmidt Mumm et al., 1997; Diamond, 2001;

Boiron et al., 2003; Phillips and Evans, 2004; Hanley and Gladney, 2011; Garofalo et al., 2014). Fluids enriched in CO_2 in these environments can carry significant concentrations of metals such as As, Cu, Au, Pd, reaching 10 s–100 s ppm, as shown by the rapidly growing body of fluid inclusion compositional data (e.g., Hanley and Gladney, 2011; Garofalo et al., 2014; Rauchenstein-Martinek et al., 2014). Furthermore, fluid inclusion records show that metal deposition, particularly in epithermal Au–Ag and shallow orogenic Au deposits (e.g., André-Mayer et al., 2002; Heinrich, 2007; Velásquez et al., 2014), is often related to fluid boiling or unmixing phenomena, leading to the formation of CO_2-rich vapor phases. Despite the ubiquitous presence of CO_2 in hydrothermal systems, its role on metal behavior during fluid evolution remains largely unknown or, to the least, controversial.

On one hand, it is well known that the fluid immiscibility domain in a water-salt system is largely extended in T–P space in the presence of CO_2 (e.g., Takenouchi and Kennedy, 1964; Bowers and Helgeson, 1983; Barton and Chou, 1993; Lowenstern, 2001; Bakker, 2009). In this process, CO_2 is usually considered as an inert component, following the very low capacity of CO_2-dominated, as compared to H_2O-dominated, supercritical fluids or vapors to solubilize ionic compounds such as salts (e.g., NaCl; Zakirov et al., 2007) and metal oxides (e.g., SiO_2, Newton and Manning, 2009; references therein), whose solubility is driven by hydration phenomena (e.g., Pokrovski et al., 2013). On the other hand, supercritical (>31 °C) pure CO_2 is also known as an efficient solvent for certain organic compounds and thiol and phosphoryl complexes of metals, a property used in industry for purification of organics and metal extraction from aqueous solution (e.g., Glennon et al., 1999; Erkey, 2000; Yang et al., 2010). It remains hypothetical, however, whether a similar solvation phenomenon may operate in natural vapor–liquid systems for metals forming sulfide complexes (e.g., Pokrovski et al., 2008). Compared to water-salt-sulfur vapor–liquid and fluid-melt systems, for which a large amount of experimental data and robust models on vapor–liquid partitioning of various metals has been acquired in the past 10 years (see Simon and Ripley, 2011; Pokrovski et al., 2013 for recent reviews), there are only few direct data on metal vapor–liquid partitioning in the presence of CO_2. For example, Webster et al. (1989) reported partition coefficients of a large set of lithophile elements (ranging from Li to U) between a fluid and a topaz rhyolite melt at 800–950 °C and 2 kbar to systematically decrease by a factor of 5–10 with increasing CO_2 content to ~50 mol% in the fluid. More recently, Tattitch et al. (2015) measured Cu distribution in a S-free felsic melt-brine-vapor system at 900 °C and