Structure and stability of cadmium chloride complexes in hydrothermal fluids

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ABSTRACT

The identity and stability of aqueous species formed by cadmium in H_2O–Na/LiCl–HCl–HNO_3 solutions were investigated using in situ X-ray absorption spectroscopy (XANES and EXAFS) at 20–450 °C and 1–600 bar, combined with solubility measurements of CdO and CdS solids at 350–400 °C and 300–600 bar. Results show that aqueous Cd speciation is dominated by the cation $Cd(H_2O)_6^{2+}$ in acidic Cl-free solutions, and by chloride species $CdCl_m(H_2O)_n^{2-m}$ over a wide range of temperatures ($20 \leq T \leq 450$ °C), acidities ($1 \leq pH \leq 8$), and chloride concentrations ($0.04 \leq m_{Cl} \leq 18$ mol/kg H_2O). EXAFS spectra from chloride solutions show that with increasing T and m_{Cl} the average number of Cl atoms increases from 1 to ~3 (± 0.6), accompanied by a decrease of the number of O from 6 to ~1 (± 0.7), in the nearest coordination sphere around Cd. Average Cd–Cl distances in Cd complexes vary in the range 2.41–2.52 (± 0.02) Å, increasing with increasing m_{Cl} and decreasing with increasing T, while Cd–O distances remain constant within errors at 2.30 (± 0.05) Å in the whole T and m_{Cl} range investigated. This evolution of the Cd atomic environment is accompanied by changes in geometry of the dominant Cd–O/Cl species from octahedral-like to tetrahedral-like with increasing T and m_{Cl}, as shown by XANES spectra analyses. These structural data are consistent with the formation of octahedral $Cd(H_2O)_6^{2+}$ and $CdCl(H_2O)_5^{+}$ and tetrahedral $CdCl_2(H_2O)_2^{0}$, $CdCl_3(H_2O)^{-}$ and $CdCl_4^{-}$ species at $T \leq 200$–300 °C and $m_{Cl} \leq 18$. At $T > 300$ °C, aqueous Cd speciation is dominated by two complexes, $CdCl_2$ $(H_2O)_2^{0}$ and $CdCl_3(H_2O)^{-}$ in a wide m_{Cl} range (0.04–5m). The stability constants of these complexes, derived from solubility measurements at 400 °C and 600 bar are ~6 orders of magnitude higher than available HKF-model predictions based on low-T data. The new data on aqueous Cd complexes may be used for interpretation of Cd/Zn ratios measured in natural hydrothermal saline fluids and volcanic vapors in which the greater stability of Cd chloride species as compared to their Zn analogs is likely to be responsible for the elevated Cd/Zn ratios in comparison to crustal rocks and Cl-poor waters.

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1. Introduction

The present study is aimed at better quantifying the identity, stability and structure of cadmium aqueous complexes responsible for Cd transport by hydrothermal fluids. This knowledge is crucial for understanding the behavior of Cd during the formation of ore deposits, for improving ore prospecting and treatment technologies involving hot solutions, and for setting up valuable strategies for remediation of polluted sites, and safe treatment and storage of cadmium industrial wastes. The major source of Cd in the environment is the mining and treatment of Zn–Pb–Cu hydrothermal ores where Cd is commonly present as an isomorphic substitution in Zn-bearing minerals due to the close chemical and crystallographic properties of these metals. The continental crust contains on average

80 ppb of Cd, which is 3 orders of magnitude lower than for Zn, with Cd/Zn mass ratios showing little variations between different rocks (Cd/Zn = 0.001–0.003, Heinrichs et al., 1980; Rudnick and Gao, 2003). However, the behavior of Cd may diverge significantly from that of Zn in hydrothermal processes involving hot aqueous fluids. For example, hydrothermal sphalerites (ZnS) are usually rich in Cd, with Cd/Zn ratios of 0.01 to 0.2, and complete solid solutions CdS–ZnS were described in polymetallic ores and fumarole minerals (e.g., Axelsson and Rodushkin, 2001; Tombros et al., 2005; Chaplygin et al., 2007; Gottesmann and Kampe, 2007; Cook et al., 2009). Volcanic gases also selectively concentrate cadmium vs zinc, exhibiting Cd/Zn ratios of 0.1 to 1.0 (Pennisi et al., 1988; Symonds and Reed, 1993; Rubin, 1997), which is 2 to 3 orders of magnitude higher that the average crustal value cited above. This makes the Cd/Zn ratio a potentially useful geochemical indicator of hydrothermal/volcanic activity and fluid origin, sources, and evolution. However, in contrast with Zn, the Cd behavior in hydrothermal fluids is very poorly known. To interpret rigorously cadmium transport by aqueous fluids at elevated temperatures and pressures (T–P) and to compare it with Zn we need to know

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the solubility of Cd-bearing minerals and the chemical status of this metal in the fluid phase.

The main natural ligands capable of transporting Cd under hydrothermal conditions are OH^-/H_2O, Cl^-, and HS^-/H_2S. In aqueous solution, the Cd^{2+} cation undergoes hydrolysis with formation of $Cd(OH)_n^{2-n}$ hydroxide complexes, where $1 \leq n \leq 4$. The stability constants of these species at ambient T–P were extensively studied and reported in numerous thermodynamic reviews (Baes and Mesmer, 1976; Archer, 1998; Martell and Smith, 1998). Based on available data and theoretical correlations with other metals, Shock et al. (1997) reported thermodynamic properties of $Cd(OH)_n^{2-n}$ at elevated T–P. However, the predicted concentrations of Cd hydroxide species in equilibrium with oxyhydroxide phases at near-neutral pH are unexpectedly high, attaining 10's ppm at elevated T ($\geq 300 °C$), which is 1–3 orders of magnitude higher than recent experimental determinations for similar base metals such as Zn (Bénézeth et al., 2002) and Cu (Palmer et al., 2004). The role of sulfur in Cd transport at hydrothermal conditions is not sufficiently known (Rickard and Luther, 2006). Experimental studies on Cd–S systems were performed only at ambient T–P (e.g., Ste-Marie et al., 1964; Daskalakis and Helz, 1992; Wang and Tessier, 1999). Although cadmium has a stronger chemical affinity to the sulfide ligand compared to hydroxide, the abundance of Cd–S complexes at elevated T–P is limited by both the weakening of the sulfide complexes stability with increasing T (Rickard and Luther, 2006; Tagirov et al., 2007), and the low sulfur concentrations, typically less than 0.1–0.5 wt.% in most hydrothermal fluids (Barnes, 1979). In contrast, chloride is a far more abundant ligand in hydrothermal fluids, with concentrations attaining 10–30 wt.% (Barnes, 1979). Thus, it is very likely that chloride complexes play a dominant role in the Cd transport in hydrothermal–magmatic settings, similarly to other major base metals like Zn, Fe, Pb, and Ag.

Many experimental and computational studies have demonstrated the formation in aqueous solution of chloride complexes $CdCl_n^{2-n}$, where $1 \leq n \leq 4$. Experimental data for these complexes have been obtained at $T \leq 100 °C$ mostly using potentiometry, and consistent stability constants for Cd chloride complexes at near-ambient temperatures are reported (see reviews by Sverjensky et al., 1997; Archer, 1998; Martell and Smith, 1998; and references therein). The distribution of Cd–Cl species as a function of Cl concentration at 20 °C and 1 bar calculated using these data is shown in Fig. 1a. In contrast, at high T–P the thermodynamic properties of cadmium chloride complexes are very poorly constrained. To the best of our knowledge, only one experimental work on $CdCl^+$ at $T \leq 250 °C$ in weakly saline solutions was published (Palmer et al., 2000). As for the stability constants of Cd–Cl complexes at supercritical temperatures, only theoretical predictions from low-T data using the HKF model are available (Fig. 1b, Sverjensky et al., 1997).

The structures of cadmium chloride complexes in aqueous solution were studied at ambient T–P using X-ray diffraction (XRD), Nuclear Magnetic Resonance (NMR), Raman, Infrared, and X-ray absorption spectroscopies (e.g., Bol et al., 1970, Waters et al., 1973; Drakenberg et al., 1978; Ackerman et al., 1979; Caminiti et al., 1980; Paschina et al., 1983; Mosselmans et al., 1996; Seward and Driesner, 2004). Most of these studies agree about a) the presence of water molecules in the first coordination shell of Cd in its chloride species $CdCl_n(H_2O)_m^{2-n}$, and b) Cd coordination change from octahedral to tetrahedral with increasing Cl concentration in solution. It follows from these studies that the cadmium cation (Cd^{2+}) and low-ligand number Cl complexes ($CdCl^+$) are octahedral, and $CdCl_4^-$ is likely to be tetrahedral. The octahedral-to-tetrahedral transition occurs upon the formation of the second ($CdCl_2^0$) or third ($CdCl_3^-$) chloride complex, depending on the solvent medium (Arhland, 1979; Paschina et al., 1983). Very scarce structural data are, however, available for Cd–Cl complexes at T above ambient. The existing reports using X-ray absorption spectroscopy (XAS) have explored very limited T and Cl concentration ranges ($mCl \leq 1$ mol/kg H_2O, $T \leq 250 °C$, Mosselmans et al., 1996; Seward and Driesner, 2004), and do not allow derivation of the identity and stability of the dominant Cd–
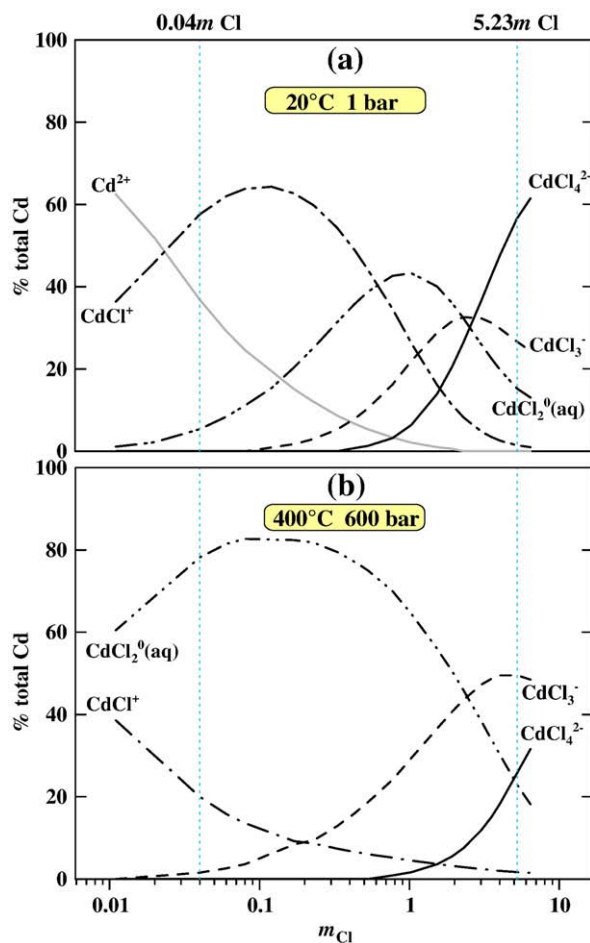

Fig. 1. Distribution of Cd species in a NaCl–HCl aqueous solution as a function of total Cl concentration at (a) 20 °C/1 bar and (b) 400 °C/600 bar from Sverjensky et al. (1997). The vertical dashed lines correspond to the minimum and maximum Cl concentrations studied in this work at temperatures above ambient.

Cl complexes over the range of hydrothermal T–P–pH conditions and fluid compositions.

Here we combined in situ XAS and solubility measurements to study systematically Cd–Cl complexing over a wide T–P and Cl concentration range (20–450 °C, 1–600 bar, 0–18 mol Cl/kg H_2O). Our results provide new insights into the identity, stability and structure of aqueous chloride complexes responsible for Cd transport by hydrothermal fluids.

2. Materials and methods

2.1. Experimental samples, conditions and analytical techniques

In situ XAS measurements were performed on two nitrate Cd $(NO_3)_2$–HNO_3 and six chloride $CdCl_2$–HCl–NaCl aqueous solutions at $T = 20$–450 °C and $P = 1$–600 bar. In addition, several concentrated $CdCl_2$–HCl–LiCl aqueous solutions (up to $18m$ Cl) were measured at 20 °C and 1 bar. All solutions were prepared by weight from Cd $(NO_3)_2 \cdot 4H_2O$, $CdCl_2 \cdot H_2O$, NaCl, LiCl, HNO_3, HCl and deionized water. Solution compositions are reported in Tables 1, 2 and 3 in molality units (m = number of moles of each solute per kg of water). Spectroscopic experiments were complemented by batch-reactor solubility measurements of monteponite (CdO, cubic) and greenockite (CdS, hexagonal) in pure water and similar NaCl–HCl–H_2O solutions at 350–400 °C and 300–600 bar. A commercial CdO solid (Fluka, ≥99%) was treated before the experiments. First, the initial powder was washed several times with deionized water to remove ultrafine particles. Then, the slurry was aged