LETTER

Zinc transport in hydrothermal fluids: On the roles of pressure and sulfur vs. chlorine complexing

BARBARA ETSCHMANN^{1,*}, WEIHUA LIU², ROBERT MAYANOVIC³, YUAN MEI², STEVEN HEALD⁴, **ROBERT GORDON⁵, AND JOËL BRUGGER¹**

¹School of Earth, Atmosphere and Environment, Monash University, Clayton, Victioria 3800, Australia ²CSIRO Mineral Resources Flagship, Clayton, Victoria 3168, Australia

³Department of Physics Astronomy and Materials Science, Missouri State University, Springfield, Missouri 65897, U.S.A.

⁴Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, U.S.A.

⁵Moyie Institute & Department of Physics, Simon Fraser University, Burnaby, British Colombia, Canada

ABSTRACT

We provide an experimental confirmation of the suggestion, based on thermodynamic simulations and extrapolations (Zhong et al. 2015), that Zn is transported in the form of chloride complexes in most acidic, shallow hydrothermal systems; while bisulfide complexes become increasingly important in deep, pH neutral to basic hydrothermal systems. We used in situ X-ray absorption spectroscopy (XAS) diamond-anvil cell experiments to determine Zn(II) speciation in a 1 m NaHS + 0.2 m HCl solution in contact with sphalerite. XANES data indicate that Zn coordinates to oxy/hydroxyl/chloride ligands from room temperature up to and including 200 °C, and then at higher temperatures (≥300 °C) and pressures (>2 kbar) it changes to complexing with sulfur. Our data confirm that bisulfide complexes become increasingly important in neutral-alkaline solutions at high pressure and temperature, due to an increase in sulfur solubility and to favorable entropy contributions for bisulfide vs. chloride complexes.

Keywords: Zinc, sulfur, chloride, hydrothermal, high temperature and pressure

INTRODUCTION

Knowledge of metal complexation is important for predicting the solubility, transport, and deposition of metals leading to the formation of hydrothermal ore deposits. Most zinc (Zn) deposits share a hydrothermal origin. As chloride is the most abundant anion in hydrothermal fluids (Yardley 2005) and the sulfide mineral sphalerite (ZnS) is by far the most important Zn ore mineral, the complexation of Zn(II) with chloride and sulfur ligands has been studied extensively (Ruaya and Seward 1986; Bourcier and Barnes 1987; Plyasunov and Ivanov 1991; Anderson et al. 1998; Tagirov et al. 2007; Tagirov and Seward 2010).

Advances in in situ synchrotron-based X-ray absorption spectroscopy (XAS) and ab initio molecular dynamics simulations (AIMD) provide us with increasingly reliable views of the speciation and thermodynamics of metal complexes at the molecular level (Brugger et al. 2016). For example, Mei et al. (2015) combined AIMD simulations with in situ XAS data to demonstrate that Zn(II) is bonded to Cl predominantly in a tetrahedral geometry up to 400 °C and 1 kbar, with a trigonal planar geometry appearing above 500 °C (35% trigonal planar at 600 °C), and were able to use this new speciation model to reinterpret available solubility data (e.g., Ruaya and Seward 1986; Bourcier and Barnes 1987), demonstrating that discrepancies among the different interpretations of the experimental data arose from erroneous assumptions about Zn(II) complexing rather than experimental errors. A subsequent study (Mei et al. 2016) demonstrated that Zn is coordinated with S in tetrahedral $[Zn(HS)_n(H_2O)_{4-n}]^{2-n}$ complexes up to 300 °C and 1 kbar, with trigonal planar species predicted to become predominant at

* E-mail: barbara.etschmann@monash.edu

lower temperatures than in chloride solutions (i.e., at 400-500 °C for Zn in a 2 m NaHS solution).

The thermodynamic properties proposed by Mei et al. (2015, 2016) suggest that Zn(II) bisulfide complexes grow in importance with increasing temperature in neutral-alkaline solutions, while chloride species are dominant at lower temperatures. This is consistent with the geochemical modeling of Zhong et al. (2015a) that predicted that chloride complexes will predominate in most shallow(<~4 km) rock-buffered hydrothermal systems, while bisulfide complexes become increasingly important at high P-T (>10 km), due to an increase in sulfur solubility (>3 molal at $T \ge 500$ °C) and favorable entropy contributions for bisulfide vs. chloride complexes in aqueous fluids (Mei et al. 2013). These predictions are based on data collected in fluids containing either chloride or hydrosulfide. This study tests the above predictions to determine the predominant Zn species in a mixed Cl+S fluid.

EXPERIMENTAL METHODS

X-ray absorption near edge structure (XANES) data were collected using a hydrothermal diamond-anvil cell (HDAC) at beamline 20-ID at the Advanced Photon Source (APS) at Argonne National Lab, Illinois. The APS is a 7 GeV ring with a maximum current of 102 mA. Beamline 20-ID is an undulator beamline with a Si(111) monochromator with an energy resolution ($\Delta E/E$) of 1.4×10^{-4} (at 10 keV). A focused beam size of 5 µm² was used. The incident and transmitted beam intensities I_0 and I_1 were measured using ion chambers. A four-element Si-drift detector, used for detecting fluorescence data, was positioned at 90° to the incident X-ray beam.

Solutions were prepared using: NaHS(s) (Alfa Aesar), ZnBr2 (GFS, reagent grade), S (Alfa Aesar, 99.5%), ZnCl₂ (Sigma, reagent grade), HBr (48%, Sigma), and HCl (37% Sigma). The requisite amounts were diluted/dissolved in water to prepare the solutions listed in Supplemental¹ Table S1. A stopped PTFE solution cell was used to measure XAS data for the standard solution (Sol2, Supplemental¹ Table S1) under ambient conditions, to aid comparison with data collected previously at 1 kbar at the European Synchrotron Research Facility (ESRF; Grenoble, France)

FIGURE 1. (a) Experimental setup on beamline 20-ID. (b) View of a sample containing solid and air bubble. The sample is located in a 500 µm Re-gasket. The diamond is fluorescent under the X-ray beam; as a result, the outer edge of the diamond is "glowing," and the green line across shows X-rays traveling through the diamond above the gasket. The black circle in the center is a recess drilled into the top diamond, which allows for solution measurement by the micro-beam traveling parallel to the gasket. (c–d) A stacked first derivative of the normalized XANES spectra (c) large volume and (d) HDAC data. Note the white line and the maximum of the first derivative shifts to lower energy with decreasing coordination number and ligand (S vs. O/Cl). (Color online.)



(Mei et al. 2016). Solutions were loaded with a small piece of sphalerite (Picos del Europa mine, Spain; sample M4983, Museum Victoria) into the modified Bassett-style HDAC (Bassett et al. 2000; Yan et al. 2011). XANES data were collected in situ up to 500 °C and ~4.5 kbar upon heating. The solution, loaded using a micro-syringe, was contained in a cylindrical hole (500 µm in diameter) drilled in a rhenium gasket of 125 µm thickness (Fig. 1). Similar to previous studies (e.g., Mayanovic et al. 2002), the HDAC was mounted on a rotating stage on the XAS experimental table with a vertical optical window, allowing simultaneous optical observation of the sample from the top using a microscope and video camera, and XAS measurement with the X-ray beam entering horizontally from the side via a laser-drilled recess (150 µm diameter, 100 µm deep) through one of the anvils (Figs. 1a and 1b). A temperature controller (PES Enterprises Inc.) was used to control the temperature to within ±1 °C, based on two thermocouples positioned next to the bottom and top diamonds and sealed with zirconia cement. The pressure at elevated temperature was approximated using the equation of state (EOS) of sodium chloride solutions (Driesner and Heinrich 2007) with similar stoichiometric ionic strength as the experimental solutions, based on the observed homogenization temperatures (Supplemental¹ Table S1).

As noted in previous HDAC studies (e.g., Mayanovic et al. 1999; Bassett et al. 2000; Hong et al. 2009), diffraction from the diamond interferes with the XAS signal. To overcome this, the HDAC was rotated and spectra were collected at a number of angles with differences of 1–3°. Changing the angle changes the location of the diffraction peaks, allowing the data to be deglitched following the procedures described by Mayanovic et al. (1999) and Hong et al. (2009).

AB INITIO MOLECULAR DYNAMICS SIMULATIONS

To extend the pressure range beyond those in the experiments to conditions typical of lower crust/upper mantle and shallow subduction zones, AIMD simulations of Zn(II)-Cl-HS complexes were run at 100 °C, 1.5 kbar and 500 °C, 1.5–20 kbar. AIMD simulations were performed using the Car-Parrinello MD code "CPMD" ver-

sion 3.17.1 (Car and Parrinello 1985). A box containing 1 Zn²⁺, 5 HS⁻, 1 Cl⁻, 4 Na⁺, 111 H₂O was used for each simulation. Details of the calculation procedures are given in Mei et al. (2015, 2016).

XANES results

XANES spectra reflect (1) the oxidation state of the target atom, (2) the geometry, and (3) composition (nature of ligands) of the surrounding coordination sphere. The positions of the absorption edge and of the white line (historically defined as the most intense peak just above the edge in the spectrum) tend to shift as a function of these parameters (Penner-Hahn 2005; Bunker 2010). These shifts can be accounted for electrostatically: (1) The higher the oxidation state, the higher the charge on the target atom, and the higher the X-ray energy required to eject a core electron. (2) Six ligands will induce a higher charge in the vicinity of the central atom compared to four ligands; thus, octahedral complexes tend to have a white line at a higher energy than tetrahedral complexes. (3) Metal-bisulfide complexes tend to have a white line at a lower energy than metaloxide/halide complexes. S has a lower electronegativity than O/Cl, so it induces a lower formal charge on the metal atom.

Figures 1c and 1d show the stacked first derivative, and Supplemental¹ Figures 1a and 1b show the stacked normalized Zn *K*-edge XANES spectra in H₂O/OH⁻/Cl⁻/HS⁻ solutions (Supplemental¹ Table S1). Data shown in Figure 1c and Supplemental¹ Figure 1a were collected previously using a large volume autoclave (Mei et al. 2015, 2016) and clearly demonstrate the shift to lower energy in both the white line and the position of the peak of the first derivative of the XANES due to a change in the geometry of the complexes, from octahedral to tetrahedral to trigonal planar (SolsB, SolsC, SolsD; see Supplemental¹ Table S1), followed by a further shift to lower energies when the complexing ligand is changed to HS⁻ (SolE) from Cl⁻/H₂O/OH⁻, with increasing temperature. Sphalerite solubility in SolE was estimated to be 13(3) mmolal at 500 °C, 1 kbar, which compares well with the predictions using Zn bisulfide complexes properties from Mei et al. (2016) (70 mmolal; details in Supplemental¹ Table S1).

Reassuringly, the data collected with the HDAC show the same trend as those collected with the large volume autoclave (Figs. 1c–1d and Supplemental Figs. 1a–1b). The results for the Cl-free Sol10 (sphalerite + 2 m NaHS + S) are identical to those collected previously (SolE), and indicate the presence of Zn(II) bisulfide complexes at high temperature as a result of prograde solubility. It should be noted that it was necessary to add extra S into the system for Sol10 (HDAC) compared to SolE (autoclave). Attempts using just the NaHS solution + sphalerite resulted in the dissolution of the Re gasket; geochemical modeling demonstrated that the S-free solution (e.g., pH_{400 °C} = 7.5) is much more basic than the S-bearing solution (pH_{400 °C} = 4.4). Excess sulfur both ensures buffering of the S content of the fluid despite reaction with the gasket and a pH closer to neutral (4.8 at 400 °C, 2.95 kbar).

The only source of sulfur in Sol6 (sphalerite in 0.2 m HCl) was due to the dissolution of sphalerite. Under these conditions the concentration of available chlorine was so much higher than that of sulfur that it dominated complexation to Zn; acidic pH also decreases the stability of bisulfide complexes, since $H_2S(aq)$ predominates over HS^- [reaction $HS^- + H^+ = H_2S(aq)$].

The most exciting result from the HDAC experiments is that Sol5 (sphalerite in 1 m NaHS + 0.2 m HCl) clearly demonstrates a change in ligand type from Cl⁻/H₂O/OH⁻ at ambient up to and including 200 °C to HS⁻ at temperatures \geq 300 °C. Note that according to available thermodynamic properties (review in Zhong et al. 2015, supplemented by Mei et al. 2015, 2016), Zn bisulfide complexes should dominate Zn speciation even at room temperature in Sol5; given the basic pH of the solution (Supplemental¹ Table S1), and given the small amount of experimental data available under these conditions (Tagirov and Seward 2010), this could indicate the importance of hydroxide complexes yet to be fully characterized.

AIMD results

The results of simulations of Zn(II) speciation in solutions containing 2.5 m HS⁻ and 0.5 m Cl⁻ at experimental pressures and at 20 kbar are listed in Supplemental¹ Table S2. The simulations show that (1) at 100 °C, 1.5 kbar, fourfold tetrahedral complexes are stable; (2) at 500 °C, 1.5 and 4.5 kbar threefold complexes predominate with fourfold complexes being present for a small percentage of the time; and (3) at 500 °C, 20 kbar fourfold species once again predominate. It was not possible to observe ligand exchange between Cl⁻/HS⁻/H₂O as the exchange kinetics are too slow to be observed by AIMD on the scale of picoseconds, even at elevated temperatures (Mei et al. 2015, 2016).

At low pressures (\leq 4.5 kbar), the AIMD results are consistent with experimental measurements. The increase in coordination from three [Zn(HS)₃] to four [Zn(HS)₄²] ligands of the Zn bisulfide complexes with increasing pressure is similar to that observed previously with increasing HS⁻ concentration (Mei et al. 2016).

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Much like higher HS⁻ concentrations, higher pressures enhance the stability of the $Zn(HS)_4^{2-}$ complex, which in turn enhances Zn solubility in sulfur-rich fluids at high pressures.

DISCUSSION

The hypothesis offered by Zhong et al. (2015a), stating that chloride is the dominant ligand controlling Zn mass transfer at low *P*-*T* conditions whereas sulfur becomes increasingly important at higher *P*-*T* conditions, has been verified experimentally. Our XANES results show that when sufficient sulfur and chlorine are available, in neutral-alkaline solutions, Zn bonds preferentially to OH⁻/H2O/Cl⁻ at lower *P*-*T* conditions and then with HS⁻ with increasing *P*-*T* conditions, (e.g., Sol5, calculated pH 25 °C = 7.4).

This can be accounted for on a macroscopic scale by noting that the reduction of the dielectric constant of water with increasing temperature (from 78 at 25 °C to 18.3 at 500 °C and 4.5 kbar, Fernandez et al. 1995) drives complexing of metal species toward having lower overall charge (eventually neutral charge) with increasing temperature. This can be achieved in two ways: (1) the geometry changes from octahedral to tetrahedral to trigonal, thereby decreasing the overall charge of the complex, and (2) the bond polarity decreases, i.e., Zn will preferentially bond with ligands with decreasing electronegativity with increasing temperature (Pauling electronegativity: Zn = 1.65, O = 3.44, Cl = 3.16, S = 2.58).

On a microscopic level, the increase in entropy associated with (1) reduction in coordination number (Crerar et al. 1985; Susak and Crerar 1985) and/or (2) reduction of the number of hydration waters (i.e., less solvation) of Cl⁻ and HS⁻ is the impetus for forming these metal-Cl⁻/HS⁻ complexes (Sherman 2010). The reduction of hydration waters of HS⁻ is larger than that of Cl⁻ (Sherman 2010; Mei et al. 2013) resulting in a preference for complexing to HS⁻ compared to Cl⁻. In these and previous experiments (Mei et al. 2015, 2016), it was found that Zn speciation transitions to a lower coordination with S (trigonal complex at 300 to 400 °C) at a lower temperature than with Cl (evidence for trigonal complex around 500 °C). However, this is the first direct experimental demonstration that given sufficient amounts of Cl and S in the aqueous system, Zn undergoes a transformation from predominant chloro/aqua ion to bisulfide complexing with increasing *P* and *T* conditions.

AIMD calculations show that at 20 kbar the coordination of Zn(II) reverts toward tetrahedral, which is associated with an increase in the number of bisulfide ligands coordinated to Zn. The effect of pressure on mineral solubility is complex (e.g., Crerar et al. 1985; Brugger et al. 2016). The type of coordination change affecting Zn complexing as a function of pressure is not taken into account by popular extrapolation algorithms (e.g., Sverjensky et al. 2014). In this case, the change in coordination will tend to increase Zn solubility in S-rich fluids with increasing pressure: MD simulations suggest that this effect counterbalances a general trend toward stronger dissociation at high pressures (Seward and Barnes 1997) driven by pressure-dependent changes (i.e., solution density) in the hydration of the free ions (Cl⁻ and HS⁻).

IMPLICATIONS

The new experiments provide the first experimental confirmation that Zn(II) bisulfide complexes may dominate Zn transport in high-temperature neutral-alkaline fluids, including metamorphic fluids (e.g., Zhong et al. 2015b; Mei et al. 2016). MD simulations suggest that pressure-driven coordination changes may be important in controlling Zn speciation (and hence solubility) in deep geological fluids, e.g., subduction zones. Sulfate/polysulfide/bisulfide equilibria in a subduction zone is a subject of intense scrutiny and debate (e.g., Debret and Sverjensky 2017; Rielli et al. 2017). Pons et al. (2016) used the fact that the fractionation of stable Zn isotope between mineral and fluid is sensitive to the predominant Zn(II) complexes (Fujii et al. 2011) to infer that Zn(II) sulfate complexes may be important for Zn transfer from slab to mantle as a result of slab dehydration and deuteric mantle metasomatism. Debret and Sverjensky (2017) used thermodynamic modeling to show that the predominance of sulfate vs. bisulfide ligand in fluids resulting from serpentinite dehydration depends upon the amount of dissolved sulfide (pyrrhotite) at 20 kbar and 630–660 °C. Our study range at high pressure using diamond anvil cell. Review of Scientific Instruments 80, 073908 (11 p.).

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Endnote:

¹Deposit item AM-19-16719, Supplemental Material. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2019/Jan2019_data/Jan2019_data.html).

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confirms that under conditions where reduced sulfur predominates

in solution, Zn(HS)²/₄ (Fujii et al. 2011) and/or Zn(HS)²/₃ (Mei et al.

2016) are the most likely Zn complexes accounting for Zn mobility.

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