



Speciation and thermodynamic properties of zinc in sulfur-rich hydrothermal fluids: Insights from *ab initio* molecular dynamics simulations and X-ray absorption spectroscopy

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Abstract

Chlorine and sulfur are the main elements involved in the complexing of metals in ore-forming fluids. The nature and thermodynamic properties of the Zn(II)–Cl complexes have been investigated by previous experimental and theoretical studies and are now well established up to high temperatures (600 °C). In contrast, the role of bisulfide complexes for zinc speciation in sulfur-bearing fluids remains poorly known, and a better understanding of Zn(II)–HS complexation is required for modeling zinc transport in magmatic and metamorphic fluids and for optimizing the hydrometallurgical processing of sulfide ores.

We have conducted *ab initio* molecular dynamics (MD) simulations to calculate the speciation of Zn(II)–HS complexes from ambient to hydrothermal-magmatic conditions (25–600 °C, up to 2000 bar). These theoretical calculations were complemented by X-ray absorption spectroscopy (XAS) measurements of Zn(II) in HS[−]-rich solutions at 200–500 °C and 600–1000 bar. The speciation and geometrical properties predicted by the *ab initio* MD simulations and the *in situ* XAS data are in excellent agreement. Upon heating from room temperature to 250 °C, Zn(II) speciation in HS[−]-rich solutions shows a transition from the sixfold octahedral hexaaquo complex [Zn(H₂O)₆]²⁺ to fourfold tetrahedral [Zn(HS)_{*n*}(H₂O)_{4−*n*}]^{2−*n*} complexes (*n* = 1–4). *Ab initio* MD simulations also show that at temperatures > 250 °C, the threefold trigonal-planar [Zn(HS)₃][−] complex becomes increasingly stable, and predominates in S-rich solutions; in contrast, chloro-complexes display a tetrahedral geometry at 25–500 °C, while trigonal planar ZnCl₃[−] predominates at temperatures > 500 °C. The stability constants of Zn(II)–HS complexes were calculated by thermodynamic integration of constrained *ab initio* MD simulations at 200, 350 and 600 °C. The stability constants generated from this study predict that zinc can be transported by HS[−] at high temperature in reduced, neutral to alkaline solutions, while Zn chloride complexes dominate in acidic fluids.

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1. INTRODUCTION

Most of the World's resources of transition metals such as Zn, Pb, Cu, Co or Fe are mined from hydrothermal ore

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deposits. Understanding the formation, weathering, and hydrometallurgical processing of these ores requires a detailed understanding of the behavior of these metals in hydrothermal fluids, and their partitioning between minerals and fluids over a wide range of chemical and physical conditions. Zn(II) chloride complexes are assumed to be responsible for zinc transport in most crustal fluids (e.g., Brugger et al., 2003; Liu et al., 2012). Numerous experimental and theoretical studies have been carried out to determine the speciation and thermodynamic properties of Zn(II)–Cl complexation in fluids under a wide range of temperature and pressure (e.g., Ruaya and Seward, 1986; Bourcier and Barnes, 1987; Plyasunov and Ivanov, 1991; Anderson et al., 1998; Yardley, 2005; Liu et al., 2007). Our recent study (Mei et al., 2015a) also emphasized the importance of Zn(II)–Cl complexation, and provided an updated view of the speciation and thermodynamic properties of Zn(II) chlorocomplexes up to 600 °C, 5 kbar that is consistent with most experimental data and with the results from *ab initio* molecular dynamic (MD) simulations.

Together with chloride, bisulfide (HS^-) is probably the most important ligand in magmatic-hydrothermal (Seo et al., 2009) and metamorphic (Tomkins, 2010) fluids. A recent thermodynamic study (Zhong et al., 2015a) suggests that Zn(II)–bisulfide complexes may play an important role for zinc transport at high temperature (i.e., >500 °C). However, our understanding of the role of sulfur for zinc transport in hydrothermal fluids is still limited, since the current knowledge regarding the speciation of Zn(II) in bisulfide solutions is based upon *ex situ* measurements of sphalerite (ZnS) solubility performed over a limited range of experimental conditions (ambient to 350 °C, P_{sat} ; Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993; Tagirov et al., 2007; Tagirov and Seward, 2010). By their nature, solubility studies provide quantitative information about the Zn:S ratio in the dominant Zn(II) complexes, but no direct information on the structure of these complexes. Such information is available only at room temperature, based on voltammetric (Luther et al., 1996) and EXAFS (Helz et al., 1993) measurements, and on the theoretical study of Tossell and Vaughan (1993). Overall, these studies are in remarkable disagreement, with different stoichiometries proposed for the major species that are stable in the Zn–HS–OH system. In particular, Hayashi et al. (1990) and Daskalakis and Helz (1993) suggested that $\text{Zn}(\text{HS})_4^{2-}$ is an important species in near neutral sulfur-bearing fluids, however Bourcier and Barnes (1987) and Tagirov and Seward (2010) considered $\text{Zn}(\text{HS})_{2(\text{aq})}$ and $\text{Zn}(\text{HS})_3^-$ as predominant species in such fluids. The formation constants for important species such as $\text{Zn}(\text{HS})_{2(\text{aq})}$ differ significantly among different studies; for instance, Bourcier and Barnes (1987) gave a $\log K$ value of 15 for $\text{Zn}(\text{HS})_{2(\text{aq})}$ at 300 °C, saturated pressure, while Tagirov and Seward (2010) gave a value of 12.56 for $\text{Zn}(\text{HS})_{2(\text{aq})}$ at the same P – T condition.

This study aimed to help solve these controversies and provides new insights into Zn(II)–HS complexation using a combination of *ab initio* MD simulations and *in situ* XAS measurements of Zn(II) in bisulfide-rich solutions. In the last decade, *ab initio* MD has been applied to predict the speciation and geometries of metal complexes in

hydrothermal fluids (e.g., Cu(I)–Cl (Sherman, 2007), Au(I)–HS (Liu et al., 2011b), Cu–HS–Cl (Mei et al., 2013a), Au(I)–HS/OH/S₃ (Mei et al., 2013b)). Combining *ab initio* MD and *in situ* XAS measurement, previous studies provide comprehensive understanding of metal complexation in a wide range of temperature and pressure (e.g., Ag(I)–Cl (Pokrovski et al., 2013), Zn(II)–Cl (Mei et al., 2015a), Pd(II)–Cl–HS (Mei et al., 2015b)). We have also shown that quantitative thermodynamic properties can be obtained for the formation constants for Cu(I)–Cl–HS (Mei et al., 2013a), Zn(II)–Cl (Mei et al., 2015a) and Pd(II)–Cl–HS (Mei et al., 2015b) complexes using thermodynamic integration of constrained MD simulations.

In this study, we applied *ab initio* MD simulations to calculate the speciation and thermodynamic properties of Zn(II)–HS complexes. The structural properties calculated from *ab initio* MD are confirmed by the first *in situ* XAS fluorescence measurement of Zn(II)–HS complexes under hydrothermal conditions. This work provides the first *ab initio* MD simulations and XAS fluorescence characterization on bisulfide complexes of a divalent transition metal at hydrothermal conditions of up to 500 °C, 1000 bar. The stability constants derived from the MD simulations were applied to extrapolate the thermodynamic properties of Zn(II)–HS complexes to a wide range of T – P conditions.

2. METHODS

2.1. *Ab initio* molecular dynamics simulation

Car–Parrinello molecular dynamics (CPMD, code version 3.17.1) (Car and Parrinello, 1985) was used to conduct *ab initio* MD simulations. The CPMD method implements density functional theory (DFT) using a plane-wave basis set and pseudo-potentials to simulate the presence of the core electrons. In this study, The PBE exchange correlation-functional (Perdew et al., 1996) was employed with a cutoff gradient correction of 5×10^{-5} . Lin et al. (2012) showed that the energy profiles for liquid water calculated by PBE agree very well with higher-level *ab initio* calculations (MP2, CCSD). Vanderbilt ultrasoft pseudo-potentials in the CPMD package generated with the valence electron configuration $3d^{10}4s^2$ for Zn (Laasonen et al., 1993) were used together with plane-wave cutoffs of 25 Ry (340.14 eV). All MD simulations were performed in the NVT ensemble (Nosé, 1984). Temperatures were controlled by the Nosé thermostat for both the ions and electrons. A time-step of 3 a.u. (0.073 fs) was chosen to stabilize the simulations. The target fictitious kinetic energies were obtained by taking the converged value of a 10,000-steps simulation with no defined Nosé thermostat for electrons. A fictitious electron mass of 400 a.u. (3.644×10^{-28} kg) was used to obtain convergence of the energy of the total CP-Hamiltonians. Periodic boundary conditions were used to eliminate surface effects.

Ab initio MD simulations of Zn(II)–HS complexation were performed on constant-volume periodic cells containing 55 water molecules, 1 Zn atom, 4 or 10 HS^- ligands, and 2 or 8 Na atoms. The fluid densities were chosen to correspond to the equation of state of NaCl fluids at a similar

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