Metal Mobility in Hydrothermal Fluids: Insights from ab initio Molecular Dynamics Simulations

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Table of Contents

Abstract

Aqueous fluids are an important medium for transporting metals in the Earth's crust, and are responsible for the formation of many ore deposits. The nature and thermodynamic properties of metal complexes in hydrothermal fluids plays a key role in controlling elemental mobility and mineral solubility in natural and man-made systems. The bulk of our knowledge on metal complexation in hydrothermal fluids originates from experimental studies. Experimental studies at extreme conditions (i.e. high temperature and pressure) are challenging; they can be carried on only over limited P-T-x conditions, and require an accurate speciation model for interpretation. Molecular dynamics (MD) simulations are coming of age for studying metals in hydrothermal processes; the simulations can support the interpretation of experiments; explore conditions beyond the range over which experiments are available; and provide a molecular-level understanding of hydrothermal metal mobility.

In this thesis, *ab initio* (first principles) molecular dynamics (MD) simulations based on density functional theory were conducted to predict the stochiometries and geometries of Cu(I), Au(I) and Zn(II) complexes in solutions with different ligands (Cl^-, H_2O/OH^-, HS^-/H_2S, S_3^-) at temperatures and pressures ranging from ambient to hydrothermal/magmatic conditions. The important complexes related to metal transport in fluids with different temperatures, pressures and ligand concentrations were simulated. The simulations accurately reproduce the identities and geometries of metal complexes derived from experimental studies, where available. The *ab initio* MD also demonstrates novel complexes which have not yet been observed by experiments (i.e. $CuCl(HS)^-$, $AuS_3(HS)^-$, $AuS_3(OH)^-$, $AuS_3(H_2O)$).

The thermodynamic properties of metal-ligand association/dissociation reactions of Cu(I)-Cl-HS and Zn(II)-Cl complexes were investigated by distance-constrained MD simulations using thermodynamic integration. The predicted equilibrium constants (logK) for the ligand substitution reactions at high temperature (i.e. >= 300 ˚C) show good agreement (within 1-2 log units) with the experimental values. Although the slow kinetics at lower temperatures (i.e. < 200 ˚C) leads to a decrease in the accuracy of the predicted logKs, MD simulations can still reproduce the trends of the change of metal mobility successfully. The predictions of the stoichiometry and thermodynamic properties demonstrate the potential of MD simulations in studying metal mobility in hydrothermal fluids.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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List of publications

This PhD thesis is of publication format. Four papers constructed this PhD thesis, including

TWO PUBLISHED PAPERS

1 **Yuan Mei***; David M Sherman; Weihua Liu; Joël Brugger*, Complexation of gold in S_3^--rich hydrothermal fluids: Evidence from ab-initio molecular dynamics simulations, *Chemical Geology,* 2013, 347, 34-42

2 **Yuan Mei**; David M Sherman; Weihua Liu; Joël Brugger, Ab initio molecular dynamics simulation and free energy exploration of copper(I) complexation by chloride and bisulfide in hydrothermal fluids, *Geochimica et Cosmochimica Acta,* 2013, 102, 45-64

ONE SUBMITTED MANUSCRIPT:

3 **Yuan Mei**; David M Sherman; Weihua Liu; Joël Brugger, The effect of solution density on ion hydration and metal complexation: ab initio molecular dynamics simulation of Cu(I) and Au(I) in chloride brines (25-1000 °C, 1-5000 bar), accepted pending revisions in *Geochimica et Cosmochimica Acta*

ONE MANUSCRIPT PREPARED FOR SUBMISSION

4 **Yuan Mei;** David M Sherman; Weihua Liu; Joël Brugger, thermodynamic properties of Zn-Cl complexation from ab initio MD simulation, to be submitted to a geochemistry journal.

OTHER PUBLICATIONS RELATED TO THIS THESIS:

SUBMITTED MANUSCRIPT

A Yuan Tian; Barbara Etschmann; **Yuan Mei**; Pascal Groundler; Denis Testemale; Yung Ngothai; Joël Brugger, Speciation and thermodynamic properties of Manganese (II)

chloride complexes in hydrothermal fluids: in situ XAS study, accepted pending revisions in *Geochimica et Cosmochimica Acta*

REFEREED JOURNAL PAPERS

B Yuan Tian; Barbara Etschmann; Weihua Liu; **Yuan Mei**; Denis Testemale; Brian O'Neil; Nick Rae; David Sherman; Yung Ngothai; Stacey Borg; Joël Brugger, Speciation of Nickel (II) chloride complexes in hydrothermal fluids: in situ XAS study, *Chemical Geology,* 2012, 334, 345-363

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D **Yuan Mei,** David M Sherman, Weihua Liu and Joël Brugger, Speciation and thermodynamic properties of d10 transition metals: insights from ab-initio Molecular Dynamics simulations, *34th International Geological Congress (IGC) 2012, August 2012, Brisbane, Australia*

E **Yuan Mei,** David M Sherman, Joël Brugger, Weihua Liu, Zn-Cl Complexation in Magmatic-Hydrothermal Solutions: Stability Constants from Ab initio Molecular Dynamics, *Goldschmidt Conference 2012, June 2012, Montreal, Canada*

F **Yuan Mei,** David M Sherman, Joël Brugger, Weihua Liu, Ab initio molecular dynamics simulation of copper(I) complexation in chloride/sulfide fluids, *Goldschmidt Conference 2011, August 2011, Prague, Czech Republic*

G Weihua Liu, Barbara Etschmann, Denis Testemale, **Yuan Mei,** Jean-Louis Hazemann, Kirsten Rempel, Harald Müller, Joël Brugger, Which Ligand is the most Import for Gold Transport in Hydrothermal Fluids? An in situ XAS Study in Mixed-Ligand Solutions, *Goldschmidt Conference 2013, August 2013, Florence, Italy*

H Weihua Liu, Stacey Borg, Barbara Etschmann, **Yuan Mei**, Denis Testemale, David Sherman and Joël Brugger, Molecular-level understanding of metal transport in hydrothermal ore fluids: in situ experiments and ab initio molecular dynamic simulations, *34th International Geological Congress (IGC) 2012, August 2012, Brisbane, Australia*

I David M Sherman, **Yuan Mei**, Metal Complexation in Hydrothermal Fluids: Insights from *Ab initio* Molecular Dynamics, *Goldschmidt Conference 2011, August 2011, Prague, Czech Republic*