
XAS studies of metal speciation in hydrothermal fluids

Yuan TIAN

B.Eng. (2007), East China University of Science and Technology, Shanghai, China

*This thesis is submitted for the degree of Doctor of Philosophy
in
School of Chemical Engineering
at
The University of Adelaide*



May 2013
Adelaide, Australia

Table of Contents

Abstract	v
Declaration	vii
Acknowledgements	ix
List of publications	xi
Chapter 1	1
1.1 Metal speciation and hydrothermal ore deposits	3
1.2 Research objectives	6
1.3 Experimental approaches and advances of XAS technology	6
1.4 Thesis organization.....	11
1.5 References	12
Chapter 2	21
2.1 Introduction	23
2.2 Instrument description	24
2.2.1 Stainless steel autoclave and internal sample cell	26
2.2.2 Pressure and temperature control.....	28
2.2.3 Safety measures	29
2.3 Commissioning and results.....	30
2.4 Conclusions	36
2.5 References	37
Chapter 3	41
3.1 Introduction	43
3.2 Method.....	48
3.3 <i>Ab initio</i> XANES simulations for solid standards	49
3.3.1 Calculation method: MST vs FDM	50
3.3.2 Effect of cluster size	52
3.4 <i>Ab initio</i> XANES simulations for aqueous species	54

3.4.1	Effect of the self-consistent field (SCF) calculations	54
3.4.2	Effect of bond distance	55
3.4.3	Effect of stoichiometry and distortion	57
3.4.4	Effect of hydrogen	60
3.4.5	Contributions of second hydration shell	62
3.5	Conclusions	63
3.6	References	65
Chapter 4	71
4.1	Introduction	75
4.2	Materials and measurements	76
4.2.1	Experimental setup	77
4.2.2	XAS measurements.....	77
4.3	Results and data analysis	77
4.3.1	Results of XANES spectroscopy	77
4.3.2	EXAFS analysis.....	81
4.3.3	Density Functional Theory calculations.....	83
4.3.4	Ab initio XANES simulation	83
4.4	Discussion.....	85
4.4.1	Ni speciation in chloride brines	85
4.4.2	Thermodynamic analysis and comparison with previous studies.....	87
4.4.3	Comparison to Co chloride complexes	91
4.5	References	92
Chapter 5	95
5.1	Introduction	101
5.2	Materials and methods.....	104
5.2.1	Experimental samples	104
5.2.2	XAS Measurements	106
5.2.3	EXAFS data analysis	108
5.2.4	Density Functional Theory calculations	108
5.2.5	Ab initio XANES simulations	110
5.3	Qualitative analysis of XAS spectra.....	110
5.3.1	Effect of temperature	110
5.3.2	Effect of salinity.....	114

5.3.3	XANES spectra of bromide solutions.....	116
5.4	EXAFS refinements.....	118
5.4.1	Mn-Cl solutions	119
5.4.2	Mn-Br solutions	129
5.5	DFT calculations.....	131
5.6	<i>Ab initio</i> XANES simulations.....	132
5.6.1	Simulations for solid standards.....	132
5.6.2	Simulations of aqueous complexes.....	135
5.7	Discussion: Mn(II) speciation in chloride brines	139
5.7.1	Nature of Mn(II) chlorocomplexes	139
5.7.2	Thermodynamic analysis	141
5.7.3	Comparison with Fe(II) chloride complexing	147
5.8	Annexes	148
5.8.1	Single crystal x-ray diffraction for (NEt ₄) ₂ MnCl _{4(s)}	148
5.8.2	DFT optimized geometries for Mn(II) complexes.....	150
5.8.3	Classical Molecular Dynamics (MD) simulation	155
5.9	References	158
Chapter 6	169
6.1	Ni(II) speciation in hydrothermal brines	171
6.2	Mn(II) speciation in hydrothermal brines.....	172
6.3	<i>Ab initio</i> XANES simulations to explore structure of hydrothermal solutions	173
6.4	Future work.....	174
6.5	References	176
Appendix A	179
Appendix B	199
Appendix C	203
Appendix D	223

NOTE: Statements of authorship appear in the print copy of the thesis held in the University of Adelaide Library.

Abstract

Knowledge of metal speciation and thermodynamic properties underpins our capability to model metal transport and deposition in natural and engineered systems. Using synchrotron-based X-ray Absorption Spectroscopy and high temperature – high pressure experimental techniques, this project aims to elucidate nickel and manganese speciation in hydrothermal chloride solutions, and obtain the thermodynamic properties for predominant species.

Ab initio XANES simulation methods were used in this study to provide independent or complementary information about the nature (stoichiometry and geometry) of aqueous complexes. Application of this technique to the calculation of XANES spectra of Mo(VI) complexes in hydrothermal systems confirmed that $[\text{MoO}_4]^{2-}$ is stable in neutral and basic solutions over a wide range of temperature and salinity, and chlorinated Mo complexes (e.g., $[\text{MoCl}_2\text{O}_2(\text{H}_2\text{O})_2]_{(\text{aq})}$, $[\text{MoOCl}_4]_{(\text{aq})}$) exist in strongly acidic solutions. XANES simulations of Te complexes added additional evidence that $[\text{Te}(\text{OH})_3]$ and $[\text{TeO}_3]$ species predominate in basic and acidic solutions, respectively, and that the deprotonation process to convert $[\text{Te}(\text{OH})_3]$ to $[\text{TeO}_3]$ is associated with a distance contraction for the Te-O bond.

Ni(II) speciation in hydrothermal brines was investigated over a wide range of temperatures (25-434 °C) and fluid compositions (0-7.68 m Cl⁻) at 400 and 600 bar. Quantitative XAS data interpretation revealed that Ni(II) chloroqua complexes undergo a structural transition from octahedral at room temperature to distorted tetrahedral at elevated temperatures. Both heating and an increase in salinity promote the stability of tetrahedral complexes relative to octahedral complexes. The $\text{NiCl}_{2(\text{aq})}$ species exists in both octahedral $[\text{NiCl}_2(\text{H}_2\text{O})_4]_{(\text{aq})}$ and tetrahedral $[\text{NiCl}_2(\text{H}_2\text{O})_2]_{(\text{aq})}$ forms, with the ratio of octahedral to tetrahedral decreasing at

high temperature (> 200 °C). The highest order Ni chloride complex identified in this work is not the fully chlorinated $[\text{NiCl}_4]^{2-}$ but the tri-chloro mono-aqua complex $[\text{NiCl}_3(\text{H}_2\text{O})]^-$, confirmed by both EXAFS analysis and XANES simulations.

A similar coordination change of Mn(II) chloroaqua complexes has been quantitatively identified by analysis of both XANES and EXAFS data collected between 30 to 550 °C at 600 bar, with chlorinity ranging from 0.100 to 10.344 m. Octahedral species predominate at room temperature within the whole salinity range and persist up to ~ 400 °C in low salinity solutions ($m_{\text{Cl}} < 1$ m), and tetrahedral species become significant at temperatures above 300 °C. Compared with Fe(II) chloride complexation, the octahedral to tetrahedral structural transition occurs at higher temperature for Mn(II) complexes. A combination of EXAFS refinements, Density Functional Theory calculations and *ab initio* XANES simulations confirmed that at elevated temperatures (≥ 400 °C) the highest order chloride complex predominating in highly saline brines ($m_{\text{Cl}} > 3$ m, Cl:Mn ratio > 53) is $[\text{MnCl}_3(\text{H}_2\text{O})]^-$ with $[\text{MnCl}_4]^{2-}$ being unstable through all T-P-salinity range, while a lower order chlorocomplex, $[\text{MnCl}_2(\text{H}_2\text{O})_2]_{(\text{aq})}$, is the major species in low salinity solutions ($m_{\text{Cl}} < 0.5$ m, Cl:Mn ratio < 10). The differences regarding to the stoichiometry and stability of highest order metal chloride complexes identified in this study, $[\text{NiCl}_3(\text{H}_2\text{O})]^-$ and $[\text{MnCl}_3(\text{H}_2\text{O})]^-$, and in previous studies (i.e., $[\text{CoCl}_4]^{2-}$ and $[\text{FeCl}_4]^{2-}$) may play a role in the fractionation between metals with closely related geochemical properties in hydrothermal systems (e.g., Ni/Co; Mn/Fe).

Overall, the combination of XANES and EXAFS data provided us with a molecular level understanding of Ni and Mn speciation in hydrothermal brines and improved our capability for modeling metal mobility in the Earth's crust.

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.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Signature:

Date: 29-05-2013

Acknowledgements

I always feel lucky that I made the right decision to come to down under to pursue something I was really interested in 3.5 years ago, because I was introduced to a great project and some great people, although I had a steep learning curve in the beginning of this project, which is far away from what I've learnt for my undergraduate study. This PhD experience is a unique journey in my life when it comes to the final stage, and everything in the past three and a half years comes to my mind all together.

This thesis has been benefited from so many people. Firstly, I am extremely grateful to all my supervisors: A/Prof. Joël Brugger, Dr Yung Ngothai, Dr Weihua Liu, and A/Prof. Brian O'Neil for their infinite patience, invaluable discussions, unreserved help, and constant encouragement to my research. Without these key factors, this thesis would not be able to come into being.

I am particularly thankful to the scientists based in SA Museum Dr Barbara Etschmann, Prof. Allan Pring, Dr Ben McHenry, Dr Peter Elliot, Dr Mike Snow and other scientists Dr Stacey Borg, Dr Fang Xia, Dr Pascal Groundler, Dr Denis Testemale, Prof. David Sherman, Dr Yves Joly, Dr Frank Reith and PhD fellow Blake Tooth for their kind suggestions and assistances to my research and critical discussions and comments for some research articles, which significantly improved the quality of this project. I am also grateful to Jason Peak and Michael Jung, the technicians based in School of Chemical Engineering workshop, for building and maintaining the HP-HT hydrothermal autoclave for this project. I thank Nick Rae and beamline scientists Dr Bernt Johannessen, Dr Chris Glover for their contributions to the intensive experiments at Australian Synchrotron, and Dr Denis Testemale for the

experiment at ESRF. A special thank is attributed to Dr Haipeng Wang (previously Associate Professor of Curtin University of Technology), who provided valuable assistance to my PhD admission and scholarship applications, as well as suggestions of doing research. Thanks a lot to those who helped me with administrations via the School of Chemical Engineering of the University of Adelaide and Mineralogy Division of SA Museum.

I would like to acknowledge Australian Synchrotron and European Synchrotron Radiation Facility for providing precious beamtime, Australian International Synchrotron Access Program for travel funding, and iVEC for the EPIC advanced computing resource. I also acknowledge ASI scholarship from the University of Adelaide. This thesis has been examined by Prof. John Mavrogenes and Prof. Terry Seward, whose helpful reviews and comments are greatly appreciated.

Last but not least, I thank my dear wife Yuan Mei for accompanying me in Adelaide and this thesis would not be completed without her endless understanding and patience, in particular during the last six months of my PhD. I thank all my families in China for their continual encouragement and support. I wish this thesis will comfort my grandparents in the heaven.

List of publications

Part of the thesis has been published in the following peer-reviewed conference paper and abstract.

1. **Tian, Y.**, Brugger, J., Liu, W., Borg, S., Etschmann, B., O'Neill, B., Testemale, D., Hazemann, J-L., Glover, C., Ngothai, Y., Jung, M., Peak, J., 2010. High-temperature and pressure spectroscopic cell for in-situ XAS study of supercritical fluids at the Australian Synchrotron, Chemeca 2010, Adelaide, S. A., Australia. (Copyright of this paper belongs to RMIT Publishing, Appendix A)
2. **Tian, Y.**, Brugger, J., Liu, W., Etschmann, B., Borg, S., Testemale, D., O'Neill, B., Ngothai, Y., 2011. Speciation and Thermodynamic Properties of Manganese(II) and Nickel(II) Chloride Complexes in Hydrothermal Fluids: In situ XAS Study. Goldschmidt Conference Abstract, August 14-19, 2011, Prague, Czech Republic. (published in Mineralogical Magazine 75, 2011; copyright of this abstract belongs to the Mineralogical Society of Great Britain and Ireland, Appendix B)

The following peer-reviewed journal paper and manuscript are based on this PhD project, and they comprise the main body of this thesis (chapters 4 and 5):

3. **Tian, Y.**, Etschmann, B., Liu, W., Borg, S., Mei, Y., Testemale, D., O'Neill, B., Rae, N., Sherman, D.M., Ngothai, Y., Johannessen, B., Glover, C., Brugger, J., 2012. Speciation of nickel (II) chloride complexes in hydrothermal fluids: In situ XAS study. Chemical Geology 334, 345-363. (Copyright of this paper belongs to Elsevier Ltd.)
4. **Tian, Y.**, Etschmann, B., Mei, Y., Grundler, P., Testemale, D., Hazemann, J-L., Elliott, P., Ngothai, Y., Brugger, J., Speciation and thermodynamic properties of

Manganese (II) chloride complexes in hydrothermal fluids: *in situ* XAS study.
(under review for *Geochimica Cosmochimica Acta*)

The XANES simulation work (chapter 3) of this PhD project contributes to the following peer-reviewed research paper and manuscript:

5. Borg, S., Liu, W., Etschmann, B., **Tian, Y.**, Brugger, J., 2012. An XAS study of molybdenum speciation in hydrothermal chloride solutions from 25–385 °C and 600 bar. *Geochimica et Cosmochimica Acta* 92, 292-307. (Copyright of this paper belongs to Elsevier Ltd., Appendix C).
6. Grundler, P., Brugger, J., Etschmann, B., Helm, L., Liu, W., Spry, P., **Tian, Y.**, Testemale, D., Pring, A., Speciation of aqueous tellurium(IV) in hydrothermal solutions and vapors, and the role of oxidized tellurium species in gold metallogenesis. (in revision for *Geochimica Cosmochimica Acta*, Appendix D)