



A review of the coordination chemistry of hydrothermal systems, or do coordination changes make ore deposits?

Joël Brugger^{a,*}, Weihua Liu^b, Barbara Etschmann^a, Yuan Mei^{a,b}, David M. Sherman^c, Denis Testemale^d

^a School of Earth, Atmosphere and the Environment, Monash University, Clayton, 3800, VIC, Australia

^b CSIRO Mineral Resources, Clayton, VIC 3168, Australia

^c School of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK

^d CNRS, Université Grenoble Alpes, Institut NEEL, F-38000 Grenoble, France

ARTICLE INFO

Article history:

Received 12 June 2016

Received in revised form 11 October 2016

Accepted 13 October 2016

Available online 18 October 2016

Keywords:

Coordination chemistry

Hydrothermal fluids

In situ spectroscopy

Geochemical cycling

Ore deposits

Mineral solubility

Molecular dynamics

ABSTRACT

The hydration and complexation of metals in hydrothermal fluids are key processes controlling the mobility of elements in the Earth's crust, leading to the formation of ore deposits from which the World's supply of Fe, Mn, Ag, Au, Pd, Cu, Zn, Co, Pb, U, and Mo is mined. In the past 20 years a large amount of in situ spectroscopic data, complemented by increasingly accurate ab initio molecular dynamic simulations, have dramatically improved our understanding of the nature and geometry of the metal complexes that are responsible for metal transport in the upper crust. This new information underpins a "Coordination Chemistry" approach to ore transport and deposition.

In order to highlight the unifying principles brought about by the concepts of coordination chemistry, we present a *periodic table of metal coordination chemistry in hydrothermal fluids* based on a review of the literature and new XAS data on the hydration of the uranyl ion in hydrothermal fluids, and the pressure dependence of Ni(II) and Zn(II) complexing. The different coordination geometries of metal complexes control some of the first order behaviours of these metals in hydrothermal systems. In particular, (i) complexes with low coordination number and open structures (i.e., linear and trigonal pyramidal) have an enhanced affinity for low-density, vapour-like fluids, relative for example to tetrahedral and octahedral complexes; and (ii) fractionation and changes in solubility are associated with changes in coordination geometry caused by changes in pressure, temperature, and ligand availability. For example, first row divalent transition metals as well as Cd(II) all occur as chloride-poor, octahedral complexes at low T, low salinity, and tetrahedral-like chloride-rich complexes at high T, high salinity in chloride brines. However, the octahedral–tetrahedral transition occurs at different conditions for different metals, and this can drive fractionation between geochemical pairs such as Zn/Cd, Fe/Mn and Co/Ni.

This review highlights the central role of entropy in driving the formation of metal complexes and changes in coordination geometry as a function of temperature and, to a lesser extent, pressure. Changes in coordination geometry are associated with large changes in entropy. Hence, coordination changes usually occur rapidly as a function of temperature (few 10's of °C), and can result in rapid changes in mineral solubility. These effects need to be taken into account when extrapolating the thermodynamic properties of metal complexes to high temperature and high pressure. A molecular-level understanding of metal speciation hence underpins the development of more accurate models of reactive-transport over wide ranges in pressure, temperature, fluid composition and physical states.

© 2016 Elsevier B.V. All rights reserved.

Contents

1.	Introduction	220
2.	A wealth of new information: towards a <i>molecular level</i> understanding of metal transport in hydrothermal fluids	221
2.1.	Spectroscopic studies of complexes and complex-forming reactions under hydrothermal conditions	221
2.1.1.	In situ spectroscopy	221
2.1.2.	A note on beam damage	223

* Corresponding author.

E-mail address: joel.brugger@monash.edu (J. Brugger).

2.2.	Molecular simulations	224
3.	Review of coordination of metals in hydrothermal fluids	224
3.1.	Titanium, zirconium and hafnium	224
3.2.	Vanadium	225
3.3.	Niobium and tantalum	226
3.4.	Chromium, molybdenum and tungsten	226
3.5.	Iron and manganese, nickel and cobalt, zinc and cadmium: transition metals existing mainly as octahedral and tetrahedral aqua- and chloro-complexes	227
3.6.	Copper, silver and gold	230
3.7.	Mercury	232
3.8.	Platinum group elements (PGE)	232
3.9.	Gallium	232
3.10.	Indium	233
3.11.	Thallium	233
3.12.	Germanium	233
3.13.	Tin	233
3.14.	Lead	234
3.15.	Arsenic, antimony and bismuth	234
3.16.	Selenium, tellurium (and polonium)	235
3.17.	Rare earth elements, yttrium and scandium	235
3.18.	Uranium and thorium	237
4.	Discussion	238
4.1.	Metal transport in hydrothermal systems – a view from coordination chemistry	238
4.1.1.	A periodic table for hydrothermal geochemistry	238
4.1.2.	Effects of temperature and salinity	239
4.1.3.	Effects of pH and redox state	241
4.1.4.	Effect of pressure	241
4.1.5.	Coordination chemistry controlled by ligands	242
4.2.	Driver for metal complexation in hydrothermal systems: key role of translational entropy	242
4.3.	A few key issues in hydrothermal geochemistry	244
4.3.1.	Sulfur versus chloride complexing	244
4.3.2.	Liquids and vapours	244
4.3.3.	Charged versus neutral complexes – the dielectric diiktat?	245
5.	Conclusions and perspectives	245
	Acknowledgements	245
	Appendix A. Supplementary data	245
	References	245

1. Introduction

Most of the World's metals (Fe, Mn, Ag, Au, Pd, Cu, Zn, Co, Pb, U, Mo, ...) are mined from hydrothermal ore deposits. These ore deposits either form as a result of the flow of aqueous fluids within the Earth's crust and the ability of these fluids to carry metals in soluble form (Heinrich et al., 1996), or are often modified by geofluids (Altree-Williams et al., 2015). Ore-forming fluids cover wide ranges in temperature (25 to >600 °C), pressure (0.1 to >500 MPa) and compositions ranging from nearly pure water, to low density 'vapours' rich in volatiles such as CO₂, CH₄, H₂O or SO₂, or to complex 'hydrated melts' with >50 mol% salt (NaCl, KCl, CaCl₂, FeCl₂). Aqueous fluids play a key role in controlling the composition of the Earth's crust by redistributing metals as a result of dehydration reactions during regional metamorphism or subduction (Bebout and Penniston-Dorland, 2016; Zhong et al., 2015b), or during exsolution from rising magmas (Heinrich et al., 2004).

A quantitative understanding of metal transport and deposition under geological conditions (e.g., via reactive-transport modelling) is important for our understanding of crustal geochemistry, and is key to sustaining mineral exploration (predictive mineral discovery). This quantitative understanding underpins the optimisation and development of environmentally sustainable hydrometallurgical methods for processing ores of ever increasing complexity and decreasing concentration (Brugger et al., 2010; Seward and Driesner, 2004). Hydrothermal fluids also are important in a number of physical chemistry and engineering applications (e.g., corrosion in power plants, geothermal energy, use of supercritical water as a green solvent for material synthesis, catalysis; Grunwaldt et al., 2003).

At a fundamental level, mineral solubility is controlled by (i) the crystal chemistry and stability of the minerals (lattice energy); (ii) the physicochemical properties of aqueous electrolyte solutions; and (iii) the thermodynamic and molecular properties of the aqueous species of metals (Crerar et al., 1985). At the birth of thermodynamics in the late 19th century (Gibbs, 1873), little information was available about the structures of metals in solution, and Alfred Werner (1866–1919) won the 1913 Nobel Prize in Chemistry for proposing the correct octahedral configuration of some transition metal complexes (Werner, 1893). However, it was well known at that time that metals react with ligands to form complexes, because of the effect of these complexes on mineral solubility. As illustrated in Fig. 1a, the activity of a complex increases in a linear fashion with respect to the activity of the ligand on a log-log plot, with the slope of the line equal to the ligand:metal ratio. In thermodynamic models of aqueous solutions, the role of water as a ligand is often ignored; in other words, the thermodynamic models assume that the activity of water ($a_{\text{H}_2\text{O}}$) is equal to one when it comes to complex-forming reactions. This is reflected by the fact that dissolved ions or metal complexes are written for example as Co²⁺ and CoCl₂(aq), ignoring the coordinated water molecules. This convention is still overwhelmingly used today by hydrothermal geochemists – and by many inorganic chemists, geochemists, and engineers alike (Bethke, 2008).

In their seminal study, Susak and Crerar (1985) observed a change in coordination geometry from octahedral to tetrahedral in the aqueous complexes of divalent transition metals (Fe, Co, Ni, Cu) upon heating and upon increasing chloride concentration, based on semi-quantitative in situ spectroscopic UV–vis measurements. This

Download English Version:

<https://daneshyari.com/en/article/5782994>

Download Persian Version:

<https://daneshyari.com/article/5782994>

[Daneshyari.com](https://daneshyari.com)