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



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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-richer 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.

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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 CO_2 , CH_4 , H_2O or SO_2 , 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 (aH_2O) 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 Co^{2+} and $CoCl_2(aq)$, 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:

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