The coordination chemistry of hydrothermal systems

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The hydration and complexation of metals in hydrothermal fluids are key processes controlling the mobility of elements in the Earth's crust, leading for example to the formation of ore deposits from which the World's supply of Fe, Mn, Ag, Au, Pd, Cu, Zn, Co, Pb, U, Mo is mined. In the past 20 years a large amount of *in situ* spectroscopic data, in particular synchrotron X-ray absorption spectroscopic data, complemented by increasingly accurate *first principle* 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 hydrothermal geochemistry. We present a *periodic table of metals coordination chemistry in hydrothermal fluids* based on a review of the literature to illustrate the unifying principles brought upon by the concepts of coordination chemistry.

We show that the different coordination geometries (e.g. linear versus tetrahedral versus octahedral) of metal complexes control some of the first order properties of these metals in hydrothermal systems, such as their relative affinity for low-density, vapour-like fluids. Recently, the diffential mobility of Zr in aqueous fluids and hydrated melts in subduction environments was related to changes in coordination geometry. For some elements, large fractionation and solubility gradients are associated with changes in coordination geometry brought upon by changes in pressure, temperature, and ligand availability (activity). These changes also affect metal ratios in hydrothermal fluids, including the ratios of geochemical pairs such as Zn/Cd, Fe/Mn, and Co/Ni.