

Ion association and metal complexation in hydrothermal fluids: from quantum chemistry to geology

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Reactive transport simulations of fluid-rock interactions enable us to test models of ore formation. However, such simulations depend on our thermodynamic models for the partitioning of metals between melts, fluids and vapour phases. Complexation of metals by Cl^- and HS^- (and S_3^{2-}) ligands in the fluid phase exerts a fundamental control on how mineral solubilities change with temperature and fluid composition. Our understanding of such complexation reactions has been based on speciation models of mineral solubility data along with extrapolations using Born model equations of state (e.g., SUPCRT). However for this approach to be reliable, we need independent confirmation of the important complexes (e.g., CuCl_2^- , ZnCl_4^{2-} etc.) that are present. Moreover, we need to be in a PT regime where the fluid can be approximated as a dielectric continuum; this will break down at low fluid densities and high temperatures where the dielectric constant of water is uncertain.

In recent years, we have been able to gain a molecular-level insight on hydrothermal fluids using ab initio molecular dynamics. From these simulations, we are able to sample the microstates of a system and estimate the free energy of formation of metal complexes. One of the fundamental physical insights that emerge from this work is that metal complexation and ion association in hydrothermal fluids at high temperature is driven by changes in translational entropy. This concept, along with knowledge of the coordination chemistry and hydration of metals in solution, explains why the dominant speciation of Zn changes from $\text{Zn}(\text{H}_2\text{O})_6$ to ZnCl_4^{2-} with increasing temperature while the speciation of Cu changes from CuCl_3^{2-} to CuCl_2^- . Translational entropy also explains the increased ion-pairing in low density fluids and vapors to yield species such as NaCuCl_2 . Although new molecular insights on hydrothermal fluids are emerging, there are still some major theoretical problems that remain untouched. Perhaps most important is the partitioning of metals between fluids and melts.