

Metal speciation in hydrothermal fluids: Insights from *ab initio* molecular dynamics

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The solubilities of metals in crustal fluids is enhanced at high temperature by the formation of complexes with ligands such as Cl^- and HS^- . Understanding the nature and thermodynamic properties of metal complexes in hydrothermal fluids is crucial for predicting solubilities of minerals in natural and man-made systems.

Ab initio molecular dynamics simulations provide a means to determine the nature and stabilities of metal complexes under conditions that are beyond experimental practicality. This approach is made possible by the availability of high-performance computing resources and the implementation of density functional theory. However, we still need to use approximate exchange-correlation functionals (GGA), and a fundamental question is the whether such functionals can provide us with geochemically useful accuracy. Moreover, we must extrapolate our results to other conditions (e.g., infinite dilution) in order to compare our results to existing thermodynamic models and experiment.

We have tested this approach on Cu [1] [2], Au [2], Zn [3], and Pd [4] complexing in chloride- and sulfur-rich ore fluids under extreme T-P conditions. We find very encouraging agreement with experiment; this suggests that the level of theory (i.e., the generalised gradient exchange-correlation functional) that we are using is adequate for these systems. The simulations also helped to resolve some uncertainty in the interpretation of experimental data. Coupled with experimental studies, the MD simulation give molecular-level insights into the chemical processes responsible for the formation of ore deposits. We are now able to explore PT regimes where experiments are impractical.

[1] Mei et al., 2013, *Geochim. Cosmochim. Acta*, **102**, 45–64

[2] Mei et al., 2014, *Geochim. Cosmochim. Acta*, **131**, 196–212

[3] Mei et al., 2015, *Geochim. Cosmochim. Acta*, **150**, 265–284

[4] Mei et al., 2015, *Geochim. Cosmochim. Acta*, in press