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Molecular dynamics simulation of hydrothermal fluids

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One of the fundamental questions in geochemistry is how crustal fluids transport metals leading to the formation of ore deposits. Metals are complexed by ligands such as Cl^-, HS^-, F^- in geological fluids at high pressure–temperature (P-T) to dissolve ore minerals. To predict metal transport in fluids of different compositions, thermodynamic models of mineral solubility and metal complexation are essential. To model fluid thermodynamics, traditional approaches employ classical continuum methods, treating water as a dielectric continuum based on Born's solvation model in 1920s. From the Born model, the HKF (Helgeson-Kirkham-Flowers) equation-of-state (EOS) was derived in 1970s and has been widely used to extrapolate complexation stability constants to elevated P-T if the dielectric constant of water is available. Until now, this has been the state-of-the-art model in hydrothermal aqueous fluids. However, these dielectric continuum models of aqueous solutions can only be used to extrapolate the solvation free energies of known species; they cannot predict the formation of new chemical species that may occur at high P-T. Recent advancements in first-principles computational methods and faster computers now allow us to model the water molecules explicitly therefore model the atomistic interactions of metals and ligands accurately in geochemical fluids. Complemented by in-situ X-ray Absorption Spectroscopy (XAS) studies, this approach has dramatically improved our understanding of element behaviour and chemical processes of hydrothermal fluid.

Ab initio molecular dynamics simulations enable us to use quantum chemistry (in the form of density functional theory) to explore the speciation of elements and the energetic profile of ion-pairing reactions. Over the past 15 years, we have tested this approach on metal complexes (Cu/Au/Zn/Pd/Pb/Mo/W/La/Y complexing in $Cl^-/HS^-/F^-/NH_3/SO_4^{2-}/S_3^-$) and successfully calculated the thermodynamic properties of different metal complexes as a function of P-T. This allows us to explore P-T regimes of fluids where the Born model breaks down (e.g., mantle fluids) to predict the formation of chemical species for which there is no reference data that can be used to extrapolate. In this presentation, we will review our research on molecular dynamics simulation of hydrothermal fluids, with new advances and perspectives in molecular modelling methods and application.