

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

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Complexation of metals by  $\text{Cl}^-$  and  $\text{HS}^-$  ligands in hydrothermal fluids is a fundamental process in the evolution of the Earth's crust and the formation of ore deposits. Current thermodynamic models of complexation equilibria under hydrothermal conditions depend on extrapolations of experimental data using equations of state based on the Born model of solvation. Thermodynamic parameters for aqueous species are often provisional estimates based on systematic correlations between fundamental properties such as entropy, volume, ionic radius etc. Computational molecular simulations, however, can be used to test current thermodynamic models, predict metal speciation, and even estimate thermodynamic properties. For a condensed fluid, molecular dynamics simulations can be used to sample the configurational degrees of freedom in order to predict properties as a function of pressure and temperature. Simulations of dilute solutions, however, require very large systems (1000's of atoms) and very long (> 1 ns) simulation times; such calculations are only practical by treating the atomic interactions using classical two- or three-body interatomic potentials. However, classical potentials seem to be unreliable for describing metal-ligand interactions, especially for transition metals and metalloids such as  $\text{Sn}^{+2}$ ,  $\text{Au}^{+3}$ ,  $\text{Cu}^{+2}$  and  $\text{Cu}^+$ . 'Ab initio molecular dynamics' treats the molecular motions classically but the atomic interactions quantum mechanically. Although these simulations are only practical for systems with 100's of atoms over short times (< 100 ps), they are giving fundamental new insights on metal speciation in hydrothermal fluids. Here, we describe simulations of Cu, Zn, Sn, Au, and Ni in NaCl- and HS-bearing aqueous fluids up to 350 °C. We show that predicted structures and speciation are in close agreement with experiment. Based on our simulations, we propose that the major driving force for metal complexation in hydrothermal fluids is the change in translational entropy between reactants and products. Entropies and free energies of complex formation can be estimated using thermodynamic integration and metadynamics. Applications of these techniques to Zn-Cl and Cu-Cl-HS stability constants will be presented.

## Collection and determination of suspended particulate trace metals: The US GEOTRACES Intercalibration cruises

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As part of the GEOTRACES Intercalibration and Methods Development effort, we have been working to optimize techniques for the accurate and precise determination of suspended particulate trace metals (TMs) from full water column profiles in various oceanic regimes. The goal has been to determine the best particle collection and analysis methods for future GEOTRACES ocean basin sections and to carry out laboratory intercalibration to arrive at community consensus on analytical methods and results. We will present results from the Atlantic and Pacific Intercalibration cruises (IC1 and IC2; 2008-09), with a focus on the feasibility of accurate and precise determination key Geotraces TMs as well as other TMs on small volume (~10L) samples collected from rosette-mounted Go-Flo bottles. We will summarize our findings with respect to filter type, practical performance, blanks and potential artifacts such as dissolved metal adsorption. Details of the filtration methodology will be described, with an important emphasis on minimizing element-dependent particle settling artifacts and determining appropriate procedural blanks. Digestion methods for particulate samples will be evaluated and results from an interlaboratory intercalibration exercise will be presented, with a summary of ICP-MS analytical approaches. Results for samples collected using 5-10L Go-Flo bottle samples will be compared with parallel samples collected with large-volume *in situ* pumps.