



## **Thermodynamic modeling of deep Earth fluid-rock interactions**

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I will first lay out the need for theoretical thermodynamic modeling and how it can be used to help address interesting deep Earth problems, as well as being extremely useful as a tool to aid in the planning and interpretation of experimental studies at high temperatures and pressures. Next, I will focus on the basis for calculating the standard Gibbs free energies of aqueous species as functions of temperature and pressure. This treatment includes a summary of how to make estimations even when experimental data are lacking. The calculated standard state free energies give us standard state thermodynamic activities. In turn, these activities are linked to measurable concentrations by activity coefficients. A summary of current approaches to the estimation of aqueous activity coefficients will be described, including approximations that enable the treatment of mixed volatile and multi-solute fluids. Finally, examples will be discussed of the application of all of the above to place subduction zone fluid-rock interactions on a forward modelling basis. The examples include the following: models of the importance of organic species with oxidation states of carbon ranging from -4 to +4 coexisting in subduction zone fluids at pressures greater than about 30 kb; prediction of the variable speciation of nitrogen in subduction zone fluids and implications for the origin of the Earth's atmosphere; a new theory for the formation of diamond by pH drop at constant redox conditions; and a model for the breakdown of antigorite in subduction zones leading to the generation of highly oxidizing fluids. Additional applications have focused on predictions of rock solubility and pH changes in metasomatic fluids, the use of theoretical modeling to interpret solubility and speciation experiments, and comparisons with the predictions of ab initio molecular dynamics for aqueous complexing reactions. The results of all these examples illustrate the need for obtaining a fundamental understanding of aqueous complexation between ions, and ions and neutral species, in subduction zone fluids. Such an understanding can only come about by integration of the results of experimental solubility and speciation studies with thermodynamic and ab initio molecular dynamic modelling studies that can be iteratively compared with the results of petrologic and field studies of subduction zone rocks.