

Aqueous fluids at high pressures and temperatures: Insights from molecular simulations and experiments

SANDRO JAHN

GFZ German Research Centre for Geosciences,
Telegrafenberg, 14473 Potsdam, Germany
(jahn@gfz-potsdam.de)

Aqueous fluids are involved in most geochemical processes at the Earth's crust and upper mantle. Fluid-rock interactions trigger important processes such as weathering, the formation of ore deposits or metamorphic reactions. To understand the function of aqueous fluids in these geological processes, we need to characterize their molecular structure at the relevant conditions of pressure, P , temperature, T , and composition, x . Speciation is probably the key parameter that links many properties of interest, e.g. mineral solubilities, electrical conductivities and chemical activities, but also element partitioning and isotopic fractionation between fluids and minerals. Due to the structural disorder and the particle mobility, a single experimental method (e.g. diffraction or different types of spectroscopy) is usually not sufficient to fully determine the molecular structure of a fluid. Furthermore, the structure of the fluid changes continuously with P , T and x . Thus, experiments need to be performed *in situ*, which often poses additional challenges. Molecular simulations have become a powerful complementary approach to study fluid structure and properties. Especially *ab initio* techniques that are free of empirical parameters have the accuracy and general applicability to be fully predictive even at extreme conditions. In this talk, the synergetic effects of combining molecular modeling and experimental approaches to study properties of aqueous fluids at extreme conditions will be highlighted. I will present results of recent *ab initio* molecular dynamics simulations (see e.g. [1]) and link them to spectroscopic or diffraction data. Recent modeling efforts to understand and predict isotopic fractionation between different species in the fluid or between fluids and minerals will be discussed.

[1] Jahn & Wunder (2009) *Geochim. Cosmochim. Acta* **73**, 5428–5434.

Tracing sources and cycling of phosphorus in Peru Margin sediments using oxygen isotopes in phosphates

DEB P. JAISI* AND RUTH E. BLAKE

Department of Geology and Geophysics, Yale University, PO
Box 208109 New Haven CT 06520
(*correspondence: deb.jaisi@yale.edu)

Because of the differential reactivity of sedimentary phosphate phases in response to diagenesis, dissolution/precipitation and biological cycling the oxygen isotope ratios of phosphate ($\delta^{18}\text{O}_p$) can carry a distinct signature of these processes, as well as inform on the origin of specific P phases. Here we present results of sequential sediment extraction (SEDEX) analyses combined with $\delta^{18}\text{O}_p$ measurements, aimed at characterizing authigenic and detrital phosphates from Peru Margin sediments collected during ODP Leg 201. Our results show that the $\delta^{18}\text{O}_p$ values of authigenic phosphate vary between 20.2 and 24.8 ‰ and can be classified into at least two major groups: authigenic phosphate precipitated at/near the sediment-water interface in equilibrium with paleo-water oxygen isotope ratios ($\delta^{18}\text{O}_w$) and temperature, and phosphate derived from hydrolysis of organic matter (P_{org}) with subsequent incomplete to complete re-equilibration and phosphate precipitated possibly deeper in the sediments column. The $\delta^{18}\text{O}_p$ values of detrital phosphate, which vary from 7.7 to 15.4 ‰, suggest two possible terrigenous sources and their mixtures: phosphate from igneous/metamorphic rocks and authigenic phosphate precipitated in source regions in equilibrium with $\delta^{18}\text{O}_w$ of meteoric water. More importantly, original $\delta^{18}\text{O}_p$ of at least one phase of authigenic phosphates and all detrital phosphates are not altered by diagenesis and other biogeochemical changes within the sediment column. These findings help to understand the origin P phases and paleoenvironmental conditions.