

# **Molecular Insight into Hydrothermal Solution Geochemistry**

**T.M. Seward**

Institut für Mineralogie und Petrographie, ETH-Zentrum, 8092 Zürich, Switzerland;  
(tseward@erdw.ethz.ch)

Aqueous fluids under extreme conditions of temperature and pressure occur ubiquitously throughout the Earth's crust and upper mantle. Throughout geological time, they have been and still are responsible for the transport of enormous amounts of heat and chemical mass within the crust. They discharge extensively at the Earth's surface and comprise one of the fundamental mechanisms by which the deep Earth communicates chemically with Earth's oceans and atmosphere and hence, with our biosphere. High temperature – high pressure water and aqueous solutions are intimately involved in magmatism, volcanism, metamorphism, tectonism and ore formation. Furthermore, they have probably played a defining role in the biomolecular syntheses which determined the origin of life chemistry in seafloor hydrothermal environments on our early Earth. Despite the importance of high temperature – high pressure aqueous fluids in so many fundamental Earth processes, our knowledge of many aspects of aqueous solution chemistry under extreme conditions remains sparse and in many cases, primitive.

Aqueous solutions in the Earth's crust are multicomponent electrolyte solutions. Perhaps the most fundamental aspect of aqueous solution chemistry is ion-solvent interaction, that is to say, the hydration of dissolved species by solvent molecules. Water is a hydrogen bonded solvent and the nature of ion-solvent interaction in hydrothermal systems is determined for a given ionic or molecular species by changes in hydrogen bonding as a function of temperature and pressure (Seward and Driesner, 2004).

In hydrothermal fluids, this changing nature of ion hydration plays a fundamental role in determining many properties such as ion mobility and conductivity, viscosity, ion association and metal complex equilibria, fluid phase equilibria, stable isotope ( $^{18}\text{O}/^{16}\text{O}$  and D/H) fractionation effects and mineral solubility and precipitation

(e.g. Seward et al, 1999; Driesner and Seward, 2000; Newton and Manning, 2000; Suleimenov and Seward, 2000; Ho et al, 2001). In particular, changing ion hydration as a function of temperature and pressure, leads to fundamental changes in water activity in aqueous solutions. For example, the number of first shell water dipoles coordinated to the  $\text{Sr}^{2+}$  ion in aqueous solution decreases from 8 to about 4 as temperature increases from ambient to near critical conditions at pressures near the saturated vapour pressure (Pfund et al, 1994; Seward et al, 1999). This dehydration is associated with a contraction of the first shell  $\text{Sr}^{2+}$ -oxygen(water) distances by about 0.05 Å.

For a simple anion such as iodide, the first shell iodide-oxygen(water) distance increases with increasing temperature as the number of coordinated water ligands decrease (i.e. the ion dehydrates) (Seward et al, 2005). These effects will be discussed in some detail with application to geochemical phenomena occurring in the Earth's crust. In addition, the implications for the stability of biomolecules under hydrothermal conditions will also be discussed.

## References

- Driesner T. and Seward T.M. (2000) *Geochim. Cosmochim. Acta* 64, 1773-1784.
- Ho P.C., Palmer D.A. and Gruskiewicz M.S. (2001) *J. Phys. Chem. B* 105, 1260-1266.
- Newton T.C. and Manning C.E. (2000) *Geochim. Cosmochim. Acta* 64, 2993-3005.
- Pfund D.M., Darab J.G., Fulton J.L. and Ma Y. (1994) *J. Phys. Chem.* 98, 13102-13107.
- Seward T.M., Henderson C.M.B., Charnock J.M. and Driesner T. (1999) *Geochim. Cosmochim. Acta* 63, 2409-2418.
- Seward T.M. and Driesner T. (2004) In: *Aqueous Systems at Elevated Temperatures and Pressures: Physical Chemistry in Water, Steam and Hydrothermal Solutions* (D.A. Palmer, R. Fernandez-Prini and A.H. Harvey, eds.) Elsevier, chap. 5, 149-182.
- Seward T.M., Henderson C.M.B., Charnock J.M. and Suleimenov O.M. (2005) *Geochim. Cosmochim. Acta* (submitted).