

# Molecular Aspects of Water Activity in Hydrothermal Solutions: Insight from X-ray Absorption Spectroscopy, Molecular Dynamics and Stable Isotope Fractionation

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Crustal hydrothermal fluids are multicomponent electrolyte solutions which may contain appreciable concentrations of volatile components such as CO<sub>2</sub> as well as high concentrations of halide salts. Such fluids are responsible for the transport, precipitation and redistribution of chemical components throughout the crust and upper mantle. Mineral solubilities in high temperature and pressure salt solutions are sensitive to changes in water activity (1) as a result of association equilibria (e.g. ion pairing and cluster formation). In addition fundamental changes occur in the nature of ion-solvent interaction which lead to a contraction of first shell hydration waters around alkali and alkali earth metal cations. For example, molecular dynamics simulations and Exafs data indicate that the first shell cation-oxygen(water) distances for Na<sup>+</sup> and Sr<sup>2+</sup> (2,3) decrease by up to 0.05Å over the temperature range from 25 to 35°C at saturated vapour pressures. The associated increase in bond energy is reflected in the enhanced fractionation of <sup>18</sup>O water of up to one per mil into the solvation shell environments of 4 molal NaCl and KCl solutions (4). The cation-oxygen(water) bond shortening may be associated with a decrease in the number of first shell co-ordinated

water molecules (e.g. Na<sup>+</sup>, Ag<sup>+</sup>, Sr<sup>2+</sup>)(2,3,5) whereas for other cations such as Cd<sup>2+</sup>, the number of first shell waters remains constant even though the Cd<sup>2+</sup>-oxygen(water) distance contracts(6). Knowledge of such changes in association equilibria and ion hydration in water solvent as a function of temperature and pressure is important to our understanding of silicate mineral dissolution and deposition by deep crustal fluids.

- Aranovich Lya, Newton RC, *Contrib.Mineral.Petrol.*, **125**, 200-212, (1996).  
Charnock JM, Dobson BR, Driesner T, Seward TM & Tironi IG, *Geochim. Cosmochim. Acta*, **62**, 2095-3107, (1998).  
Driesner T & Seward TM, *Geochim.Cosmochim.Acta*, **64**, 1773-1784, (2000).  
Seward TM, Henderson CMB & Charnock JM (submitted)  
Seward TM, Henderson CMB, Charnock JM, Driesner T., *Geochim.Cosmochim Acta*, **63**, 2409-2918, (1998).  
Seward TM.,Henderson CMB, *Geochim.Cosmochim.Acta*, **60**, 2273-2282, (1996).