

Iodide Ion Hydration in Aqueous Solution to 360°C: Insight from XAS and Ab Initio MD

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The interaction of solute species with solvent molecules is a fundamental aspect of aqueous solutions and changes with increasing temperature and pressure in response to changes in the hydrogen bonding of water solvent. The varying nature of ion hydration in hydrothermal systems plays an important role in many geochemical processes including water stable isotope fractionation, mineral solubility and precipitation, metal complexing and transport reactions.

Anion-solvent interaction is still poorly known at elevated temperatures and pressures and no data exist for iodide solvation above ambient temperatures (Seward and Driesner, 2004). We have therefore studied the first shell hydration of iodide using X-ray absorption spectroscopy from 35 to 350°C at equilibrium vapour pressures. The Exafs of 1.00m RbI as well as 0.10m CsI and SrI₂ was measured using a high temperature X-ray optical cell containing silica glass and/or cvd diamond windows. With increasing temperature from 35 to 350°C, iodide-oxygen(water) distance increased from 3.56 to 3.61Å as the first shell waters are "dragged" away from the iodide ion by expanding bulk water solvent to which they are hydrogen bonded. Over the same temperature range, the number of first solvation shell waters apparently decreases from 7 to 4.

We have also performed ab initio molecular dynamics simulations using the Car-Parinello scheme (Car and Parinello, 1985). The present density functional theory calculations utilised norm-conserving pseudopotentials of Troullier and Martins (1991) to describe the core of all atoms except for hydrogen for which a von Barth-Car analytical pseudopotential was used. The simulation cell was cubic with periodic boundary conditions containing 32 waters and one iodide ion. At 27°C, the iodide-oxygen(water) distance was 3.53Å and increased to 3.59Å at 350°C, in good agreement with our results from XAS.

Car R. and Parinello (1985) Phys. Rev. Lett. 55, 2471.
Seward T.M. and Driesner T. (2004) In: Aqueous Systems at Elevated Temperatures and Pressures (Elsevier), chap. 5.
Troullier and Martins (1991) Phys. Rev. B, 43.

Fluid-mediated re-equilibration and self-irradiation in complex U-Th-rich assemblages of pegmatites: A case from Norway and implications for U-Th-Pb dating of ore deposits.

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In most rocks, uranium and thorium are concentrated in favorable crystallographic sites in few minerals such as zircon, monazite, titanite, and rarely uraninite, thorianite, thorite / huttonite, euxenite. These minerals are submitted to intense self-irradiation that can lead to amorphization and also modify their environment by irradiating the host minerals. Here, we focus on accessory minerals in rare-metal-rich pegmatites from southern Norway (Kragersø, Iveland-Evje); some of these minerals are rich in U (e.g. up to 15wt % for euxenite). A complex paragenesis of zircon + monazite + xenotime + euxenite was studied by multiple methods including optical and electron microscopy and U-Pb geochronology (SIMS and LA-ICP-MS). Observations show that complex relationships exist between the different minerals (especially zircon-euxenite) and the various processes (alteration by fluids and radiation effects) which have repercussions on the U-Th-Pb geochronology response. Irradiation (self and out), destroy the crystal lattice (amorphization) promoting the alteration of more or less destroyed parts. Amorphization induces volume increase, leading to the formation of cracks which eventually connected into a network through the rock. This fracturing allows fluid circulation, and promotes alteration of source minerals and dispersion of elements (e.g. Pb and U). Our results demonstrate however that monazite and xenotime crystals, even altered, have a greater potential for U-Th-Pb dating [1].

[1] Seydoux-Guillaume *et al.* (2012) *Chem. Geol.* **330-331**, 140-158.