

Towards computer simulation of element complexation in subduction zone fluids

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Field-based evidence as well as laboratory experiments suggest rare earth elements (REE) can form chloride, fluoride, hydroxide and sulphate complexes in hydrothermal fluids. In addition to effects of pressure and temperature, the presence and concentrations of these ligands are thus likely to play a critical role in determining REE mobility in subduction zones. But to date, the atomic-scale processes controlling elemental solubilities are poorly understood.

Pending accompanying high-pressure, high temperature mineral-fluid trace element partitioning experiments, we are investigating the configurations and energetics of REE complexes dissolved in H₂O at elevated pressures and temperatures using electronic structure theory.

A thermodynamic cycle was developed to obtain relative hydration free energies of REE ions using density functional theory. The first solvation shell is explicitly defined and the remaining part of the solvent is modelled using a polarisable continuum model, which can be augmented to mimic a broad pressure and temperature range.

Calculated relative hydration free energies for trivalent REE ions with eight- and nine-fold coordinated explicit first hydration shells show good agreement with experimental literature values at room pressure and temperature. The hydration free energy is more negative for smaller complexes (heavy REE) relative to larger complexes (light REE). We explore the energetics and geometries of lesser charged and neutral REE-anion complexes dissolved in H₂O. Preliminary results show enhanced REE complexation in the presence of anions.

With increasing temperature and pressure, the difference in hydration energies between HREE and LREE ions increases. If this were to dominate the thermodynamics, smaller complexes (HREE) would remain in solution in preference to larger complexes (LREE). This seems counter-intuitive given the observed high LREE/HREE ratios observed in island arc volcanics. Co-existing solids, either bulk or surface, must play a dominating role in controlling REE signatures.

Laser microprobe depth profiling of ⁴He diffusion in Durango Apatite

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To further demonstrate the utility of laser ablation methodologies in (U-Th)/He thermo- and geochronology [1] an artificial diffusion profile of ⁴He in Durango apatite has been studied by depth profiling.

A >200µm thick slab, cut from a larger apatite crystal, was polished and then heated under vacuum in a diffusion cell [2] at 400°C for 45 minutes. The slab was put in the laser chamber of the noble gas extraction line, and using a 193nm Excimer laser the sample was ablated with a 100µm spot size in 6µm depth increments. After gas purification and cryogenic separation, the ⁴He was analyzed by ion counting on a GVI Helix SFT mass spectrometer.

Fig. 1 shows that the experimental results match well with the calculated model loss curve based on experimentally derived bulk diffusion coefficients [3]. This result supports the experimental results of Farley [3] and demonstrates convincingly that laser ablation also provides an opportunity to resolve natural ⁴He diffusion and α-ejection profiles directly.

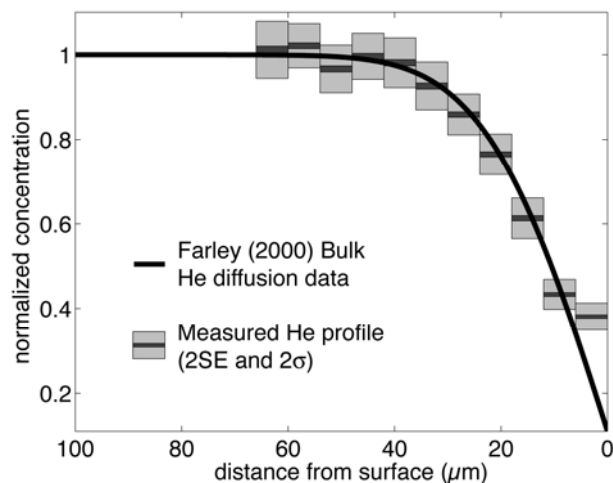


Figure 1: The measured ⁴He diffusion profile compared to the calculated apatite model loss curve.

[1] Boyce *et al.* (2006) *GCA* **70**, 3031-3039. [2] Farley *et al.* (1999) *An. Chem.* **71**, 2059-2061. [3] Farley (2000) *JGR* **105**, 2903-2914.