

Rutile solubility in supercritical NaAlSi₃O₈-H₂O fluids

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Subduction zones are important settings for chemical cycling. The transfer of material in subduction zones is often the result of a water-rich fluid; however, the nature of these fluids and their capacity for mobilizing key trace elements, such as Ti, remains uncertain. A central question is: Are these fluids silicate-rich or dilute solutions, or can intermediate fluids act as metasomatizing agents? Previous work on Ti has focused on hydrous melts or water-rich solutions [1-5]. We present new results of an experimental study on rutile (TiO₂) solubility in supercritical, intermediate NaAlSi₃O₈-H₂O fluids.

Experiments were conducted in a piston-cylinder apparatus at 900°C and pressures between 0.9 and 2.2 GPa for a range of fluid compositions. At pressures within the supercritical regime (1.0-2.0 GPa) rutile solubility was determined by electron probe microanalysis of the quench glass; at <1.0 and >2.0 GPa, solubility was determined both by analysis of quench glass and rutile weight loss.

Rutile solubility shows a non-linear increase with increasing Na-Al silicate in the fluid. At 1.25-1.5 GPa, rutile solubility shows a strongly sigmoidal dependence on fluid composition, implying that dissolved Na-Al silicates enhance Ti solubility in fluids. Rutile solubility also shows a non-linear decrease with increased pressure at a given composition. This pressure effect is diminished at high water content (~70%), where solubility values begin to converge for supercritical fluids. Overall, relatively high solubility (~1000s ppm) of rutile in the supercritical fluids give insight into the magnitude and mechanism for mobilizing Ti and other HFSEs in subduction zones and other high pressure metasomatic environments.

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Interactions of metal cations with mineral/water and organic-containing mineral/water interfaces studied by second harmonic generation

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The interactions of several metal ions – Ca(II), Sr(II), Ba(II), Zn(II) and Cd(II) – with model environmental interfaces are investigated using the Eisenthal $\chi^{(3)}$ method for second harmonic generation (SHG) [1]. SHG is used to evaluate adsorption at silica/water and carboxylic acid functionalized silica/water interfaces [2, 3]. Utilizing a dynamic flow system and the sensitivity of SHG to interfacial potential, we track metal binding in real time.

Results show that adsorption reaches steady-state conditions in a few minutes and is fully reversible. Adsorption isotherms are obtained for the metal ions at each interface and fit with the Gouy-Chapman and triple-layer models to obtain adsorption free energies ranging from –18 to –36 kJ/mol. Interfacial potentials, adsorbate number densities, interfacial charge densities are also obtained from the SHG experiments. For the alkaline earth metals, the adsorption free energies and adsorbate number densities for the silica/water interface increase with atomic number. The carboxylic acid functionalized interface displays lower adsorption free energies but higher maximum adsorbate number densities than the bare silica/water interface, which is consistent with acid deprotonation due to metal ion adsorption. Our SHG experiments provide valuable quantitative data that can be used in computational geochemistry for model validation.

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