Rutile solubility in albite-H₂O fluids at high P and T: Implications for HFSE mobility in subduction zones

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Ti and other HFSE are considered immobile in high-P fluids, but rutile is common in eclogite-facies veins. Rutile occuring with vein Na-Al-silicates motivates experiments on the role of NaAlSi₃O₈ (Ab) dissolved in H_2O on rutile solubility at 800-900°C and 0.5-1.5 GPa. At 800°C, 1 GPa, hydrothermal piston-cylinder (HPC) methods[1] indicate that rutile solubility rises linearly from 19 ± 7 ppm (1 σ) in pure H₂O to 275±10 ppm at 8.8 wt% Ab. Results give higher solubility than reported by [2] using hydrothermal diamond-anvil cells (HDAC). The discrepancy was examined by measuring rutile solubility in Ab-H₂O in HDAC by synchrotron XRF at ESRF, ID22. Ti solubility rose from 159±11 to 210±5 ppm with Ab increasing from ~2.5 to 8 wt % (P=0.7-1.1 GPa), in agreement with our HPC results but not [2]. The role of Ab is important. Rutile solubility in supercritical Ab-H₂O (HPC, 900°C, 1.5 GPa) increases from 85 ppm in pure H_2O to ~1500 ppm at the critical composition ($X_{Ab} \sim 0.09$); solubility rose further to ~5000 ppm at albite saturation ($X_{Ab}=0.52$). Independent evidence points to polymerization of Na-Al-Si species in solution at these conditions[3], which implies that the solubility increase with X_{Ab} is controlled by access to more energetically favorable sites in the polymers. As a preliminary test, we carried out Ti K-edge XANES at APS (GSECARS) on quenched hydrous rutile-saturated Ab glasses (X_{Ab} =0.29-0.50). Ti pre-edge at 4970.5±0.1 eV and 0.23±0.01 normalized intensity indicates coordination by oxygen that is ~95% octahedral and 5% tetrahedral[4], in contrast to IVcoordinated $Ti(OH)_4$ in H_2O . Evidently, the higher Ti solubility arises from the change in coordination afforded by dissolved Ab components. Ti, and by extension HFSE, are surprisingly soluble in realistic subduction-zone fluids.

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Changes in ion pairing across the H₂O liquid-liquid transition: Implications for planetary fluids

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Compression of H_2O at ambient temperature leads to a transition at 0.2-0.4 GPa from low-density water (LDW) to high-density water (HDW) [1,2] due to second coordination-shell collapse [3] or interstitial H_2O [4]. This transition may play an important role in fluid-rock interactions in cold, deep planetary settings, such as the interiors of the icy moons of Jupiter and Saturn. To explore potential effects, we studied pressure-dependent variation in contact ion-pairing in MgSO₄ solutions at 23°C by Raman spectroscopy using hydrothermal diamond-anvil cells. Solutions were 0.5, 1.75 and 2.0 *m*, as determined by freezing-point depression. Pressure (*P*) was determined from the frequency shifts of the 206 cm⁻¹ line of quartz [5].

Raman spectra in the region of the OH stretching mode of H₂O were collected for 2.0 m MgSO₄ and deconvoluted into 3 components. Frequencies of all peaks (1 atm positions: ~3280, \sim 3450, \sim 3580 cm⁻¹) decrease linearly with P. A well-resolved decrease in linear slope at 0.4 GPa is interpreted to record the liquid-liquid transition. A negative correlation between frequency and P is consistent with strengthening of hydrogen bonding with compression; the lower slope at >0.4 GPa implies less strengthening with P in HDW. Spectra in the v_1 - SO_4^{2-} region were deconvoluted into 2 components, $v_1^{CIP} \approx 993$ cm⁻¹ (contact ion pairs, CIP), and $v_1^* \approx 980$ cm⁻¹, which includes Raman-indistinguishable contributions from free SO4²⁻ ions and single and doubly solvent-separated ion pairs [6]. Values of v_1^* increase linearly with P, and also display a well-resolved slope break at ~0.4 GPa. The fraction of CIPs decreased with P to 0.4 GPa, but the trend reversed at >0.4GPa, signifying increasing CIPs with P in HDW. Salt reassociation with P in deep, cool environments – e.g., beneath the ocean floors of icy satellites - will enhance the progress of dissolution reactions relative to expected values based on LDW, and result in higher mineral solubility in HDW.

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