

Water solubility in octahedrally-coordinated silicates

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The incorporation of water in nominally anhydrous silicates is associated with mechanical weakening, lowered melting points, and can serve as a significant volatile reservoir in the planet. We have performed first-principles calculations addressing the substitution mechanism of H₂O in octahedrally coordinated silicates. The solubility of H₂O in these silicates results from combining static calculations with a statistical-mechanical model for the entropy of solution. We address the H₂O solubility in three silicates: stishovite (SiO₂), Mg- and Ca- perovskite, with H solution mechanisms constrained by charge balance in the structure. In the CMASH system, the only stable solution mechanisms are Al+H = Si or 2H=Ca or Mg.

The OH bond in octahedrally coordinated silicates varies between 1.02Å and 1.2Å, with only the OH bond in stishovite lengthening with increasing pressure. The incorporation of 3.1 mol% H₂O in each mineral accounts for minimal density decrease (<1%) and a 4.1%, 2.2% and 1.5% decrease of the bulk modulus (K₀) for stishovite, MgSiO₃ and CaSiO₃, respectively. The decrease of K₀ is comparable to the effects of vacancy-compensated aluminum incorporation.

In all cases, the solution enthalpy is positive, such that solubility of H₂O and Al₂O₃ is an entropy-driven process. In MgSiO₃, we find a total solubility of aluminum of about 15-20 mol % at 25 GPa and 2000 K. The solubility of water in stishovite exceeds 0.3 wt% H₂O at 25 GPa and 1500 K, increasing with increasing pressure and temperature. This accounts for the transport of water equivalent to the mass of the oceans over the age of the Earth. The solubility of H₂O in both Mg- and Ca-perovskite is significantly lower, with solubilities less than 100 ppm H₂O at pressures and temperatures equivalent to the top of the lower mantle, accounting for a mass of water equivalent to about 1% of the Earth's oceans.

Reference

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