

Effect of sodium salt on rutile solubility in aqueous fluids: Insights into titanium transport in subduction zones

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Most arc tholeiitic and calc-alkaline basalts display TiO_2 and Zr concentrations exceeding those that could be derived from partial melting of depleted mantle [1]. This peculiar geochemical signature indicates that small amounts of Ti and Zr are transported from a slab and added to the source mantle by aqueous fluids, hydrous melts, or supercritical fluids [1]. The titanium transport from the slab to the mantle wedge could be controlled by the solubility of TiO_2 in fluids. However, our knowledge of TiO_2 solubility and speciation in aqueous fluids with complicated compositions remains insufficient. We investigated the solubility of rutile (TiO_2) in $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$, $\text{NaHCO}_3\text{-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, and $\text{NaF-H}_2\text{O}$ fluids at high temperatures up to 1012 °C and approximate pressures up to 1.7 GPa by in-situ observations of the complete dissolution of rutile crystals in a hydrothermal diamond anvil cell (HDAC). We compared the rutile solubility in NaF solutions with previous data and additionally examined the enhancing effect of ligands such as OH^- , CO_3^{2-} , HCO_3^- , and SO_4^{2-} on the solubility.

In-situ observations of the dissolving rutile grain at a constant temperature of 800 °C for 13 minutes showed that the equilibration was achieved in a few minutes after the target temperature was attained at a heating rate of $\sim 30\text{ }^\circ\text{C min}^{-1}$. To avoid the kinetic delay of dissolution, we reduced the heating rate to $\sim 3\text{ }^\circ\text{C min}^{-1}$ when the heating temperature approached approximately 50 °C within the complete dissolution temperature. The addition of the sodium salts (Na_2CO_3 , NaHCO_3 , Na_2SO_4 , and NaF) to H_2O resulted in a remarkable increase in the solubility of rutile as compared to those in pure H_2O previously determined with the piston-cylinder method. The solubility of Ti in 1.0 *m* Na_2CO_3 solution increased by a factor of ~ 40 , while the NaF solutions showed a less enhancing effect than previously expected. Because the addition of those sodium salts to fluids is assumed to increase Na^+ ions and the anionic species and change pH in the fluids, the enhanced rutile solubility can be explained by the formation of Ti aqua hydroxo-complexes or Ti complexes with sodium or the anionic ligands. This dissolution mechanism contributes to interpreting the extraordinary high Ti mobility in alkaline carbonic fluids within exhumed high- to ultrahigh-pressure terranes in orogenic belts. In addition, the speciation of Ti might control whether the dissolved Ti is trapped by precipitation at the slab-mantle interfaces or transported by metasomatic fluids into the mantle wedge.

Reference: [1] Schmidt and Jagoutz (2017) *Geochem. Geophys. Geosyst.*, 18, 2817–2854.

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