LETTER

Very low solubility of rutile in H₂O at high pressure and temperature, and its implications for Ti mobility in subduction zones

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ABSTRACT

The solubility of rutile in H₂O has been measured at 1000–1100 °C, 1–2 GPa. The data indicate that solubility is very low over the investigated range, with a maximum of 4.7 millimol/kg H₂O at 1100 °C, 2 GPa. The data were fit with the equation log _m _Ti = 4.892 – 10470/T + 0.1923P, where _m _Ti is Ti molality, T is in Kelvins, and P in GPa. When compared to previous results, the new data indicate substantially lower solubility, opposite pressure dependence, and thermodynamic properties of the reaction rutile = TiO₂,aq that are now consistent with other oxide hydrolysis reactions. Calculations of Ti transport during mantle metasomatism by H₂O in subduction zone environments predict much lower Ti mobility at all conditions. These results offer strong support for models of Ti retention in eclogites during slab devolatilization, and require that examples of significant Ti mass transfer be explained by complexing agents in solution, most likely aluminosilicate complexes.

INTRODUCTION

Rutile (TiO₂), a common accessory mineral in eclogites and other high-pressure rocks (e.g., Philippot and Selverstone 1991; Van Baalen 1993; Rubatto and Hermann 2003), plays a central role in controlling the distribution high-field-strength elements (HFSE) in the Earth (Kamber and Collerson 2000; Rudnick et al. 2000). A key step in the terrestrial cycling of Ti (and other HFSE) occurs in subduction zones. There, fluid-rock interaction leads to retention of these elements in eclogitic rutile, producing a Ti-enriched reservoir that is subducted into the deep Earth, and complementary Ti-depleted arc magmas that are returned to the surface (Brenan et al. 1994; Foley et al. 1999; Rudnick et al. 2000). This model is based in part on the widely held view that the solubility of rutile is quite low in H₂O-rich subduction-zone fluid.

However, the assumption of low rutile solubility in H₂O is problematic. Experimental data suggest that the solubility of rutile in H₂O may actually be relatively high (Ayers and Watson 1993). For example, at 1000 °C, 1 GPa, the data of Ayers and Watson (1993) indicate that Ti concentration at rutile saturation is 0.2 molal, or >50 times more soluble than Al at corundum saturation (Tropper and Manning 2004), and similar in magnitude to the solubility of quartz in H₂O at mid-crustal metamorphic conditions (e.g., ~600 °C, 0.5 GPa; Manning 1994). Moreover, Ayers and Watson (1993) found that rutile solubility decreases strongly with increasing pressure (P) at constant temperature (T). This result differs from other simple minerals such as quartz, corundum, calcite, and anhydrite (Manning 1994; Caciagli and Manning 2003; Newton and Manning 2004; Tropper and Manning 2004). Such behavior would greatly enhance Ti transport by H₂O moving from slab to wedge, and lead to rutile precipitation near the arc-magma source region (Ayers and Watson 1993). Rutile formation in the mantle wedge reduces the retention of Ti in eclogites and is inconsistent with the high rutile solubility and low Ti contents of arc basalts (Ryerson and Watson 1987). Thus, whereas complexing with other ligands and dissolved silicate may also influence Ti mobility in subduction zones, the existing data on the solubility of rutile in H₂O pose a fundamental dilemma.

To address this problem, we measured the solubility of rutile in H₂O at 1000–1100 °C, 1–2 GPa. The new data indicate that rutile solubility is significantly lower than given by previous solubility measurements, and that the P dependence of solubility is opposite in sign. These results indicate that dilute aqueous solutions have an extremely low capacity to dissolve and transport Ti at high P and T, which supports models of HFSE retention in the slab during devolatilization.

EXPERIMENTAL METHODS

Two types of rutile were used as starting materials. Initial experiments were conducted with sintered rutile made by firing TiO₂ powder (Fisher Co.) at 1000 °C over three days, with repeated grinding. X-ray diffraction verified the absence of additional phases. In subsequent experiments, we used pure, translucent, clear-to-yellowish, flux-grown rutile crystals, with lattice constants of a = 4.5933 Å and c = 2.9592 Å.

In experiments using sintered rutile, the powder was pressed into a small pellet and placed in an inner Pt capsule, which was welded at one end, crimped at the other, and multiply punctured to facilitate H₂O penetration. The capsule and ~35 μL H₂O were then sealed in a welded Pt capsule with 3.5 mm OD, 0.20 mm wall thickness, and held at 115 °C for ≥3 h to check for leakage. In experiments on single crystals, a polished chip of flux-grown rutile was placed in a folded Pt-envelope, which was lightly crimped to allow H₂O entry. Loading procedures were otherwise identical. We initially omitted the inner capsule from experiments on single crystals, but occasional breakage and significant growth of new grains during runs indicated that the second capsule was needed to segregate the starting rutile from the main fluid reservoir and to minimize TiO₂ transport during experiment (see below).

All experiments were conducted in an end-loaded, piston-cylinder apparatus using 25.4 mm diameter furnace assemblies. Each capsule was placed horizontally in the furnace, packed in NaCl or BN, and covered with a piece of Pt foil to prevent puncture by the thermocouple. Experiments below the NaCl melting curve employed graphite-NaCl furnace assemblies (Bothlen 1984). Furnaces in