An experimental study of OH solubility in rutile at 500–900 °C, 0.5–2 GPa, and a range of oxygen fugacities

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ABSTRACT

The solubility of OH in pure synthetic rutile was experimentally constrained at 0.5–2.0 GPa and 500–900 °C, in equilibrium with four oxygen fugacity (f_{O_2}) buffering mineral assemblages: hematite-magnetite (HM), nickel-nickel oxide (NNO), cobalt-cobalt oxide (CCO), and iron-wüstite (IW). The hydroxyl concentration ([OH], in parts per million H_2O by weight) of equilibrated rutile crystals was characterized by FTIR spectroscopy. Measurements at 1 GPa at individual f_{O_2} buffers demonstrate that [OH] in rutile depends strongly on temperature: at HM, [OH] increases from 48 to 267 ppm as temperature rises from 500 to 900 °C, whereas at NNO, [OH] increases from 108 to 956 ppm over the same temperature range. The [OH] in rutile also increases strongly with decreasing f_{O_2} at any pressure and temperature, and exhibits a slight, linear, positive dependence on pressure at a given temperature and f_{O_2}. The observed systematic dependences on pressure, temperature, and f_{O_2} indicate that hydrogen substitutes into rutile as hydroxyl, (OH), via forward progress of the reaction $Ti^{4+}O_2 + \frac{1}{2}H_2O = Ti^{3+}O(OH) + \frac{1}{4}O_2$. Our measured [OH] values are significantly greater than those determined in previous studies on finer-grained, polycrystalline rutile, which likely suffered diffusive loss of H during quenching. This is supported by our observation of narrow, OH-depleted rims on otherwise high-OH run products, pointing to minor but important diffusive H loss from crystal rims during quenching. Fitting of isothermal variations in composition with f_{O_2} at 1 GPa and temperature indicates nearly ideal, multi-site mixing of the TiO_2-$TiOOH$ solid solution. A fit to the entire data set suggests standard volume, enthalpy, and entropy of the hydration reaction of, respectively, 1.90 ± 0.48 cm³/mol, 219.3 ± 1.3 kJ/mol, and 19.9 ± 1.4 J/(mol·K) (1σ uncertainty). These constraints form the basis for use of [OH] in rutile as a thermobarometer and oxybarometer in experimental and natural systems. The moderate to high [OH] in nominally anhydrous rutile at all investigated temperatures, pressures, and f_{O_2} values imply that Ti^{3+} may be higher than previously suspected in some terrestrial geologic settings.

Keywords: Rutile, experimental petrology, infrared spectroscopy, oxygen fugacity, hydroxyl, nominally anhydrous minerals