AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

High-pressure and high-temperature titanium solution mechanisms in silicate-saturated aqueous fluids and hydrous silicate melts

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ABSTRACT

In the system Na₂O-Al₂O₃-SiO₂-H₂O-TiO₂, the behavior of Ti-containing structural complexes has been determined in H₂O-saturated silicate melts and in coexisting silicate-saturated aqueous fluids as well as in silicate-rich supercritical fluids to 900 °C and 2225 MPa. Titanium speciation in aqueous fluids in the system TiO₂-H₂O was also characterized. All measurements were carried out in situ at the desired temperature and pressure using confocal microRaman and microFTIR spectroscopy. The experiments were carried out in an Ir-gasketed hydrothermal diamond-anvil cell (HDAC) with K-type thermocouples for temperature measurement and the Raman shift of 1130 cm⁻¹ synthetic diamond to monitor pressure.

In the system Na₂O-Al₂O₃-SiO₂-H₂O-TiO₂, four or five O atoms surround a central Ti⁴⁺ cation in melts, fluids, and supercritical fluids. In this environment, the titanium solubility mechanism is the same for melt, fluid, and single-phase liquid and can be described with the equation, 4Q₄(Na)₄H₂O + TiO₂ ↔ 4Q₄(HNa) + Q₇(Na). Subscripts denote the nature of central cation, superscripts, the number of bridging oxygens, and the symbol(s) in parentheses the type(s) of cation(s) that form bonds with nonbridging oxygen in the Q-species. The ΔH of this reaction is on the order of several tens of kJ/mol. Because of the structural similarity of Ti-complexes in hydrous silicate melts and silicate-rich aqueous fluid, the fluid/melt partition coefficients also resemble one another. The partition coefficient is between 0.1 and 1 and is positively correlated with temperature, pressure, and Al/(Al+Si) of the silicate melt or aqueous fluid. In the chemically simpler system TiO₂-H₂O, titanium in aqueous fluid occupies the central position in oxygen polyhedra surrounded by approximately six O atoms. Here, the enthalpy change for the solution reaction is between 50 and 60 kJ/mol absent pressure corrections for volume differences between TiO₂ in rutile and in aqueous solution. The Ti concentration in aqueous fluid is on the order of fractions to a few tens of parts per million. This solubility is orders of magnitude lower than in Ti solubility in silicate-saturated aqueous fluid in the system Na₂O-Al₂O₃-SiO₂-H₂O-TiO₂ at similar pressures and temperatures.

In natural environments such as high-grade metamorphic terranes and subduction zones, aqueous fluids are silicate-saturated. Such fluids are more efficient solvent refractory oxides, perhaps by 2–3 orders of magnitude for an oxide such as TiO₂ than inferred from their solubility in pure H₂O fluids.

Keywords: Aqueous fluid, titanium, partitioning, silicate melt, solution mechanism

INTRODUCTION

Characterization of transport mechanisms of TiO₂ in the Earth’s interior is important because Ti-minerals such as rutile can serve as sinks for trace elements often used to model magmatic and metamorphic processes (e.g., Ryerson and Watson 1987; Brenan et al. 1994; Rudnick et al. 2000; Zack et al. 2002). For example, TiO₂ may be dissolved in fluid derived from a dehydrated subducted slab and transported by such fluid into the overlying mantle wedge to a source region of partial melting. This process is dependent on the solubility and solution mechanisms of Ti⁺ in the fluid.

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In the simple TiO₂-H₂O system, Ti solubility in aqueous fluids is on the order of fractions to of tens of parts per million in the pressure and temperature regime corresponding to the Earth’s upper mantle (Audétat and Keppler 2005; Antignano and Manning 2008). However, this solubility is not only temperature and pressure dependent, but is obviously also affected by other solutes (Audétat and Keppler 2005; Antignano and Manning 2008). Systematic studies of the relationships between additional solutes and Ti solubility in aqueous fluids, however, have not been carried out. Experimental studies of solution mechanism(s) of Ti-bearing components in aqueous fluids, which are needed to model fluid-mediated Ti-transport in the Earth’s interior, are even less comprehensive.

The scarcity of experimental data on solubility and solution mechanisms (structure) of Ti-bearing components in aqueous fluids at high pressure and temperature is, in part, because oxide contents of aqueous fluids are altered upon their return to ambi-