

**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  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2$ , the behavior of Ti-containing structural complexes has been determined in  $\text{H}_2\text{O}$ -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  $\text{TiO}_2-\text{H}_2\text{O}$  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  $^{13}\text{C}$  synthetic diamond to monitor pressure.

In the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2$ , four or five O atoms surround a central  $\text{Ti}^{4+}$  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,  $4\text{Q}_{\text{Si}}^1(\text{Na})4\text{H}_2\text{O} + \text{TiO}_2 \leftrightarrow 4\text{Q}_{\text{Si}}^0(\text{HNa}) + \text{Q}_{\text{Ti}}^0(\text{Na})$ . 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  $\Delta H$  of this reaction is on the order 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  $\text{Al}/(\text{Al}+\text{Si})$  of the silicate melt or aqueous fluid. In the chemically simpler system  $\text{TiO}_2-\text{H}_2\text{O}$ , 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  $\text{TiO}_2$  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  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2$  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  $\text{TiO}_2$ , than inferred from their solubility in pure  $\text{H}_2\text{O}$  fluids.

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