



**Experiment title: Rutile solubility in aqueous solutions at high temperature and pressure**

**Experiment number:**  
EC 52

**Beamline:**  
ID22

**Date of experiment:**  
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**Date of report:**  
27.8.06

**Shifts:**  
12

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*Received at ESRF:*

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**Report:**

Silicate melts and aqueous fluids play a key role in the evolution of the Earth's crust and mantle. Melt and fluid generation and subsequent ascent are major geologic processes in the crust and in subduction zones, leading to large-scale mass and energy transfer in Earth's interior and abundant volcanic activities on the surface. Knowledge of the physical and chemical properties of these systems is essential for a better understanding and modeling of these processes. Elements like Ti are important tracers of the sources of magmas that erupt at the Earth's surface. A key step in the terrestrial cycling of Ti (and other HFSE) occurs in subduction zones. Data on the solubility of rutile in H<sub>2</sub>O at high pressure and temperature, however, are controversial (Ayers and Watson 1993, Tropper and Manning, 2005; Audetat and Keppler, 2005).

We used micro-XRF spectroscopy at high temperature and pressure using a hydrothermal diamond-anvil cell (HDAC) to determine the solubility of rutile in aqueous fluids at in-situ conditions. The XRF spectra were collected using the Si (111) double-crystal monochromator at an excitation energy of 10 keV. The beam was focussed at the fluid in the sample chamber of the HDAC using the KB-mirror optics. The XRF spectra were acquired at 90° to the incoming beam using a Si(Li) 13-element detector. Due to the HDAC geometry, only 4 elements detected a signal from the sample volume. As expected, spectra recorded by the central detector element showed the best signal-to-background ratio. The intensity of the Ti fluorescence signal collected by the central element was already sufficient to perform these experiments. Addition of the signal from the other 3 elements did not improve the signal quality significantly, probably due to the lower Ti K $\alpha$  fluorescence signal-to-background ratio in these spectra. The setup was calibrated by measuring Ti standard solutions loaded into the sample chamber of the HDAC. The lower limit of detection for Ti was about 3 ppm or 5E-05 mol/kg. The maximum temperatures and pressures of the experiments were 800°C and ca. 1.3 GPa.

Several rutile dissolution experiments were performed for aqueous fluids containing a NaAlSi<sub>3</sub>O<sub>8</sub> (albite) or Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> (sodium-trisilicate) component. A rutile grain and the silicate component as a glass chip of known volume were added at the start of an experiment, and the desired fluid composition was attained by adjusting the water/glass ratio in the sample chamber. The silicate glass dissolved completely in the fluid at high temperature and pressure. The Ti concentrations in the fluid obtained at 800°C and various fluid compositions are shown in Fig. 1. The data for fluids containing albite component do not display a strong

dependence of the Ti content on the fluid composition. The Ti contents are consistent with results from weight-loss experiments (Antignano et al. 2005) and much higher than solubilities determined for pure water (Audétat & Keppler 2005, Tropper & Manning 2005). Solubilities for the sodium-tri-silicate bearing fluids are even higher and display a strong dependence on the amount of dissolved silicate component.

Although equilibration kinetics were considered to be fast for these experiments (Audétat & Keppler 2005) we observed an increase of the Ti concentration in  $\text{H}_2\text{O}+\text{NaAlSi}_3\text{O}_8$  fluids with time for repeated analyses at a given temperature (Fig. 2). This time dependence was not noticed until all the data were processed after the beamtime session. For these results, even the last recorded Ti molalities might not represent the equilibrium concentrations. They also imply that the data reported by Audétat & Keppler (2005) might strongly underestimate equilibrium concentrations due to undetected effects of the dissolution kinetics.

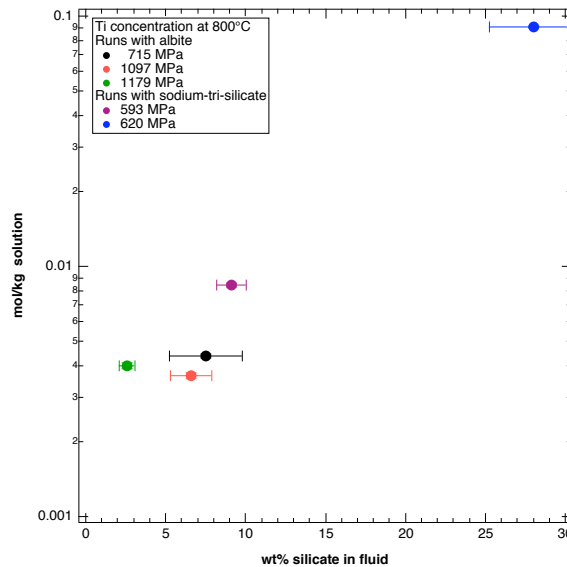


Figure 1: Ti concentrations at 800°C in an aqueous fluid during dissolution of rutile as a function of the concentration of the dissolved silicate component (at pressures indicated).

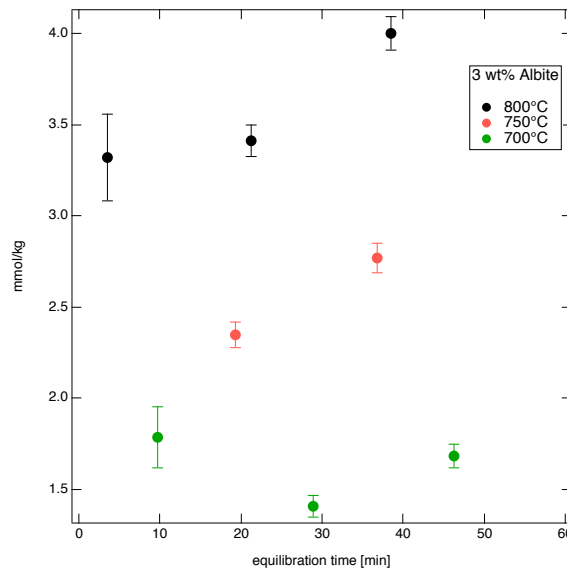


Figure 2: Temporal evolution of the Ti molality in an aqueous fluid containing 3 wt% of albite component during dissolution of rutile at 700, 750, and 800 °C.

### References:

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 Ayers JC, Watson EB (1993) *Contributions to Mineralogy and Petrology*, 114, 321-330.  
 Tropper P, Manning CE (2005) *American Mineralogist*, 90, 502-505.

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