Ti partitioning in quartz coexisting with rutile to evaluate the metamorphic *P–T* paths of ultrahigh-temperature granulites

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The Ti-in-quartz thermometers (Wark & Watson 2006; Kawasaki & Osanai 2008) were based on the thermodynamic property of quartz that the solubility of TiO_2 increases with temperature. We propose the new thermobarometer for ultrahigh-temperature granulites calibrated from the experimentally reversed data. We employed the three types starting materials: (1) mineral mixture of rutile and quartz saturated in TiO_2; (2) glass; and: (3) mixture of rutile and TiO_2-free silica mineral.
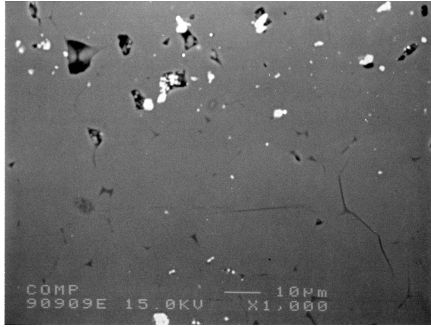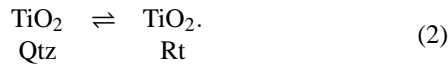

Fig. 1   Back scattered electron image (BSEI) of a run product (no. 090909E) synthesized quartz (dark) and rutile (bright) from glass at 15 kbar and 800 °C for 3764 hours in the Pt capsule. White bar, 10 μm.

The Ti would substitute for the tetrahedral Si in quartz:

$$\begin{array}{ccc} SiO_2 & \rightleftharpoons & SiO_2 \\ Qtz & & Rt \end{array} \qquad (1)$$

and

$$\begin{array}{ccc} TiO_2 & \rightleftharpoons & TiO_2. \\ Qtz & & Rt \end{array} \qquad (2)$$

We apply the infinite dilute solution model (Henry's law) to TiO_2 component in quartz in equilibrium with rutile. The TiO_2 content of quartz, $X_{TiO_2}^{Qtz}$, is given by the following Arrhenius-type equation:

$$\ln X_{TiO_2}^{Qtz} = (\Delta H_{TiO_2}^{o} + P\Delta V_{TiO_2}^{o})/RT$$
$$- (\Delta S_{TiO_2}^{o}/R + \ln k_{TiO_2}^{Qtz}), \qquad (3)$$

where $\Delta H_{TiO_2}^{o}$, $\Delta S_{TiO_2}^{o}$, $\Delta V_{TiO_2}^{o}$, $\ln k_{TiO_2}^{Qtz}$, P, T and R are changes of enthalpy, entropy and volume at the standard state of interest, the Henry's coefficient, pressure, temperature and gas constant, respectively (Kawasaki & Osanai 2008)

We conducted the reversal experiments under the pressures from atmospheric pressure to 2 GPa and temperatures from 800 to 1500 °C using the electric furnace and piston-cylinder apparatus at Ehime University. Durations were $4 - 3764$ hours. Temperature was calibrated by the melting point of gold at 1064.18 °C and was measured by the use of a Pt/Pt-13%Rh thermocouple placed at the top of the sample space and at the outer side in contact with the reaction tube in the furnace. The run temperature was controlled by the measurement of the outer-side temperature of the reaction tube, and was kept constant within ± 1 °C of the nominal values. Pressures in the piston-cylinder apparatus were calibrated by the phase transformation of Bi I–II at room temperature (2.55 GPa; Hall, 1971) and by the quartz-coesite transition at 1000 °C (2.94 GPa; Bohlen & Boettcher, 1982).
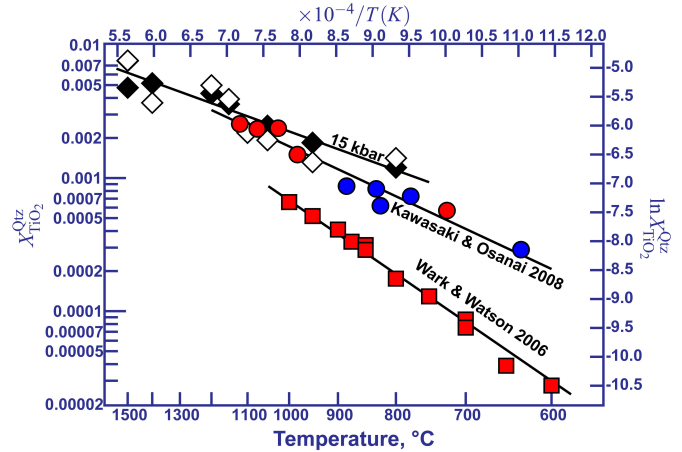

Fig. 2   Experimental results at 15 kbar and previous works (Wark & Watson 2006; Kawasaki & Osanai 2008).

One of the run products are shown in Fig. 1. Experimental results are compiled in Fig. 2 comparing the previous works (Wark & Watson 2006; Kawasaki & Osanai 2008). From the present experiments we obtain the pressure-temperature dependence of the solubility of TiO_2 in quartz:

$$RT \ln X_{TiO_2}^{Qtz} = -8504(733) - 4.975(480)T$$
$$- 39.7(167)P \qquad (4)$$

where $X_{TiO_2}^{Qtz}$ is the mole fraction of TiO_2, or the number of Ti atoms per formula unit based on a two-oxygen atom normalization. Pressure and temperature are given in kbar and Kelvin. This equation is very powerful to evaluate the metamorphic temperatures for ultrahigh-temperature granulites. The metamorphic temperatures evaluated by the present thermometer are in good agreement with those obtained by the empirical thermometer. The previous Ti-in-quartz thermometer gives about 200 °C higher temperatures than those estimated by the present and empirical thermometers, potentially because of underestimates and erroneous thermodynamic treatments of Ti solubility in quartz in the previous calibration.

References

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