TiO_2 solubility in garnet coexisting with orthopyroxene, quartz and rutile: Ti-in-garnet thermometer for ultrahigh-temperature granulites

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It has been widely recognised that needle rutile pricipitates from originally Ti-rich garnet during decompression or cooling retrograde metamorphism (Ague Eckert 2012; Hwang et al 2007; Proyer et al 2013; van Roermund et al 2000). We can evaluate metamorphic *P–T* conditions and/or paths by analysing the TiO_2 content of garnet. We present here a Ti-in-garnet thermometer for ultrahigh-temperature granulites calibrated from experimentally reversed data of the TiO_2 solubility in garnet coexisting with orthopyroxene, rutile and quartz at pressures 7–23 kbar and temperatures 850–1300 °C.

Although the previous study (Kawasaki Motoyoshi 2007) suggested that the Ti would substitute for the tetrahedral Si, we confirm that the combined substitution $Ti^{VI}Al^{IV} \rightleftharpoons Al^{VI}Si^{IV}$, quasi-chemically equivalent to Ti ⇌ Si from the viewpoint of the bulk composition of garnet, is predominant rather than the coupled substitutions $M^{VI}Ti^{VI} \rightleftharpoons Al^{VI}Al^{VI}$ (M: Ca, Mg, Fe) on the octahedral site. This indicates that the Ti occupation is restricted only octahedral site in garnet. The chemical formula of the Ca- and Ti-poor ultrahigh-temperature garnet can be expressed as $M_3Al_2Si_{3-x}Ti_xO_{12}$, which indicates that the relation of Si + Ti = 3 is never the evidence of the Si ⇌ Ti substitution on the tetrahedral site.

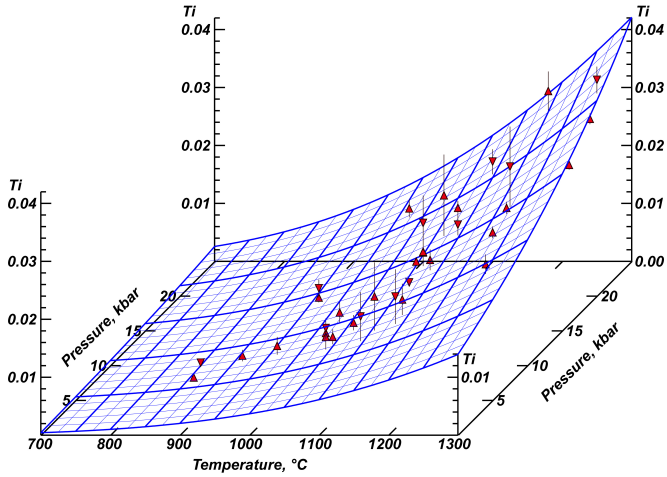

Figure 1. N_{Ti} (O = 12)–*P*–*T* diagram. ▲, Ti-increase runs. ▼, Ti-decrease runs. Vertical bars, $\sigma_{N_{Ti}}$.

The TiO_2 solubility in garnet coexisting with orthopyroxene, quartz and rutile is expressed by

$$\underset{\text{Grt}}{M_3Al_2Si_3O_{12}} + \underset{\text{Rt}}{TiO_2} \rightleftharpoons \underset{\text{Grt}}{M_3[TiAl]\{Si_2Al\}O_{12}} + \underset{\text{Qtz}}{SiO_2} \quad (1)$$

$$\underset{\text{Opx}}{[MAl]\{AlSi\}O_6} + \underset{\text{Rt}}{TiO_2} \rightleftharpoons \underset{\text{Opx}}{[MTi]\{Al_2\}O_6} + \underset{\text{Qtz}}{SiO_2} \quad (2)$$

$$\underset{\text{Opx solid solution}}{[M_2]\{Si_2\}O_6 + [MAl]\{AlSi\}O_6} \rightleftharpoons \underset{\text{Grt}}{M_3Al_2Si_3O_{12}} \quad (3)$$

Solubilities of TiO_2 in both orthopyroxene and quartz are out of this study and will be published elsewhere.

The TiO_2 content of garnet, expressed by the chemical reaction (1), increases with temperature and pressure (Fig. 1), though the pressure dependence is small and is given by the following equation:

$$-17777 + 0.964T + 139.5P = T \ln \frac{N_{Ti}^2}{(2 - N_{Ti})(3 - N_{Ti})}, \quad (4)$$

where N_{Ti} is the number of Ti atoms (O=12). Temperature *T* and pressure *P* are given in Kelvin and kbar, respectively. If we ignore the pressure-dependence, Ti-in-garnet is formulated as:

$$-19413 + 3.589T = T \ln \frac{N_{Ti}^2}{(2 - N_{Ti})(3 - N_{Ti})}. \quad (5)$$

This equation is available to compare the retrograde metamorphic temperatures of granulites if the pressure variation is limited to ±3 kbar, although the obtained temperatures have slightly large standard errors.

The present thermometers are useful to estimate retrograde metamorphic conditions. We apply those to ultrahigh-temperature garnets within the orthopyroxene granulite from McIntyre Island (Kawasaki et al 2002), Napier Complex and those within the leucocratic garnet–sillimanite gneisses from Rundvågshetta (Kawasaki et al 2011) and Skallevikshalsen (Kawasaki et al 2013), Lützow-Holm Complex, yielding retrograde metamorphic temperatures of 910 °C at 11.2 kbar, 844 °C at 6.1 kbar and 852 °C at 7.3 kbar, respectively.

References

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