Solubility of TiO$_2$ in garnet and orthopyroxene: Ti thermometer for ultrahigh-temperature granulites

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Abstract We report the TiO$_2$ solubility in garnet and orthopyroxene coexisting with rutile calibrated from experimental data at pressures 7–20 kbar and temperatures 850–1300°C in two Antarctic granulite systems. The Ti would substitute for the tetrahedral Si, whereas we could not find positive evidence of the coupled substitution of M-Ti (M is Mg or Fe) for Al-Al in octahedral sites as well as the interstitial substitution of □-Ti (□ is a vacancy) for M-M in triangular-dodecahedral sites of garnet at ultrahigh-temperature (UHT) metamorphic conditions. The TiO$_2$ content of garnet increases with temperature and decreases with pressure. In orthopyroxene Ti substitutes for atoms in the tetrahedral and octahedral sites. The Ti content of orthopyroxene increases with temperature and increases with pressure. Titanium solubility in garnet and orthopyroxene is not so sensitive to pressure change as compared with temperature dependence given by following empirical equations:

$$\ln \left(X_{\mathrm{Ti}}^{\mathrm{Grt,IV}}/X_{\mathrm{Si}}^{\mathrm{Grt,IV}} \right) = -15366/T + 5.962 \text{ and } \ln \left(X_{\mathrm{Ti}}^{\mathrm{Opx,IV}}/X_{\mathrm{Si}}^{\mathrm{Opx,IV}} \right) = -11367/T + 3.107,$$

where X is the mole fraction of Ti or Si on the tetrahedral sites and temperature is given in Kelvin.

Introduction

Exsolution lamellae of rutile are often observed in the porphyroblastic garnet, orthopyroxene, sapphirine, osumilite, K-feldspar (mesoperthite) and quartz of the UHT granulites from Napier complex, East Antarctica (Kawasaki and Motoyoshi, 2000; Osanai et al., 2001; Osanai and Yoshimura, 2002) and also found in garnet and clinopyroxene of the ultrahigh-pressure (UHP) eclogites and peridotites as well as ilmenite rods in olivine (Dobrzhinetskaya et al., 1996; Song et al., 2004). Some authors have proposed the hypothesis that TiO$_2$ dissolves into silicates at peak metamorphism and then rutile precipitates from the TiO$_2$-saturated hosts during the subsequent retrograde decompression metamorphism (Dobrzhinetskaya et al., 1996; Green et al., 1997; Song et al., 2004) or cooling metamorphism (Wark and Watson, 2006; Kawasaki and Osanai, 2007).

In this paper we present the new experimental data at 15–20 kbar and 1200–1300°C in the SiO$_2$–TiO$_2$–Al$_2$O$_3$ doped McIntyre granulite (Kawasaki and Motoyoshi, 2000) system, and compile the previously published data on the high-pressure and high-temperature phase relations of the Runvågshetta granulite (Kawasaki and Motoyoshi, 2005) at pressures 7–15 kbar and temperatures 850–1150°C to determine the pressure-temperature dependence of the TiO$_2$ solubility and to develop a Ti-geothermobarometer.

Experimental procedures

Starting materials

The starting material, which is highly saturated in TiO$_2$ (MCTQ), was prepared by adding 8 wt % Al$_2$O$_3$ + 16 wt% TiO$_2$ + 8 wt % SiO$_2$ to McIntyre granulite (Kawasaki and Motoyoshi, 2000; Kawasaki et al., 2002). The mixture was fused at 10.5 kbar and 1700°C for 2 minutes in a graphite capsule using the piston-cylinder apparatus. Chemical compositions of SiO$_2$–TiO$_2$–Al$_2$O$_3$ doped McIntyre granulite (MCTQ) and the Runvågshetta granulite (RVH) are given in Table 1.

Table 1 Chemical compositions of the SiO$_2$–TiO$_2$–Al$_2$O$_3$ doped McIntyre granulite (MCTQ) and the Runvågshetta granulite (RVH).

	MCTQ*	RVH
SiO$_2$	44.23	44.56
TiO$_2$	16.76	1.86
Al$_2$O$_3$	12.18	16.89
Cr$_2$O$_3$	0.01	0.06
FeO[†]	8.72	11.91
MnO	0.04	0.89
MgO	15.54	18.74
NiO	0.02	0.03
CaO	0.06	0.40
Na$_2$O	0.11	1.36
K$_2$O	0.04	3.34
Total	97.71	100.04
mg	0.761	0.764

*Fused at 10.5 kbar and 1700°C for 2 minutes in a graphite capsule.
[†]Total Fe as FeO.

Experimental techniques

High-pressure experiments were carried out using a 16.0 mm piston-cylinder apparatus at Ehime Univer-

Table 2. Representative electron microanalyses of run products.

Run No.	050607D		050726C		051205B	
P, kbar	15		20		17.5	
T, °C	1200		1300		1200	
Duration, hrs	266		238		106	
Phase	Opx	Grt	Opx	Grt	Opx	Grt
SiO_2	48.001	40.322	50.624	43.019	49.282	41.738
TiO_2	1.587	1.342	1.539	1.253	1.289	1.603
Al_2O_3	12.643	23.504	10.485	25.027	12.118	23.949
Cr_2O_3	0.030	0.010	n.d.	n.d.	0.026	n.d.
FeO	11.502	12.828	7.384	5.401	8.026	9.837
MnO	0.041	0.073	0.035	0.085	0.065	0.088
MgO	25.975	20.309	29.612	26.318	28.450	22.807
NiO	0.023	0.024	n.d.	0.012	n.d.	0.006
CaO	0.031	0.174	0.048	0.147	0.056	0.214
Na_2O	0.101	0.024	0.185	0.043	0.112	0.013
K_2O	0.016	0.006	0.011	0.008	0.019	0.004
Total	99.951	98.616	99.921	101.31	99.443	100.259
Number of cations for N oxygens						
N	6	12	6	12	6	12
Si	1.7010	2.9232	1.7589	2.9297	1.7260	2.9328
Ti	0.0423	0.0732	0.0402	0.0642	0.0339	0.0847
Al	0.5280	2.0083	0.4294	2.0088	0.5002	1.9834
Cr	0.0008	0.0006	—	—	0.0007	—
Fe	0.3409	0.7777	0.2146	0.3076	0.2351	0.5781
Mn	0.0012	0.0045	0.001	0.0049	0.0019	0.0052
Mg	1.3722	2.1949	1.5338	2.672	1.4854	2.3891
Ni	0.0007	0.0014	—	0.0007	—	0.0003
Ca	0.0012	0.0135	0.0018	0.0107	0.0021	0.0161
Na	0.0069	0.0034	0.0125	0.0057	0.0076	0.0018
K	0.0007	0.0006	0.0005	0.0007	0.0008	0.0004
Total	3.9961	8.0012	3.9926	8.0049	3.9938	7.9919

sity. Run conditions were pressures 15, 17.5 and 20 kbar and temperatures 1200 and 1300°C. Run durations were 106–266 hours. We used the $Ag_{70}Pd_{30}$ capsule and Mo/Pt double capsule for the sample container, two edges of which were sealed by welding. The sample container was put into a boron nitride rod, which was placed between two MgO rods in a graphite heater within a talc + Pyrex glass assembly. The hot piston-in technique was applied for all runs.

Temperatures were monitored with $Pt/Pt_{87}Rh_{13}$ thermocouple without any correction for the pressure effect on emf. During each experiment the temperature and pressure were kept constant within ± 5°C and ± 0.1 kbar of the nominal values. At the end of the run the sample was quenched by cutting off the electric power. The thermocouple reading dropped below 50°C in a few seconds and to the ambient temperature in several tens of seconds. The pressure was then released to an atmospheric pressure and the run product was recovered.

Run products

All run products were mounted in epoxy resin and polished for examination by microprobe analysis. An example of run products is shown in Figure 1. Quartz and rutile are several μms in grain size and found between grains of euhedral garnet and subhedral ortho-

pyroxene. Garnet always contains fine crystals of quartz and rare rutile. Orthopyroxene has no inclusions.

Chemical analyses

Chemical analyses of run products were made using an electron microprobe analyser JEOL JXA-8800 Superprobe at Ehime University. Standards of known composition included synthetic quartz for Si, rutile for Ti, corundum for Al, eskolaite for Cr, hematite for Fe, manganese oxide for Mn, nickel oxide for Ni, periclase for Mg, wollastonite for Ca, natural albite for Na and natural orthoclase for K. The instrumental conditions were: the accelerating voltage, 15 KV; electron beam current, 0.01μA; beam diameter, 1–2 μm estimated from the size of contamination spots by excitation during analysis. First-order K_α wavelengths were used for all oxides and data reduction used the ZAF correction procedure. Analysis of Ti was made by 30-sec measure-
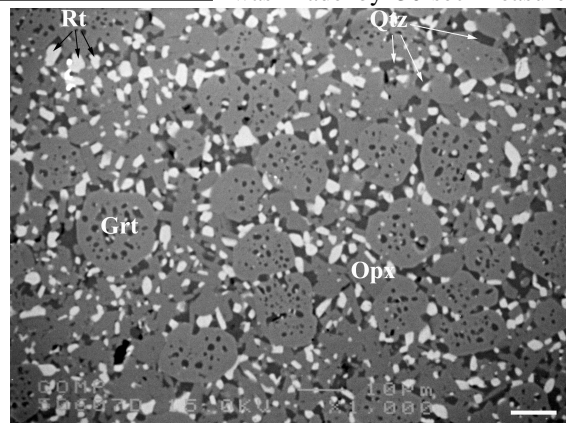

Figure 1. Back scattered electron image (BSEI) of a run product (no. 050607D) synthesized at 15 kbar and 1200°C for 266 hours in the Mo/Pt double capsule. Garnet (Grt) includes quartz (Qtz) and rutile (Rt). Orthopyroxene (Opx) is found as subhedral crystal without inclusions. White bar indicates 10 μm.

ments and the others were made by 10-sec measurements. The background correction was employed for each spot. Detection limit of Ti was about 200 ppm.

Experimental results
Stoichiometric constraints

It is clear that Ti is soluble in garnet and or-

thopyroxene. The Ti-bearing components are given by the following chemical formulae: $M_3^{VIII}Al_2^{VI}Ti_3^{IV}O_{12}$, $M_3^{VIII}M^{VI}Ti^{VI}Si_3^{IV}O_{12}$ and $\square^{VIII}M^{VIII}Ti^{VIII}Al_2^{VI}Si_3^{IV}O_{12}$ for garnet, and $M_2^{VI}Ti^{IV}O_6$ and $\square^{VI}Ti^{VI}Si_2^{IV}O_6$ for orthopyroxene. Here M = Fe, Mg;
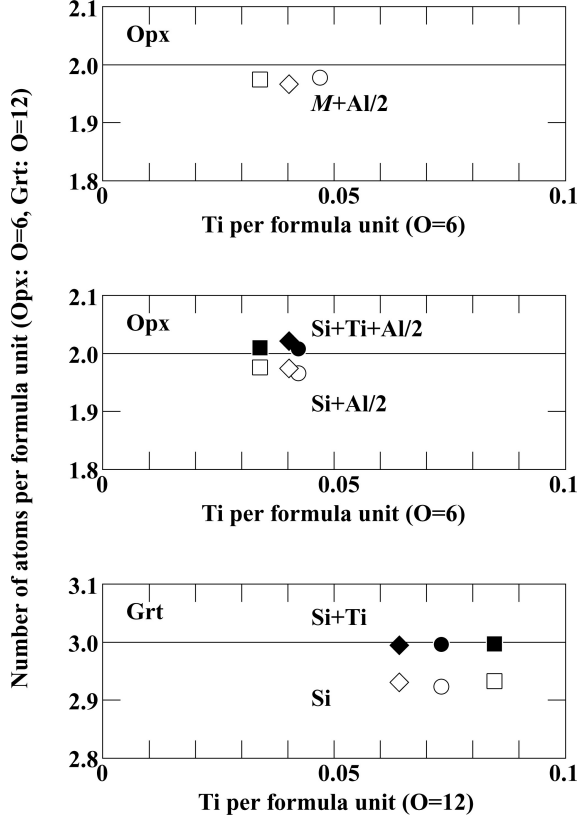

Figure 2. Plots of number of atoms in the tetra-hedral and octahedral sites vs Ti in garnet and orthopyroxene in the MCTQ system. Circles: 15 kbar/1200°C; squares: 17.5 kbar/1200°C; diamonds: 20 kbar/1300°C.

and $\square$ is the vacancy in garnet and orthopyroxene. If the Ti occupies the octahedral site, the following numeric relations should be satisfied among numbers of elements (N):

$$N_{Si}^{Grt} + N_{Ti}^{Grt} > 3, \quad (1)$$

$$N_{Al}^{Opx}/2 + N_{Si}^{Opx} + N_{Ti}^{Opx} > 2, \quad (2)$$

$$N_{Mg}^{Grt} + N_{Fe}^{Grt} > 3, \quad (3)$$

$$N_{Al}^{Opx}/2 + N_{Mg}^{Opx} + N_{Fe}^{Opx} < 2. \quad (4)$$

In Figure 2 we present these relations obtained from our present experiments in the MCTQ system. Zhang et al. (2003) reported the Ti solubility increases with pressure as $M_3^{VIII}M^{VI}Ti^{VI}Si_3^{IV}O_{12}$ accompanying increase of Si as $M_3^{VIII}M^{VI}Si^{VI}Si_3^{IV}O_{12}$ under the ultrahigh-pressure conditions (> 5 GPa). As is seen in Figure 2, the Ti in garnet would substitute

for the tetrahedral Si without substitution of the octahedral Al for pressures of the ultrahigh-temperature granulites. In orthopyroxene the Ti could occupy the tetrahedral and octahedral sites.

Figure 3 shows the experimental data of the Ti-solubility obtained from this study (MCTQ) and the previous study (RVH: Kawasaki and Motoyoshi, 2005), indicating that Ti in garnet and orthopyroxene increases with temperature. The Ti content would decrease with pressure in garnet and increase with pressure in orthopyroxene.

Thermodynamics of Ti-solubility

From the stoichiometric constraints, Ti partitioning is expressed by the following chemical reactions:

$$\underset{\text{Opx}}{M_2Si_2O_6} + \underset{\text{Rt}}{2TiO_2} \rightleftharpoons \underset{\text{Opx}}{M_2Ti_2O_6} + \underset{\text{Qtz}}{2SiO_2}, \quad (5)$$

$$\underset{\text{Grt}}{M_3Al_2Si_3O_{12}} + \underset{\text{Rt}}{3TiO_2} \rightleftharpoons \underset{\text{Grt}}{M_3Al_2Ti_3O_{12}} + \underset{\text{Qtz}}{3SiO_2}, \quad (6)$$

$$\underset{\text{Opx}}{M_2Ti_2O_6} + \underset{\text{Qtz}}{6SiO_2} \rightleftharpoons \underset{\text{Opx}}{2\square TiSi_2O_6} + \underset{\text{Opx}}{M_2Si_2O_6}. \quad (7)$$
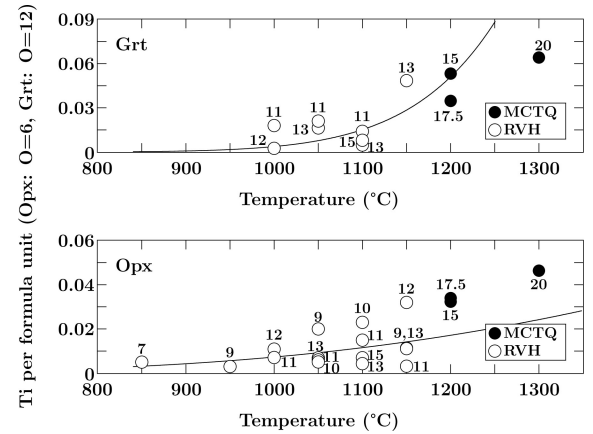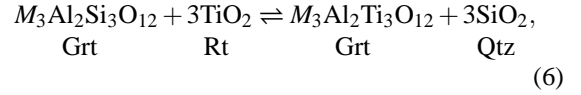

Figure 3. Solubility of Ti in garnet and orthopyroxene coexisting with rutile. Curves indicates the calculated solubility of Ti at mean pressures 15 kbar for garnet and 12 kbar for orthopyroxene by the following empirical equations:

$$\ln X_{Ti}^{Opx} = (-8810 + 1.369T + 67.1P)/T \text{ and}$$

$$\ln X_{Ti}^{Grt} = (-21310 + 13.664T - 231.3P)/T,$$

where X_{Ti}^{Grt} and X_{Ti}^{Opx} are the number of Ti atoms per formula unit narmalized by 12 and 6 oxygen atoms, respectively. Numerals indicate run pressures (kbar).

The thermodynamic treatment of the substitution of Ti on the octahedral sites is not established for the present. The Ti partitioning on the tetrahedral sites

given by the reactions (5) and (6) are formulated by

$$-\Delta G_5 = RT \ln \frac{a_{M_2Ti_2O_6}^{Opx}(a_{SiO_2}^{Qtz})^2}{a_{M_2Si_2O_6}^{Opx}(a_{TiO_2}^{Rt})^2}$$

$$\simeq 2RT \ln \frac{X_{Ti}^{Opx,IV}}{X_{Si}^{Opx,IV}} \qquad (8)$$

$$-\Delta G_6 = RT \ln \frac{a_{M_3Al_2Ti_3O_{12}}^{Grt}(a_{SiO_2}^{Qtz})^3}{a_{M_3Al_2Si_3O_{12}}^{Grt}(a_{TiO_2}^{Rt})^3}$$

$$\simeq 3RT \ln \frac{X_{Ti}^{Grt,IV}}{X_{Si}^{Grt,IV}}, \qquad (9)$$

where a and X are the activity and mole fraction, respectively. Here we assume $a_{TiO_2}^{Rt} \simeq a_{SiO_2}^{Qtz} \simeq 1$ (Kawasaki and Osanai, 2007).
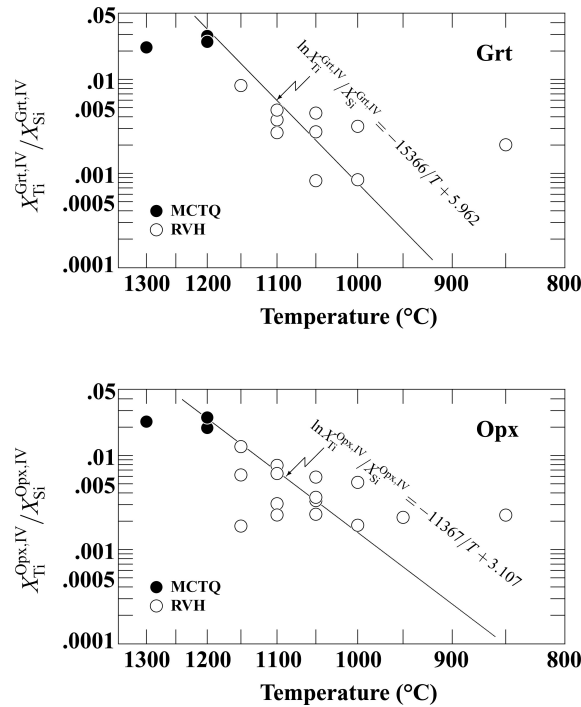

Figure 4. Temperature dependence of Ti in garnet and orthopyroxene. Curves indicates the calculated solubility of Ti, ignoring the pressure dependence.

Discussions and conclusions

Temperature dependence of the Ti-solubility is calculated from the experimental data given in Figure 3 under Equations (8) and (9):

$$\ln\left(X_{Ti}^{Grt,IV}/X_{Si}^{Grt,IV}\right) = -15366/T + 5.962 \qquad (10)$$

and

$$\ln\left(X_{Ti}^{Opx,IV}/X_{Si}^{Opx,IV}\right) = -11367/T + 3.107. \qquad (11)$$

Results are illustrated in Figure 4. The Ti content in garnet is more dependent on temperature than that in orthopyroxene. As is clear, Ti content of garnet and

orthopyroxene increases with temperature. A good fit implies the present thermodynamic model is available to describe the Ti solubility in garnet and orthopyroxene.

Using the Ti thermometers given by Equations (10) and (11), we obtain the peak and retrograde metamorphic temperatures of McIntyre granulite as 1079 and 798°C, respectively, and the retrograde temperature of Rundvågshetta granulite as 884–921°C. These data are consistent with our previous estimates. We conclude the Ti-solubility in garnet and orthopyroxene is a useful geothermometer to evaluate the metamorphic temperature of Antarctic granulites with high precision.

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