Ti-in-garnet thermometer for ultrahigh-temperature granulites

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We propose a Ti-in-garnet thermometer for ultrahigh-temperature granulites calibrated from experimentally reversed data of the TiO2 solubility in garnet coexisting with orthopyroxene, rutile and quartz at pressures 7–23 kbar and temperatures 850–1300 °C. We confirm that the combined substitution TiVIAlIV!AlVISiIV, quasi-chemically equivalent to Ti!Si, is predominant rather than the coupled substitution MVITiVI!AlVIAlVI (M: Ca, Mg, Fe). The chemical formula of Ca- and Ti-poor garnet under ultrahigh-temperature metamorphic conditions can be expressed as M3Al2Si3−xTexO12, which indicates that the relation NSi + NTi = 3 is not an evidence of TiIV!SiIV.

The TiO2 content of garnet increases with temperature and pressure, though the pressure dependence is small, as is given by the following equation:

\[17777 + 0.964T + 139.5P = T \ln \frac{N^2_{\text{Si}}}{N_{\text{Al}}N_{\text{Si}}} ,\]

where \(N\) is the number of cation per formula unit based on a 12-oxygen atom normalisation. Temperature \(T\) and pressure \(P\) are given in Kelvin and kbar, respectively.

The present thermometer is useful to estimate metamorphic conditions. This new thermometer is applied to natural garnet in geologically and petrologically well-characterised Antarctic ultrahigh-temperature granulites. The resultant pressure and temperature estimates are consistent with those reported from granulites of these areas.

Keywords: Ti-in-garnet thermometer, Ultrahigh-temperature granulites, Ti!Si substitution, Napier Complex, Lützow-Holm Complex

INTRODUCTION

Rutile needles have been reported in pyroxenes and garnet in rocks formed at a wide range of extreme pressure-temperature conditions, for example, high-pressure layered intrusions (Moore, 1968), ultrahigh-pressure eclogites (Mposkos and Kostopoulos, 2001; Zhang and Liou, 2003; Zhang et al., 2003; Hwang et al., 2007; Griffin, 2008) and peridotites as well as ilmenite rods in olivine (Green et al., 1997; Dobrzheintskaya et al., 2000; Song et al., 2004), high-pressure granulite (Ague and Eckert, 2012), ultrahigh-pressure granulite (Larsen et al., 1998) and ultrahigh-temperature granulites (Moraes et al., 2002). We often find the exsolution lamellae of rutile in the porphyroblastic garnet, orthopyroxene, sapphire, osmiumite, K-feldspar (mesoperthite) and quartz of the ultrahigh-temperature granulites from Napier complex, East Antarctica (Kawasaki and Motoyoshi, 2000; Osanai et al., 2001). Miyake and Hokada (2013) have reported ferropseudobrookite exsolution rod within porphyroblastic quartz in garnet-orthopyroxene-bearing quartzofeldspathic gneiss from Mt. Riiser-Larsen, Napier Complex, East Antarctica. These reports indicate that the host silicates contain a large amount of TiO2 at peak metamorphism and then precipitate Ti oxides such as rutile, ferropseudobrookite and ilmenite during the subsequent decompression or cooling retrograde metamorphism. We can evaluate metamorphic P-T conditions and paths by analysing the TiO2 content of host minerals.

Sepp and Kunzmann (2001) investigated the substitution of Ti4+ for Si4+ on tetrahedral sites in clinopyroxene...
in the system CaO-MgO-SiO2-TiO2 at pressures from 1 atm to 20 kbar and temperatures from 800 to 1200 °C and concluded that the solubility of Ti increases with increasing temperature, whereas it decreases with increasing pressure. The solubility of Ti in olivine coexisting with ilmenite was experimentally calibrated by Dobrzhinetskaya et al. (2000) and Hermann et al. (2005). These two are inconsistent each other. The Ti content in olivine was found to increase with pressure (Dobrzhinetskaya et al., 2000) whereas Hermann et al. (2005) demonstrated that it decreases with pressure. The Ti-in–quartz thermometer has been experimentally calibrated by Wark and Watson, 2006; Ostapenko et al., 2007; Thomas et al., 2010; Huang and Audéat, 2012) and empirically (Kawasaki and Osanai, 2008) calibrated for the temperature estimation of ultrahigh-temperature granulites. Zhang et al. (2003) and Dwarzski et al. (2006) reported that the TiO2 solubility increases with pressure in majoritic garnet. Kawasaki and Motoyoshi (2007) reported that the TiO2 content in garnet coexisting with orthopyroxene, rutile and quartz increases with increasing temperature and decreasing pressure, but the pressure dependence is not so sensitive.

In this paper we present new TiO2 solubility data of garnet coexisting with orthopyroxene, rutile and quartz at 7–23 kbar and 850–1300 °C using as starting materials two garnets from Rundvåghetta (Kawasaki and Motoyoshi, 2006) from Lützow–Holm Complex and McIntyre Island (Kawasaki and Motoyoshi, 2000) from Napier Complex, East Antarctica. Datasets indicate increasing solubility of TiO2 with temperature and pressure. We propose the Ti substitution model for Ca- and Ti-poor garnet and a new Ti-in–garnet thermometer for ultrahigh-temperature garnet obtained by the least squares fitting of polybaric–polythermal experimental data. We apply the proposed thermometer to analyse the metamorphic pressure-temperature conditions of Antarctic ultrahigh-temperature garnet.

**TI SUBSTITUTION IN GARNET**

Hereafter we employ the general formula for garnet as \((A_1)[B_2](C_3)O_{12}\), where \((A), [B], \) and \([C]\) refer to atoms on the dodecahedral \([\)\, octahedral \([\), and tetrahedral \([\)\] sites, respectively. The brackets \([\), [\, and \([\)\] are sometimes omitted for convenience as far as we don’t misunderstand.

**Previous studies**

Kawasaki and Motoyoshi (2007) proposed an empirical Ti-in–garnet thermometer based on the TiIV \(\rightleftharpoons\) SiIV substitution model. Their model is controversial. Firstly their substitution model of Ti for Si on the tetrahedral site in garnet is inconsistent with the experimental data (Zhang et al., 2003; Dwarzski et al., 2006). Zhang et al. (2003) concluded that the Ti content increases with pressure accompanying with the coupled substitutions \(\text{Ca}^2+\text{Ti}^{4+} \rightleftharpoons 2\text{Al}^{3+}\) and \(\text{Mg}^2+\text{Si}^{4+} \rightleftharpoons 2\text{Al}^{3+}\) on the octahedral site in majoritic garnet at 50–150 kbar and 1000–1400 °C. Dwarzski et al. (2006) also reported that coupled substitution \(\text{M}^2+\text{Ti}^4+ \rightleftharpoons 2\text{Al}^{3+}\) (M: Fe, Mg) on the octahedral site results in an increase in the majorite component at 30–70 kbar and 1500–1850 °C. However, such coupled substitution model to form the majorite component, which can be applied to the Ca-rich garnet at extremely high–pressures or garnet with moderate amounts of Ca coexisting with melt at ultra–high–pressures and extremely high–temperatures, should be inapplicable to Ca-poor garnet in ultrahigh-temperature garnet.

From crystal–chemical grounds Hartman (1969) argued that the Ti \(\rightleftharpoons\) Si substitution rarely occurs at tetrahedral sites. Chakhmouradian and McCammon (2005) concluded there is little evidence for tetrahedral Ti in Ti-rich garnet. Grew et al. (2013) approved that Ti occupies the octahedral position in garnet structure and proposed the end-member formulae of Ti–garnet: \(\text{Ca}_3[\text{Ti}_2]\text{Si}_3\text{O}_{12}\) for morimotoite (Ito and Frondel, 1967) and \(\text{Ca}_3[\text{TiFe}^{2+}\text{Si}]\text{Si}_3\text{O}_{12}\) for mormoitoite (Henni et al., 1995). Ma and Krot (2014) found the new Ti–garnet in which Ti occupies all octahedral site (hutcheonite, \(\text{Ca}_3\text{Ti}_2\text{SiAl}_2\text{O}_{12}\)) in the Allende meteorite. The crystallographic study of the rutile exsolution within the ultrahigh–pressure garnet by Proyer et al. (2013) indicated that titanium locates on the octahedral site and they postulated the following components for Ti–garnet: \(\text{M}_z[\text{TiAl}][\text{AlSi}_2]\text{O}_{12}\), \(\text{M}_2\text{Na}[\text{TiAl}]\text{Si}_3\text{O}_{12}\), and \(\text{M}_{2.5}\text{Ca}\{\text{TiSi}_2\text{O}_{12}\) (M: Ca, Fe, Mg; \[\)\] vacancy) as suggested by Yang and Liu (2004).

Tarte et al. (1979) documented that Ti must be distributed over tetrahedral and octahedral sites in Ti-andradite. From the petrographic study of immiscibility between Ti-rich and Ti-poor garnets in a calc–silicate hornfels, Labotka (1995) proposed the combined substitutions TiIV \(\rightleftharpoons\) SiIV; Mg2+Ti4+ \(\rightleftharpoons 2\text{Al}^{3+}\), and Mg2+ \(\rightleftharpoons\) Ca2+.

Armbruster et al. (1998) considered Ti occupies at tetrahedral position as well as octahedral. Van Roermund et al. (2000) proposed the model that Ti occupies both tetrahedral and octahedral sites from the petrological study of the ultrahigh–pressure garnet containing exsolution lamellae of rutile and ilmenite in peridotite from Otroy, Western Gneiss Region, Norway. They derived the general formula of Ti–garnet:

\[
\text{M}_z[\text{R}^{3+}_x\text{M}_y\text{Ti}_z]\{\text{Si}_{3–z}\text{Ti}_z\}\text{O}_{12} \quad (1),
\]

where \(M, \text{R}^{3+}, n, \) and \(z\) are the divalent and trivalent ions, and numbers of cations in tetrahedral and octahedral sites.
respectively. They called such garnet as the ‘super–titanic’ garnet.

Components of Ca- and Ti-poor ultrahigh-temperature garnet

Here we assume that Ti substitution is restricted only on the octahedral sites in garnet as followed by Grew et al.’s (2013) approval. The assumption is consistent with XANES data (Waychunas, 1987; Locock et al., 1995). The possible components of TiO2-bearing garnet were postulated by many authors (e.g., Ito and Frondel, 1967; Henmi et al., 1995; Van Roermund et al., 2000; Yang and Liu, 2004; Smith, 2006; Proyer et al., 2013). The components of TiO2-garnet are tabulated in Table S1 (available online from http://doi.org/10.2465/jmps.150709). Hutchisonite Ca3[Ti3]2Si3O12 (Ma and Krot, 2014) and schorlomite Ca3[Ti2][SiFe3+2]O12 (Ito and Frondel, 1967) are treated as M3[Ti2]{SiAl2}O12 (M = Ca, Mg, Fe, Mn) in our notation, and morimotite Ca3[TiFe2+]Si3O12 (Henmi et al., 1995) is treated as M3[TiM]Si3O12. These are excluded in Table S1. We omit ultrahigh-pressure Na+, vacancy-bearing garnet, including [MNa2][Si2]Si3O12, (M2□)[Si2]Si3O12 (Smith, 2006) and (Ca,Fe,Mg)2.5Si3O12 and M3[TiM]Si3O12, respectively, so that the mole fraction of M3Al2Si3O12 is given by 1 – x – y.

Ignoring the site occupancy of cations, above chemical formula is rewritten by

\[ M_3\text{Al}_2\text{Si}_3\text{O}_{12} \text{ (4).} \]

The formula is completely identical with Equation 1 postulated by Van Roermund et al. (2000) for the ‘super–titanic’ garnet derived from the assumption that Ti occupies both tetrahedral and octahedral sites. The reason why the same formulae are derived from the two different substitution models is essentially originated in the fact that the ‘octahedral’ titanic garnet M3[TiAl]2Si2Al12 is chemically equivalent to the ‘tetrahedral’ Ti-garnet M3Al2{Si2Ti}O12.

EXPERIMENTAL PROCEDURES

Starting materials

We prepared two types of ultrahigh-temperature granulite: (1) sillimanite–cordierite–sapphire grainlite from Rundvåghetta, Lützow-Holm Complex, East Antarctica (sample no. SP92011102A: Kawasaki et al., 1993; Kawasaki and Motoyoshi, 2006) and (2) orthopyroxene granulite from McIntyre Island, Enderby Land, East Antarctica (SP93022004A: Motoyoshi, 1995; Kawasaki and Motoyoshi, 2000; Kawasaki et al., 2002) to constrain the equilibrium or near-equilibrium TiO2 content of garnet. The initial TiO2 content of garnet is lower or higher than that at equilibrium or near-equilibrium. Final composition of garnet can be easily determined by means of electron microbe analyser as is discussed in the final composition of garnet subsection.

The Rundvåghetta granulite contains low–TiO2 garnet whereas the bulk composition is high and saturated in TiO2 (Table S2). We employed the finely powdered Rundvåghetta granulite (RVH) for the starting material containing the TiO2–poor garnet. Final garnet recrystallised from the the Rundvåghetta granulite always becomes enriched in TiO2. McIntyre granulite (MC0) contains rather high–TiO2 garnet (Table S2). We employed the McIntyre granulite for the starting material with TiO2–rich garnet. In addition, we prepared two TiO2–rich starting materials, namely MC3 and MC16 by adding Al2O3, TiO2, and SiO2 to the finely powdered McIntyre granulite (MC0). The McIntyre granulite series (MC0, MC3, and MC16) were fused in the Pt basket at atmospheric pressure and 1400 °C for 10 minutes under controlling oxygen fugacity fO2 by the mixed gas flowing technique in the CO2–H2 system (CO2–H2 = 0.7 t/min:0.3 t/min, log fO2 = −10.1). Three types of glass and the fine powdered McIntyre granulite were used in the experiments.

Experimental technique

High-pressure experiments were carried out using a 16.0 mm piston-cylinder apparatus at Ehime University. The
furnace assembly employed in the present study is similar to that described by Kawasaki and Motoyoshi (2000). We used a pressure medium of talc and Pyrex glass. Pulverised starting material was packed into a graphite, or into a noble metal capsule of Au, Au75Pd25 or Ag70Pd30, whose edge was welded, or into a Mo foil capsule made by rolling up Mo foil and crimping two edges with a drill. The Mo foil capsule packing with starting mix was also put into the outer Pt capsule, an edge of which was welded (Kawasaki and Motoyoshi, 2007). After dried at 120 °C overnight, another edge of a noble metal capsule was sealed by welding with carbon arc in order to prevent contamination, in particular, by H2O from surrounding talc. Four to seven sample containers were put into a boron nitride sleeve with 7.0 mm in diameter and 7.0 mm length. Identification of charge was easily made by the length of the capsule. A 13.0 mm-long semisintered MgO rods with a diameter of 7.0 mm, bored with a hole of 1.6 mm in diameter to insert a thermocouple insulator, was placed on the upper side in a graphite heater within a talc + Pyrex glass assembly. An MgO disk with 0.5 mm-thickness was placed between the top MgO rod and a boron nitride sleeve not to make the junction of thermocouple directly contact with the sample container. Powdered boron nitride was compacted to fill the space between a boron nitride sleeve and the bottom MgO rod with 5.0 mm-length, molded from fine powder and sintered at 1400 °C for 30 min.

Experiments were conducted at pressures 7–23 kbar and temperatures 850–1300 °C on the anhydrous condition. Run durations were 119–1577 hours. The hot piston-in technique was applied for all runs. At about 1 kbar the charge was heated above the softening point of Pyrex glass (about 750 °C) of the pressure–transmitting medium and was then compressed to the target pressure. Finally the sample was heated to the desired temperature. The generated pressure was measured against the oil pressure of the press. Pressure was calibrated on the basis of Bi I–II (25.5 kbar) transitions at room temperature (Hall, 1971). The quartz–coesite transformation (29.7 kbar at 1000 °C; Bohlen and Boettcher, 1982) was also used for calibration. In the present experiments, a negative correction of 12.4% was adapted to the nominal pressure value as internal friction. Run pressures in Table S3 (available online from http://doi.org/10.2465/jmps.150709) are given as the corrected values.

Temperature was monitored with Pt/Pt13Rh13 thermocouple (0.3 mm in diameter) without any correction for the pressure effect on emf. The temperatures at the top, centre and bottom in the sample space were directly measured by the use of three-junction thermocouples. It was found that a temperature gradient of about 1–2 °C/mm existed along the axial direction within the sample space at 10.6 kbar and 1400 °C (Osai et al., 1992; Kawasaki and Motoyoshi, 2000). During each experiment the temperature and pressure were kept constant within ±5 °C and ±0.1 kbar of the nominal values. The fluctuations of the electric power for heating were less than ±1% relative. 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 in about 5 minutes and the run product was recovered.

**Chemical analysis**

Chemical analysis of run products was made with the electron microprobe analyser JEOL JXA–8800 Superprobe at Ehime University, Japan, using the ZAF correction method. 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, periclase for Mg, nickel oxide for Ni, zinc oxide for Zn, wollastonite for Ca, natural albite for Na and natural orthoclase for K. The instrumental conditions were: the accelerating voltage, 15 KV; electron beam current, 5 × 10−9 A; beam diameter, 1–2 µm estimated from the size of contamination spots by excitation during analysis. First-order Ke lines were used. Analysis of Ti was made by 50-sec measurements and the others were made by 10–sec measurements. Background measurements were made by setting the spectrometer to both sides of the peak on each spot. Detection limit of Ti was about 200 ppm. Chemical composition of starting materials and garnets of Antarctic granulites is given in Table S2.

**EXPERIMENTAL RESULTS**

**Run products**

All run products were mounted in epoxy resin and polished for examination by microprobe analysis. Examples of run products are shown in Figures 1A–1D. Final Ti content of garnet was determined through the procedures describing in the final composition of garnet subsection. Blebbby (about 10 µm in grain size) and very fine rutile are found within orthopyroxene and at the garnet–orthopyroxene and orthopyroxene–orthopyroxene grain boundaries in the run products recrystallised from powdered McIntyre granulite MC0 (Fig. 1A) and in those from glass of MC3 (Fig. 1B). Garnet includes fine quartz, orthopyroxene and sometimes very fine rutile (Fig. 1A). Large euhedral garnet in some cases grew up to about 100 µm in grain size from glass of MC3 including euhedral to subhedral orthopyroxene (2–10 µm in grain size),
anhedral quartz at the core and finely needle rutile (Fig. 1B). Grain boundaries among orthopyroxene are filled by quartz and needle rutile (Fig. 1B).

Euhedral garnet recrystallised from powdered Rundvågshetta granulite contains orthopyroxene, quartz, fine rutile, and Ti-rich biotite (Figs. 1C and 1D). A 10-µm-size sapphireine contacts with orthopyroxene. Fine sapphireine (1–2 µm in grain size) within glass crystallised accompanying biotite. Subhedral spinel (~ 10 µm in grain size) recrystallised between garnet and orthopyroxene. Some large orthopyroxenes (20–50 µm in grain size) contain very fine (~2 µm) spinel (Fig. 1D). Garnet includes orthopyroxene and zircon in this charge. Euhedral sapphireine and spinel are found in glass filled space among garnet, orthopyroxene and biotite. We found quartz contacts with sapphireine and orthopyroxene. Needle rutile and zircon are found within garnet or at the grain boundary among garnet, orthopyroxene, and quartz.

Final composition of garnet

Data of the Ti-solubility in garnet are compiled in Table S3. In Figures 1A–1D we show Ti-data of garnet by $N_{\text{Ti}}/N_{\text{Si}} \times 10^4$ on the analytical point. As is seen in these figures, garnet grew over so many different inclusion phases. Garnet and orthopyroxene are reversely zoned with Mg-rich rim and Fe-rich core. These make it difficult to successfully analyse garnet for its true Ti content. We can easily determine the final (equilibrium or near-equilibrium) composition of garnet as is shown in Figure 2 (available online from http://doi.org/10.2465/jmps.150709). Garnet shows the compositional change. We consider that the final composition of garnet is approximately represented by the most Ti-rich one in the case of a recrystallisation experiment at 15 kbar and 950 °C for 1577 h (experiment no. 090604A), the starting material of which was a powdered McIntyre granulite ($X_{\text{bulk}}^{\text{Grt}}/X_{\text{bulk}}^{\text{Grt}} = 0.0031$) containing garnet with $X_{\text{bulk}}^{\text{Grt}}/X_{\text{Si}}^{\text{Grt}} = 0.0014$ ($N_{\text{Ti}} = ...$).
The final composition of garnet is $X_{\text{Grt} Ti} / X_{\text{Grt} Si} = 0.00192$ equivalent to $N_{\text{Ti}} = 0.0057$. In contrast, in the 220 experiment no. 090604B on MC3 glass, of which initial $X_{\text{bulk} Ti} / X_{\text{bulk} Si}$ is 0.0564, garnet became deplete in Ti. The final composition is $X_{\text{Grt} Ti} / X_{\text{Grt} Si} = 0.00244$ and $N_{\text{Ti}} = 0.0073$ (Fig. 2).

Thus we easily determined the final composition of garnet. In order to estimate the reliabilities of each synthetic experiment, mean standard error $\sigma$ was calculated from all analytical data on the TiO$_2$ content of garnet. The standard error is given in Table S3. The inverse squares of the standard error is assumed to be proportional to the weight of data ($1/\sigma^2 = W$: Deming, 1943). Such obtained weight was used in the least squares fittings (see the least squares fitting section).

Stoichiometric constraints
Figure 3 shows the relations among numbers of atoms Ti, Si, Al, and M (= Ca + Fe + Mg) per formula unit based on a 12-oxygen atom normalisation in garnet. The number of Si atoms monotonically decreases by the relation $N_{\text{Si}} = 3 - N_{\text{Ti}}$ with increasing number of Ti atoms. Although the present experiments show Si decreases but Al keeps constant, Ague and Eckert (2012) reported amounts of Si and Al in garnet decrease with increasing Ti content from granulate facies metapelitic rocks of the Merrimack synclinorium, Connecticut. The discrepancy in the trend of Al may be due to the $(\text{Na}_2\text{Mg}_2\text{Fe}_4)[\text{Ti}_2\text{Al}_2\text{Si}_3\text{O}_{12}]$ component in Connecticut garnet with suggestive evidences for ultrahigh-pressure metamorphism at pressures above the quartz–coesite transition predated the granulate facies metamorphism (Ague and Eckert, 2012).

The numbers of Al and M (= Ca + Fe + Mg) atoms are conserved at constant values of 2 and 3, respectively. This suggests that the combined substitution $\text{Ti}^{VI}\text{Al}^{IV} \rightarrow \text{Al}^{VI}\text{Si}^{IV}$ is predominant rather than the coupled substitution $\text{M}^{II}\text{Ti}^{VI} \rightarrow \text{Al}^{VI}\text{Al}^{VI}$ (M: Ca, Mg, Fe) in the Ca– and Ti–poor garnet under ultrahigh-temperature metamorphic conditions. We consider that the mole fraction of $\text{M}_3[\text{MTi}]\text{Si}_3\text{O}_{12}$, $y$, in Equations 3 and 4, is presumably equal to zero ($y \approx 0$). Therefore, the Ca– and Ti–poor garnet can be treated as the solid solution $\text{M}_3[\text{MTi}]\text{Si}_3\text{O}_{12} - \text{M}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. The formula of the octahedral Ti–garnet given by Equation 3 is arranged as

$$\text{(Ca,Fe,Mg)}_3[\text{Ti}_2\text{Al}_2\text{Si}_3\text{O}_{12}] \quad (5),$$

which is chemically equivalent to

$$\text{(Ca,Fe,Mg)}_3\text{Al}_2\text{Si}_3\text{O}_{12} \quad (6).$$

Here, it is worth to recall our model that the Ti occupation is restricted only to octahedral site in garnet.

Pressure and temperature dependence
Experimental results are compiled in Table S3 and illustrated in Figures 4 and 5. Figure 4 shows the $N_{\text{Ti}}$-$P$-$T$ diagram indicating the TiO$_2$ solubility in garnet increases with both pressure and temperature. In Figure 5, data of ln$K_{\text{Ti}}$ (see...
next section) plot versus $1/T$ at pressure ranges 7–11, 12–16, and 17–23 kbar, showing that $\ln K_{Ti}$ linearly decreases with the reciprocal of temperature and slightly increases with pressure. The direction of the top corner of the triangle in Figures 4 and 5 shows whether the Ti content of final garnet would increase or decrease. The data given by the upward triangle indicates Ti increases and the downward data indicates Ti decreases towards equilibrium. These figures represent that Ti in garnet increases with pressure and temperature though the increase with pressure is small.

EMPirical formuLation of Ti-in-Garnet thermomeTer for ultraHigH-temperature granulite

We found garnet, orthopyroxene, rutile and quartz in the run products on both Rundvågshetta and McIntyre granulite series. The garnet-orthopyroxene-rutile-quartz equilibria are given by the following chemical reactions:

$$M_3[Al_2Si_3O_{12}] + TiO_2 \rightarrow M_3[Al_2Si_3O_{12}] + SiO_2$$

$$M_3[Al_2Si_2O_5] + TiO_2 \rightarrow M_3[Al_2Si_2O_5] + SiO_2$$

$$M_3[Al_2Si_2O_5] + TiO_2 \rightarrow M_3[Al_2Si_2O_5] + SiO_2$$

where we assume that Ti occupies both tetrahedral (T) and octahedral (M1) sites in orthopyroxene, but never locates on the hexahedral (M2) site. We must recall a priori intracrystalline equilibrium for Ti:

$$M_3[Al_2Si_3O_{12}] + TiO_2 \rightarrow M_3[Al_2Si_3O_{12}] + SiO_2$$

Here we omit following components: $□M_2[Al_2Si_3O_{12}]$ and $□M_2[Al_2Si_3O_{12}]$, titanic pyroxenes replacing Si by Ti, which are diagnostic components of ultrahigh-pressure pyroxene (e.g., Smith, 2006).

The strict solution for the TiO$_2$ solubility in garnet should be derived from the necessary and sufficient conditions of garnet-orthopyroxene-rutile-quartz equilibria expressed by Reactions 7–10 as well as the element exchange reactions, net-transfer reactions of Al$_2$O$_3$– and TiO$_2$–solubility equilibria, which are intricately-intertwined with each other. The complete solution of these equilibria is out the present study. The solubility of TiO$_2$ in orthopyroxene in equilibrium with garnet, rutile, and quartz will be discussed elsewhere.

Now let’s establish the Ti-in-garnet thermometer from the Reaction 7. It is a matter of course that the thermometer satisfies the necessary condition but doesn’t the sufficient condition for equilibrium. The free energy change of Reaction 7 is defined as

$$\Delta G_7 = RT \ln K$$

Figure 5. $\ln K_{Ti}$ versus $1/T$ diagram. Arrowed line with numeral, calculated isobaric $\ln K_{Ti}$ curve. Upward triangle, Ti-increase run. Downward triangle, Ti-decrease run. Vertical bar, standard error of $\ln K_{Ti}$. Color version is available online from http://doi.org/10.2465/jmps.150709.
The equilibrium constant \( K \) is expressed as follows:

\[
K = \frac{X_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{X_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}}. 
\]

(13)

Kawasaki and Osanai (2008) treated activities of the coexisting rutile and quartz as \( a_{TiO_2} \simeq 1 \) and \( a_{SiO_2} \simeq 1 \), then the equilibrium constant \( K \) is expressed as follows:

\[
K \simeq \frac{X_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{X_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}}. 
\]

(14)

Although the strict thermodynamic treatment of the substitution of Ti on the octahedral sites of garnet has not yet been established at the present stage, the equilibrium constant \( K \) is rewritten by

\[
K \simeq \frac{X_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{X_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}} \times \frac{\gamma_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{\gamma_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}}. 
\]

(15)

where the definition of activity (product of composition \( \chi^a \) and activity coefficient \( \gamma^a \): \( a^a = \chi^a \gamma^a \)) is used.

According to the theory of the multisite solution (e.g., Chapter 3 of Wood and Fraser, 1977), mole fractions \( X_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12} \) and \( X_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12} \) are given by combinations of cationic mole fractions (site occupancies) on the dodecahedral (VIII), octahedral (VI), and tetrahedral (IV) sites:

\[
X_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12} = (X^{\text{VIII}}_M)^2 (X^{\text{VI}}_{Ti} X^{\text{IV}}_Al)(X^{\text{IV}}_{Si})^2 X^{\text{IV}}_Al \\
X_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12} = (X^{\text{VIII}}_M)^2 (X^{\text{IV}}_{Al})^2 (X^{\text{IV}}_{Si})^3 
\]

(16)

The equilibrium constant \( K \) in Equation 15 is

\[
K \simeq \frac{X^{\text{VI}}_{Ti} X^{\text{IV}}_Al}{X^{\text{VIII}}_M} \times \frac{\gamma_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{\gamma_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}} = K_{Ti} \cdot K_{\gamma} 
\]

(17)

where \( K_{Ti} = \frac{X^{\text{VI}}_{Ti} X^{\text{IV}}_Al}{X^{\text{VIII}}_M} \) and \( K_{\gamma} = \frac{\gamma_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{\gamma_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}} \).

As has been discussed by Wood and Fraser (1977), we assume that the non-idealities of the garnet solid solution are of similar magnitude with \( \gamma > 1 \). So the activity coefficients in the equilibrium constant given by Equation 17 cancel out:

\[
K_{\gamma} = \frac{\gamma_{M_3[TiAl]}^{\text{Gr}t}[SiAl]O_{12}}{\gamma_{M_3[AlSi]}^{\text{Gr}t}[SiAl]O_{12}} \simeq 1
\]

(18)

Then the free energy change of Reaction 7 is arranged by

\[
-\Delta G_7 \simeq RT \ln K_{Ti} 
\]

(19)

Here we must remember Equation 6 and a priori assumption that the sum of the cationic mole fraction at each site equal to the unity:

\[
N_{Al} = 2X^{\text{IV}}_{Al} + 3X^{\text{VI}}_{Al} = 2, N_{Ti} = 2X^{\text{VI}}_{Ti}, N_{Si} = 3X^{\text{IV}}_{Si}, \\
2X^{\text{VI}}_{Ti} + 3X^{\text{IV}}_{Si} = 3, X^{\text{IV}}_{Al} + X^{\text{VI}}_{Ti} + 1, X^{\text{IV}}_{Al} + X^{\text{VI}}_{Si} = 1.
\]

(20)

From these, the effective equilibrium constant \( K_{Ti} \) of the Reaction 7 is given by the following expression:

\[
K_{Ti} = \frac{N_{Al}^2}{(2 - N_{Ti})(3 - N_{Ti})} = \frac{N_{Al}^2}{N_{Al}N_{Si}}
\]

(21)

We can obtain the empirical formula for the Ti-solubility in garnet:

\[
T \ln K_{Ti} = -A + BT + CP
\]

(22)

where \( A, B, \) and \( C \) are the empirical parameters for fitting and these parameters might be related to the enthalpy, entropy, and volume changes of Reaction 7, respectively. The Equation 22 indicates that it is possible to evaluate the parameters \( A, B, \) and \( C \) by application of least squares calculations if we can obtain a sufficient number of high-quality Ti-Si-Al data of garnet coexisting with rutile and quartz in equilibrium at given physical conditions. Conversely, if we evaluate these parameters, we can estimate the equilibrium temperatures or pressures using the Ti-Si-Al data of garnet coexisting with orthopyroxene, rutile, and quartz.

**LEAST SQUARE FITTING**

We carried out the least square calculation (Deming, 1943) on the experimental data compiled in supplementary Table S3 to evaluate the empirical parameters \( A, B, \) and \( C \) of the non-linear condition function \( F \) which is arranged from Equation 22:

\[
F(X, A, B, C) = T \ln \frac{X^2}{(2 - X)(3 - X)} + A - BT + CP
\]

(23)

where \( X \) denotes the observed Ti content \( X^{\text{obs}}_{Ti} \).

The requirement of the least squares is to minimise the sum of weighted squares of the residuals, which are defined as the difference between the directly observed and calculated quantities:

\[
S = \sum W(N^{\text{obs}}_{Ti} - N^{\text{calc}}_{Ti})^2
\]

(24)

where \( W \) is the weight of data equivalent to the inverse square of the standard error of observed \( N_{Ti} \) \((W = 1/\sigma^2)\). The summation is carried out for all observations. The principle of the least squares fitting requires that the sum of the weighted squares of residuals defined by Equation 24 should be minimised with respect to the adjustable values:
\[ \delta S = 0 \] (25).

We followed the common computation procedure of the least squares calculation (e.g., Kawasaki and Ito, 1994).

The results of the least squares fitting are given by

\[
\begin{align*}
A &= 17777 \pm 1457, \quad B = 0.964 \pm 1.306, \\
C &= -139.5 \pm 49.2, \quad S/(n-k) = 6.364
\end{align*}
\] (26),

where \( n \) and \( k \) are the number of data (\( n = 35 \)) and the number of parameters (\( k = 3 \)), respectively. The \( S/(n-k) \) is an external consistency of data specifying an index measuring success and failure of the least square regression. The smaller value in \( S/(n-k) \) indicates the higher reliability of the regression. Figure 4 shows the results of least squares fitting illustrated by the \( N_{Ti}-T-P \) diagram. Figure 5 is the \( \ln K_{Ti} \) diagram at pressure ranges 7-11, 12-16, and 17-23. The curve fit is satisfactory as is seen in these figures, implying that the TiO\(_2\) solubility in garnet coexisting with orthopyroxene, rutile, and quartz can be described with reasonable precision by Equation 22 under the present experimental conditions.

**DISCUSSION**

**Geothermometer**

Substituting the evaluated values of parameters given in Equation 26 into Equation 22, we obtain the following equation for the Ti-in-garnet thermometer:

\[
T \ln K_{Ti} = T \ln \frac{N_{Ti}^2}{N_{Al}N_{Si}} \\
= -17777 + 0.964 + 139.5P
\] (27).

The pressure dependence on \( \ln K_{Ti} \) is small as compared with the temperature dependence (Fig. 5). To explain this more explicitly, we present Figure 6 (available online from http://doi.org/10.2465/jmps.150709) showing the change of \( N_{Ti} \) with pressure. The slope of the \( N_{Ti}-P \) curve, \( \partial N_{Ti}/\partial P \), increases with increasing temperature, especially it becomes slightly steep at \( T > 1000 ^\circ \text{C} \). We can read \( N_{Ti} \) changes from 0.0048 to 0.0063 when the pressure changes from 5 to 10 kbar at 1000 \(^\circ\)C, yielding that \( \partial N_{Ti}/\partial P = 3 \times 10^{-4} \text{kbar} \). This indicates that if \( N_{Ti} \) has an uncertainty of \( \pm 6 \times 10^{-4} \), the obtained pressure would have an error of about 2 kbar (see Fig. 6). The slope of the curve at constant \( K_{Ti} \) on the pressure-temperature diagram is steep and negative, \(-9.0 \approx -10.6 ^\circ \text{C/} \text{kbar} \) as shown in Figure 8. This suggests that we can evaluate \( P-T \) conditions of the ultrahigh-temperature metamorphic rocks with high precision by combining the present Ti-in-garnet thermometer and other thermobarometer with a moderate slope in pressure-temperature plane (see Fig. 8A), for example, the Fe-Mg exchange thermometer between garnet and orthopyroxene (Harley, 1984a) and/or the Al\(_2\)O\(_3\) solubility barometer in orthopyroxene coexisting with garnet (Harley, 1984b; Fitzsimons and Harley, 1994).

**Thermometer for orthopyroxene-absent granulites**

While the Ti-in-garnet thermometer given by Equation 27 is based on the orthopyroxene-free Reaction 7, the equation is derived from the orthopyroxene-present data. Equation 27 should be fundamentally applied to the garnet-orthopyroxene-rutile-quartz-bearing granulites. We cannot evaluate the discrepancy in the TiO\(_2\) content of garnet between orthopyroxene-present and orthopyroxene-absent systems because of lack of the orthopyroxene-absent data.

Figure 7 (available online from http://doi.org/10.2465/jmps.150709) shows the schematic composition-paragenesis diagram among garnet, orthopyroxene, rutile, and quartz in the TO\(_2-\)MTO\(_3-\)M\(_3\)Al\(_2\)Ti\(_3\)O\(_8\) system (\( M = \text{Ca + Fe + Mg, } T = \text{Si + Ti} \)). In ultrahigh-pressure metamorphic rocks (Fig. 7A), garnet and orthopyroxene show wide ranges of solid solution toward TO\(_2\) (Smith, 2006) and are soluble with each other. Such garnet contains fairly amounts of M\(_3\)[MSi]Si\(_3\)O\(_12\) and M\(_3\)[MTi]Si\(_3\)O\(_12\) components (Zhang et al., 2003) accompanying the coupled substitutions M\(_{IV}\)Si\(_{VI}\) \( \equiv \) Al\(_{IV}\)Al\(_{VI}\) and M\(_{IV}\)Ti\(_{VI}\) \( \equiv \) Al\(_{IV}\)Al\(_{VI}\). In the Ti-rich ultrahigh-temperature metamorphic rocks (Fig. 7B), garnet and orthopyroxene form no solid solution with TO\(_2\). Garnet shows the solid solution toward M\(_2\)Ti\(_2\)O\(_6\) component but not toward M\(_2\)Si\(_2\)O\(_6\) component accompanying the coupled substitution M\(_{IV}\)Ti\(_{VI}\) \( \equiv \) Al\(_{IV}\)Al\(_{VI}\), while orthopyroxene forms the solid solution M\(_2\)Ti\(_2\)O\(_6\)–MAl\(_2\)TiO\(_6\). In these two cases, the present Ti-in-garnet thermometer is inapplicable to the garnet-rutile-quartz (orthopyroxene-absent) rocks because the composition of garnet coexisting with orthopyroxene, rutile, and quartz is fixed while the composition of garnet depends on the bulk in the orthopyroxene-absent rocks.

In the case that TO\(_2\) component is insoluble in both garnet and orthopyroxene. Garnet never forms solid solution toward M\(_2\)T\(_2\)O\(_6\) while orthopyroxene forms M\(_2\)T\(_2\)O\(_6\)–MAl\(_2\)TiO\(_6\) solid solution (Fig. 7C), the composition of garnet represented by the point Grt of the line segment Grt–(Qtz + Rt) in the orthopyroxene-absent system is exactly equal to that given by the apex Grt of the Grt–Opx–(Rt + Qtz) triangle in the orthopyroxene-present system. This condition arises as far as only combined substitution Ti\(_{VI}\)Al\(_{IV}\) \( \equiv \) Al\(_{IV}\)Si\(_{VI}\) takes place but coupled substitutions M\(_{IV}\)Ti\(_{VI}\) \( \equiv \) Al\(_{IV}\)Al\(_{VI}\) and M\(_{IV}\)Si\(_{VI}\) \( \equiv \) Al\(_{IV}\)Al\(_{VI}\) never occur in the Ca- and Ti-poor garnet at ultrahigh-temperature metamorphic conditions.
Applications to ultrahigh-temperature granulites

We apply the present Ti-in-garnet thermometer to estimate the metamorphic conditions of Antarctic ultrahigh-temperature granulites from Tonagh Island (Harley, 1985, 1998a, 1998b; Osanai et al., 1999; Hokada et al., 1999) and McIntyre Island (Motoyoishi, 1995; Kawasaki and Motoyoishi, 2000; Kawasaki et al., 2002, 2006, 2011) and Skallevikshalsen (Yoshimura et al., 2004; Kawakami and Motoyoishi, 2004; Kawasaki et al., 2013).
The metamorphic conditions of Tonagh Island are compiled in Figure 8A. Harley (1985) estimated metamorphic conditions of Tonagh Island as 900–950 °C and 7–10 kbar (rectangle ‘Ha85’). Harley (1987) concluded metamorphic temperatures of Tonagh Island exceeded 980 °C at pressures of 7 kbar (open circle ‘Ha87’). Summary of the temperature estimation by Harley (1998b) is shown by horizontal bars labelled by ‘Ha98b’ as 980–1030 °C from coexistence of pigeonite + subcalcic pyroxene and 950–1000 °C from garnet-orthopyroxene geothermometry.

Petrological studies of sapphire–bearing aluminous gneisses by Hokada et al. (1999) implied the P–T conditions of the thermal peak as 8–11 kbar and 1030–1100 °C (grey parallelogram ‘Peak Ho99’). The estimated retrograde metamorphic P–T conditions are shown in this figure (‘Retro Ho99’). The P–T relation of the Tonagh granulite (sample no. A98012902P) determined by Hokada et al. (1999) from the garnet-orthopyroxene geothermobarometers (Harley, 1984a, 1984b; Fitzsimons and Harley, 1994) is shown by a line labelled by ‘Ho99’. This line intersects at 8 kbar and 995 °C (filled circle) with a line ‘2P’ with a $dT/dP$ slope of $-10.6 \, ^oC/kbar$ obtained obtained by applying the present Ti-in–garnet thermometer to the Tonagh garnet (sample no. A98012902P). Hokada (2001) reported that the sapphire-bearing gneiss from Tonagh Island yields equilibrium temperatures ranging from 1050 to 1110 °C using the ternary feldspar thermometer.

Tsunogae et al. (2002) indicated the Tonagh granulites experienced maximum P–T conditions up to 9 kbar and 1100 °C shown by a circle labelled by ‘Ts02’, half of which is within ‘Peak Ho99’. They found the reaction corona composed of garnet, sillimanite, cordierite, and orthopyroxene from sapphire + quartz (sample no. B98021104A) and estimated the retrograde metamorphic temperature as 800–820 °C at 8 kbar, a horizontal bar within the ‘Retro Ho99’. Tsunogae et al. (2002) also studied the carbonic fluid inclusions and obtained isochores. The isochore of quartz of sample no. B98021104A is shown by a line labelled by ‘Ts02’. The P–T relation of the TiO$_2$ solubility in garnet forming the reaction corona of B98021104A (line ‘4A’ with a $dT/dP$ slope of $-9.3 \, ^oC/kbar$) intersects at 843 °C and 7.7 kbar (filled circle) with the isochore.

Shimizu et al. (2013) estimated the metamorphic P–T path of the sapphire + quartz granulite using the pseudosection method: the granulite experienced the peak metamorphism at 950–1100 °C and 7.5–11 kbar (rectangle ‘Peak Sh13’) and followed by near-isobaric cooling toward the retrograde metamorphism at 800–950 °C and 8–10 kbar (rectangle labelled by ‘Retro Sh13’) along a counterclockwise P–T path. The present thermometer applied on garnet (sample no. B98021104AA) is shown by the line labelled ‘AA’ which passed through the retrograde P–T field estimated by Hokada et al. (1999) at the bottom–left corner of the rectangular ‘Retro Sh13’.

McIntyre Island. The McIntyre granulite (sample no. SP93022004A; Kawasaki and Motoyoshi, 2000; Kawasaki et al., 2002) consists of orthopyroxene, garnet, and quartz with minor sillimanite and accessory rutile, phlogopite, and zircon. Garnet occurs as small euhedral blebs, exsolution lamellae in orthopyroxene, and thin films around orthopyroxene, euhedral sillimanite, rutile, and phlogopite (Kawasaki and Motoyoshi, 2000). Needle rutile occurs within orthopyroxene with the same direction as the garnet lamellae. The granulite experienced peak metamorphism at temperatures 1000–1050 °C at around 11 kbar in the stability field of orthopyroxene, sillimanite and quartz (Kawasaki et al., 2002) and subsequently cooled isobarically as is shown by an arrow labelled ‘K02’ in Figure 8B toward a grey quadrilateral labelled by ‘KM00’ at temperatures 873–895 °C and pressures 10.9–11.4 kbar, resulting in the formation of garnet lamellae within orthopyroxene and garnet moats around orthopyroxene (Kawasaki and Motoyoshi, 2000). The Ti-in–garnet P–T relation with a $dT/dP$ slope of $-10.1 \, ^oC/kbar$ obtained by Equation 27 is illustrated by a line. The retrograde temperature is obtained as 910 °C if the isobaric cooling underwent at 11.2 kbar (filled circle). Harley et al.’s (1998b) estimation of metamorphic temperature at 11 kbar is illustrated by horizontal bar with open circle labelled by ‘Ha98b’.

Rundvåghetta. The metamorphic grade of the Lützow–Holm Complex increases southwestwards from the upper-amphibolite facies on the Prince Olav Coast, through a transition zone, to granulite facies in Lützow–Holm Bay (Hiroi et al., 1986; Shiraishi et al., 1989). The Rundvåghetta area, which is located close to the ‘thermal axis’ of the complex (Hiroi et al., 1991), records the highest metamorphic grade (Motoyoshi et al., 1985). The geological outline of Rundvåghetta was given by Motoyoshi et al. (1986). The diagnostic mineral assemblages of ul-

(Kawakami and Motoyoshi, 2004; Yoshimura et al., 2004; Kawasaki et al., 2013) in the Lützow–Holm Complex (Hiroi et al., 1983, Motoyoshi et al., 1985; Hiroi et al., 1986, 1991). The P–T estimation of these metamorphic rocks utilising the Ti-in–garnet thermometer given by Equation 27 are illustrated in Figures 8A–8D indicating the applicability of the method for $T > 800$ °C.
trahigh-temperature metamorphism, including spinel + quartz (Motyosyo et al., 1985), orthopyroxene + sillimanite + quartz (Kawasaki et al., 1993; Motyosyo and Ishikawa, 1997), sapphireine + quartz (Yoshimura et al., 2008) and osmiumite (Kawasaki et al., 2011), were found from this area.

Harley (1998b) estimated the peak temperature assuming \( P = 11 \) kbar using the garnet-orthopyroxene geothermobarometry (Harley and Green, 1982; Harley, 1984a; Ganguly et al., 1996; Aranovich and Berman, 1997) as is shown by a horizontal bar labelled by ‘HA98b’ in Figure 8C. Motyosyo and Ishikawa (1997) estimated the peak metamorphic conditions of about 1000 °C and about 11 kbar (open circle) and proposed the retrograde metamorphic path of the near isothermal decompression (arrow ‘MI97’). Kawasaki and Motyosyo (2006) documented the peak and retrograde metamorphic conditions as 925–1039 °C/11.5–15.0 kbar (rectangle ‘Peak K06’), 824–1010 °C/6.5–10.8 kbar (‘Retro K06’), respectively. Yoshimura et al. (2008) found the peak sapphireine + quartz assemblage as inclusions within garnet porphyroblasts and estimated the peak metamorphic conditions of 970–1055 °C and 9.5–12 kbar (rectangle) and the retrograde path (arrow ‘Y08’). Based on the occurrence of retrograde inclusions of osmiumite in garnet and the presence of a spinel and quartz assemblage, the reconstructed metamorphic \( P-T \) path for the Rundvågshetta area (Kawasaki et al., 2011) is shown by an arrow labelled by ‘K11’ in Figure 8C. The line ‘03A’ indicates the Ti–in–garnet \( P-T \) relation with a \( dT/dP \) slope of \(-9.0 \) °C/kbar obtained by Equation 27 applied to garnet (sample no. 02123003A; Kawasaki et al., 2011), which contains rutile needles. A filled circle is the retrograde temperature of 844 °C at 6.1 kbar, pressure of which was evaluated by Kawasaki et al. (2011).

Skallevikshalsen. Yoshimura et al. (2004) estimated that peak metamorphic conditions at Skallevikshalsen were 820–970 °C and 7.5–10.8 kbar as illustrated by a grey trapezoid labelled by ‘YO4’ in Figure 8D. A line labelled by ‘409’ is the Ti–in–garnet \( P-T \) relation obtained from the mafic gneiss (sample no. 99020409, Yoshimura et al., 2004). Kawakami and Motyosyo (2004) reported spinel and quartz in direct contact within a garnet porphyroblast in garnet–sillimanite gneiss and consequently estimated a metamorphic pressure of 7.5–9.0 kbar assuming a temperature of 900 °C as is shown by ‘KM04’. A line ‘804c’ applied to garnet–sillimanite gneiss (sample no. 011804c: Kawakami and Motyosyo, 2004) passes very close to the estimated conditions. Kawasaki et al. (2013) proposed the metamorphic path by an arrow labelled by ‘K13’. The line ‘801Ae’ shows the \( P-T \) relation with a \( dT/dP \) slope of \(-9.8 \) °C/kbar obtained by the present thermometer applied to the core data of the Skallevikshalsen garnet (sample no. 03011801A). Estimated temperatures of 906 and 909 °C at 8.25 kbar, average pressure by Kawasaki and Motyosyo (2004), are shown by filled circles on the lines ‘804c’ and ‘801Ae’, respectively. Rim data of sample no. 03011801A (line ‘801Ae’) is 50 °C or more lower than the final record of the retrograde metamorphic condition of 840 °C and 6.1 kbar estimated by Kawasaki et al. (2013).

CONCLUSION

The experimental determination of Ti in garnet coexisting with orthopyroxene, rutile, and quartz shows (1) combined substitution \( \text{Ti}^IV\text{Al}^V = \text{Al}^III\text{Si}^IV \) is predominant rather than coupled substitution \( \text{M}^IV\text{Ti}^V = \text{Al}^III\text{Al}^IV \) (M: Ca, Fe, Mg), (2) chemical formula of Ca– and Ti–poor garnet is given by \( \text{M}_x\text{Al}_3\text{Si}_3\text{Ti}_x\text{O}_{12} \), (3) Ti in Ca– and Ti–poor ultrahigh–temperature garnet is temperature–sensitive, (4) least–squares fitting of the experimental data leads to the calibration of a semi–empirical thermometer,

\[ 17777 + 0.964 + 139.5P = T \ln \frac{N^2_{\text{Ti}}}{N_{\text{Al}}N_{\text{Si}}} \]

with a \( dT/dP \) slope of \(-9.0 \sim -10.6 \) °C/kbar, (5) temperature sensitivity allows temperature estimation to ±20 °C, and (6) application of this thermometer to Antarctic ultrahigh–temperature garnets yields results consistent with those previously obtained by independent methods. Hence, the Ti–in–garnet thermometer supports the use of this approach to examine to other high–temperature and ultrahigh–temperature granulites for which reliable temperature estimates are lacking.

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SUPPLEMENTARY MATERIALS

Tables S1–S3, Figures 2, 6, and 7, and color version of Figures 3–5 and 8 are available on line from http://doi.org/10.2465/jmps.150709.

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