



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Earth and Planetary Science Letters 216 (2003) 591–601

EPSL

www.elsevier.com/locate/epsl

Titanium solubility in coexisting garnet and clinopyroxene at very high pressure: the significance of exsolved rutile in garnet

R.Y. Zhang^{a,*}, S.M. Zhai^b, Y.W. Fei^c, J.G. Liou^a

^a Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA

^b College of Sciences, Department of Earth Sciences, Zhejiang University, Hangzhou, Zhejiang 310027, PR China

^c Geophysical Laboratory of Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington, DC 20015, USA

Received 4 February 2003; received in revised form 19 August 2003; accepted 19 September 2003

Abstract

Exsolution microstructures including ilmenite ± garnet in clinopyroxene and rutile in garnet are common in clinopyroxenite and eclogite from the Sulu ultrahigh-pressure (UHP) terrane. In order to understand the phase relations and Ti solubility in both garnet and clinopyroxene in a natural TiO₂-bearing system, several experiments at 5–15 GPa, 1000–1400°C were carried out using the multianvil high-pressure apparatus. The Hujianlin ilmenite-rich garnet clinopyroxenite showing exsolution microstructure was selected as starting material, because it closely approaches a composition lying in the TiO₂–CaO–MgO–FeO–Al₂O₃–SiO₂ system. Except for minor melt in one experiment at 1400°C and 5 GPa, other run products contain majoritic garnet+clinopyroxene ± ilmenite (or rutile) and exhibit neoblastic texture. With increasing pressure, Ti and Ca, Mg and Si contents of neoblastic garnet increase with decreasing Al. The principal coupled substitutions are Ca²⁺Ti⁴⁺ → 2Al³⁺ and Si⁴⁺Mg²⁺ → 2Al³⁺ responding to majorite component increase. Titanium solubility (0.8–4.5 wt% as TiO₂) in garnet and Gr_{Ti}/Cpx_{Ti} ratio have a pronounced positive correlation with pressure between 5 and 15 GPa. On the other hand, the coexisting clinopyroxene contains low Ti (0.17–0.53 wt% as TiO₂), and shows no significant pressure effect. Rutile exsolution in garnet is coupled to that of pyroxene exsolution; both are exsolved from majoritic garnet on decompression. Therefore, the amount of such exsolved lamellae is a potential indicator of high-pressure metamorphism in exhumed rocks, whereas the TiO₂ content of clinopyroxene coexisting with garnet is not sensitive to pressure change.

© 2003 Elsevier B.V. All rights reserved.

Keywords: high-*P* experiment; Ti solubility; rutile exsolution; majorite; garnet clinopyroxenite

1. Introduction

Titanium-bearing minerals, such as ilmenite and rutile occurring as exsolution phases in oliv-

ine, clinopyroxene, and garnet, have been reported in some ultrahigh-pressure (UHP) peridotites and eclogites [1–5]. The effect of pressure on the Ti solubility in these phases has attracted numerous experimental studies (e.g., the Ti solubility in olivine) [6–8]. Exsolved rutile needles are common in garnets from eclogite and clinopyroxenite closely associated with ultramafic rocks in the Sulu UHP terrane ([2,3,5], and this study). Prior

* Corresponding author. Fax: +1-650-725-2199.

E-mail address: zhang@pangea.stanford.edu (R.Y. Zhang).

experiments on Ti solubility in garnet and clinopyroxene were reconnaissance in nature [9]. Both ilmenite and garnet exsolved from clinopyroxene have been recently documented in some Sulu ilmenite-rich garnet clinopyroxenites [10]. Similar intergrowths of garnet and clinopyroxene in the Granulitgebirge, Germany, have been suggested to have a very deep origin (>400 km) [11].

After olivine, pyroxene is the next most abundant phase in the upper mantle. Many experiments in the system $\text{MgSiO}_3\text{--Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ have been carried out in order to elucidate the phase relations of pyroxene and garnet at mantle conditions [12–17]. These studies indicated that the solubility of enstatite (MgSiO_3) in pyrope increases with increasing pressure, but there is considerable disagreement regarding the solubility limit of enstatite (60–83 mol%) component into pyrope [14]. Pyroxene (MgSiO_3) transforms to majorite at about 17 GPa by the coupled substitution of $\text{Mg}^{\text{VI}}\text{Si}^{\text{VI}}$ for 2Al^{VI} [13]. Ultramafic and mafic rocks have complex bulk compositions; existing experiments in the simple $\text{MgO--Al}_2\text{O}_3\text{--SiO}_2$ system can not explain the observed exsolution microstructures described above, and the pressure effect on the solubility of Ti in both clinopyroxene and garnet. In order to understand the origin of exsolution lamellae of Grt+Ilm in clinopyroxene and the Ti solubility in garnet, several experiments using a well-characterized Sulu UHP garnet clinopyroxenite as starting material were carried out. Major goals of this study are: (1) to determine experimentally parageneses and compositions of minerals as functions of pressure and temperature; (2) to explain the occurrence and characteristics of porphyroblastic garnet containing exsolved rutile needles in the Sulu UHP terrane; and (3) to discuss Ti solubility in garnet and clinopyroxene from eclogite and clinopyroxenite and its significance. Our experiments indicate that Ti solubility is positively correlated with pressure in garnet, as $M_3(\text{MTi})\text{Si}_3\text{O}_{12}$ and Si concomitantly increase as $M_3(\text{MgSi})\text{Si}_3\text{O}_{12}$ ($M = \text{Ca, Mg}$ and Fe).

2. Occurrence of exsolved Ti-bearing phases and sample description

Exsolved Ti-bearing phases are widespread in garnet and clinopyroxene from the Sulu UHP eclogite and clinopyroxenite chiefly associated with ultramafic rocks [2–5] or, to a lesser extent, within gneiss. Similar rutile lamellae are rare in the Altyn Tagh garnet lherzolites [18]. Rutile exsolution in garnets has been documented in Yangkou (near Qingdao), Junan, Rizhao and Weihai. The Yangkou ultramafic–mafic complex consists of banded garnet lherzolite (Grt+Ol+Opx+Cpx+Amp+Ilm), wehrlite (Ol+Cpx+Ilm \pm Grt+Amp), garnet clinopyroxenite (Grt+Cpx+Ilm) and eclogite (Grt+Omp+Rt) (mineral abbreviations after [19]), occurring as blocks of 10 m size in gneiss; these rocks are associated with eclogite bodies showing a transition from metagabbro to coesite eclogite [20]. These rocks exhibit banding at hand specimen and thin-section scales, defined by various proportions of olivine, Cr-bearing amphibole, clinopyroxene and garnet. The garnet clinopyroxenite and eclogite are porphyroblastic, with coarse-grained, 1–6 mm garnet setting in a fine-grained (0.15–0.5 mm) matrix of Grt, Cpx, Ilm (or Rt). Fe–Mg partitioning of Grt and Cpx and Grt–Opx barometry yield P – T estimates of 4.6 ± 0.2 GPa and $750 \pm 50^\circ\text{C}$.

Ultramafic rocks at Junan include Amp-bearing peridotite, garnet websterite and serpentinite. The peridotite is foliated and composed of oriented olivine, hornblende, enstatite and minor diopside. Garnet websterite exhibits porphyroblastic texture and was recrystallized at $700\text{--}830^\circ\text{C}$, 4.0 ± 0.2 GPa [2]. Associated eclogite shows inequigranular texture; porphyroblastic garnets range in size from 1.2 to 6 mm set in a fine-grained matrix of garnet, omphacite and minor allanite. Secondary poikiloblastic hornblende (3–6 mm) contains numerous inclusions of garnet, omphacite and rutile.

More than 10 ultramafic bodies in the southwestern Rizhao area are faulted against granitic gneiss. Most masses are totally serpentized except for two large bodies (Suoluoshu and Hujialin). The Suoluoshu body is composed of clinopyroxenite, olivine-bearing clinopyroxenite, serpentinite, and eclogite. Coarse-grained clinopy-

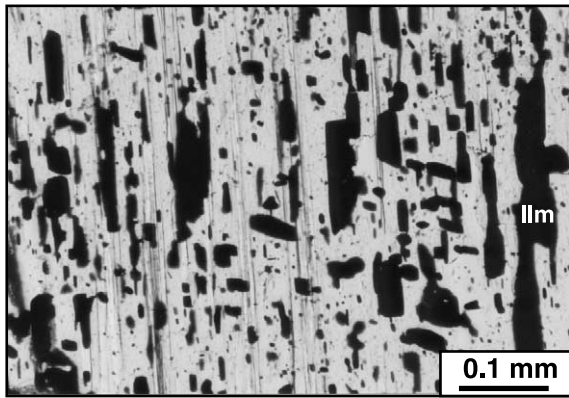


Fig. 1. Coarse-grained clinopyroxene showing exsolution lamellae of ilmenite (+Mg–Al–Cr titanomagnetite) from the Suoluoshu clinopyroxenite. Crossed polars.

roxene in clinopyroxenite contains ilmenite exsolution lamellae (Fig. 1). The eclogite layer (30 cm to several meters) within clinopyroxenite is composed of coarse-grained garnet, omphacite (~ 3 mm) and a fine-grained (0.15–0.5 mm) matrix of garnet, omphacite, quartz and rutile. Inclusions of quartz pseudomorphs after coesite (Fig. 2a) occur in coarse-grained garnets; the latter exhibit abundant exsolved rutile needles. Another example is the retrograded eclogite at Weihai, where porphyroblastic garnet relics contain both coesite inclusions and exsolved rutile needles.

In general, rutile (\pm minor apatite) needles or rods are restricted to cores and mantles of porphyroblastic garnets rather than occurring in the fine-grained matrix garnets; these rods are distributed along three crystallographically oriented planes in garnets of eclogite and clinopyroxenite

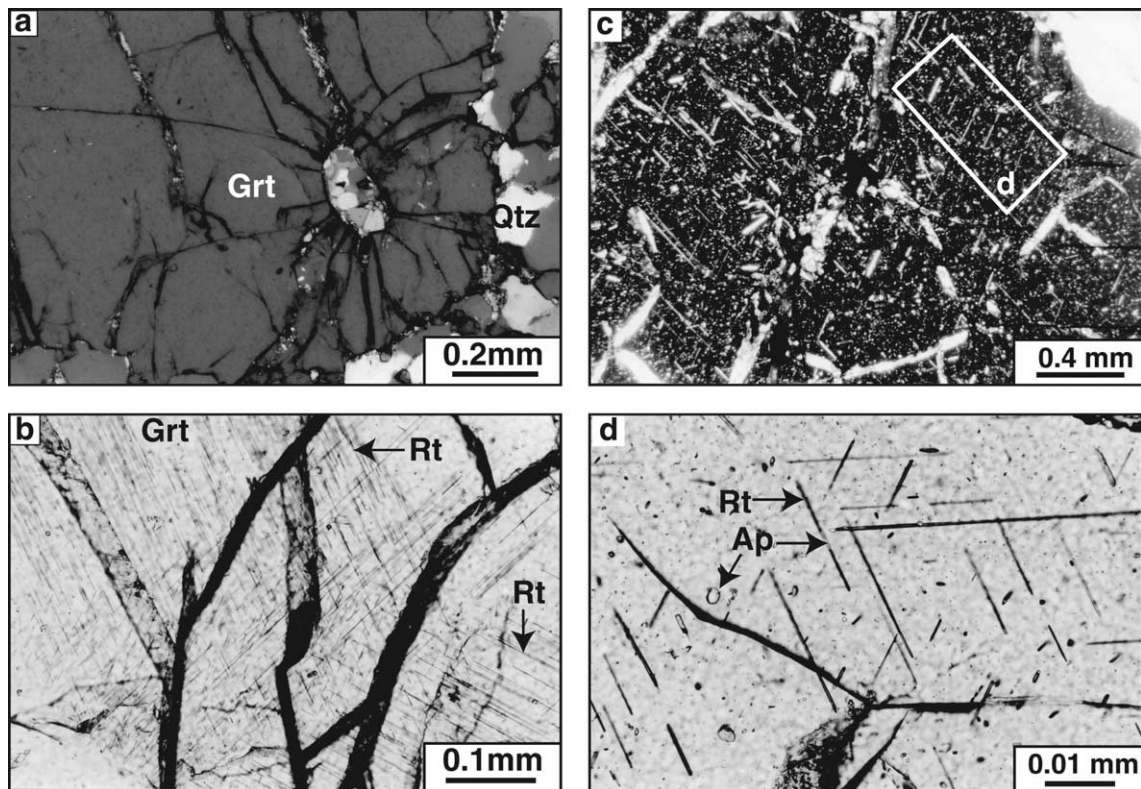


Fig. 2. Photomicrographs of garnets with exsolved rutile along crystallographically controlled planes and quartz inclusions. (a) Quartz pseudomorphs after coesite occur in porphyroblastic garnet from the Suoluoshu eclogite, Crossed polars. (b–d) Exsolved rutile rods in eclogitic garnet; (b) garnet from the Junan eclogite, plane light; (c) (crossed polars) and (d) (plane light) garnet from the Yangkou eclogite.

from the Rizhao, Yangkou, and Junan areas (Fig. 2b, c, d). Most rods are 8–300 μm long and $< 1\text{--}6 \mu\text{m}$ in diameter; apatite rods are $1\text{--}2 \times 2\text{--}10 \mu\text{m}$ in size [2,3,5]. Exsolved Cpx together with $\text{Rt} \pm \text{Ap}$ rods occur in garnet from the Yangkou eclogite as well as the Altyn Tagh garnet lherzolite. The Yangkou eclogite with majoritic garnet has been suggested to have formed at $> 7 \text{ GPa}$ based on the amount of rutile and pyroxene lamellae in garnet [5].

3. Experimental material and procedure

3.1. Starting material

The Hujialin body is composed of serpentinite and lenses of dunite and garnet clinopyroxenite.

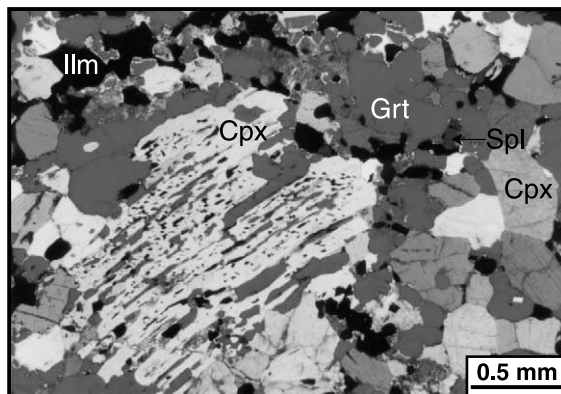


Fig. 3. Massive ilmenite-rich garnet clinopyroxenite with rare coarse-grained clinopyroxene in a fine-grained matrix consisting of clinopyroxene (Cpx), garnet (Grt), ilmenite (Ilm) and spinel (Spl). The matrix phases are identical to $\text{Cpx} + \text{Grt} + \text{Ilm} + \text{Mag} + \text{rare Spl}$ intergrowths. Crossed polars with a gypsum plate.

Table 1
Bulk and mineral analyses of starting material (Ilm-rich garnet clinopyroxenite)

Mineral	Host Cpx	Coarse-grained (0.3 vol%) exsolved phases			Matrix of Grt	Matrix of Cpx	RC ^a	Rock bulk ^b
		Grt	Ilm	Mag				
SiO ₂	54.13	39.76	0.00	0.00	39.64	55.28	48.66	46.89
TiO ₂	0.10	0.25	51.79	1.02	0.48	0.04	1.69	2.03
Cr ₂ O ₃	0.02	0.01	0.00	0.07	0.04	0.07	0.02	n.d.
Al ₂ O ₃	1.41	20.84	0.02	0.60	20.16	0.93	5.83	5.4
FeO	2.16	9.39	44.74	91.18	9.85	1.89	5.99	8.56
MnO	0.07	0.45	1.06	0.23	0.67	0.10	0.19	0.13
MgO	16.96	6.61	2.69	0.21	6.10	17.36	13.98	14.52
CaO	25.46	22.67	0.07	0.13	23.08	24.93	23.80	19.98
Na ₂ O	0.53	0.01	0.00	0.02	0.02	0.53	0.39	0.34
K ₂ O	0.03	0.00	0.00	0.00	0.01	0.01	0.02	0.15
LOI								1.19
Total	100.87	100.05	100.37	93.46	100.02	101.14	100.58	99.19
Vol	73	23	3	1				
Si	1.958	2.998	0.000	0.000	3.005	1.985	1.801	
Ti	0.003	0.014	0.971	0.029	0.027	0.001	0.047	
Cr	0.001	0.001	0.000	0.002	0.002	0.002	0.001	
Al	0.060	1.852	0.001	0.027	1.801	0.039	0.254	
Fe ³⁺			0.000	1.914				
Fe	0.065	0.592	0.933	1.000	0.624	0.057	0.185	
Mn	0.002	0.029	0.022	0.007	0.043	0.003	0.006	
Mg	0.914	0.743	0.100	0.012	0.689	0.929	0.772	
Ca	0.987	1.831	0.002	0.005	1.874	0.959	0.944	
Na	0.037	0.001	0.000	0.001	0.003	0.037	0.028	
K	0.001	0.000	0.000	0.000	0.000	0.001	0.001	
Total	4.027	8.061	2.029	3.000	8.068	4.012	4.039	

Mag (magnetite): $\text{Fe}_2\text{O}_3 = 61.53$, $\text{FeO} = 32.30$.

^a Recalculated bulk composition of $\text{Cpx} + \text{Grt} + \text{Ilm} + \text{Mag}$ intergrowths.

^b Analyzed by XRF.

Some clinopyroxenes of the garnet clinopyroxenites contain abundant exsolved garnet and ilmenite plate or rods. In order to understand phase relations between pyroxene and garnet in the natural system, Ti solubility in garnet and clinopyroxene, and origin of garnet clinopyroxenite showing exsolution microstructure, a well-investigated Ilm-rich garnet clinopyroxenite from Hujialin was selected as starting material [10]. The rock consists of rare coarse-grained clinopyroxene and a fine-grained matrix of Cpx+Grt+Ilm ± Spl ± Chl. Matrix clinopyroxene and garnet are 0.3 ± 0.1 and $0.05\text{--}0.4$ mm (most ~ 0.1 mm) in size, respectively. Ilmenite ($>5\%$) and minor green spinel occur as interstitial phases. Coarse-grained clinopyroxene (0.8–1.5 mm long) contains abundant oriented rods of garnet (20–23 vol%), ilmenite (\pm magnetite) (3–4 vol%) + a few grains of green spinel (Fig. 3). Most exsolved garnets are elongated plates or rods (up to 1.2×0.2 mm) parallel to {110} in the clinopyroxene; some exsolved garnets are variably sized bleb- and spindle-shaped grains. The ilmenite rods are 10–160 μm long; magnetite occurs as smaller, isolated rods or intergrowths with ilmenite and appears to be ex-

solved from early-formed ilmenite. The bulk compositions of the Ilm-rich garnet clinopyroxenite were analyzed by XRF (see Table 1). In order to determine whether starting minerals left in run products and whether the run products have reached equilibrium, compositions of minerals from this rock are also shown in Table 1. The rock composition is similar to recalculated bulk composition of intergrowths of Cpx (host)+Grt+Ilm (exsolved rods) except lower CaO and higher FeO.

3.2. Experimental procedure

Thin rock chips (0.1 mm thick) of the Ilm-rich garnet clinopyroxenite were checked by binocular microscope to ensure that the chips do not have fractures filled by secondary minerals. The chips were finely grounded in an agate mortar with ethanol for 2 h; the rock powder was dried in a vacuum oven at 200°C for 24 h. Six experiments were carried out using the multianvil high-pressure apparatus at the Geophysical Laboratory following the procedures described by Fei and others [17,21]. Small 8/3 and 18/11 cast assemblies were

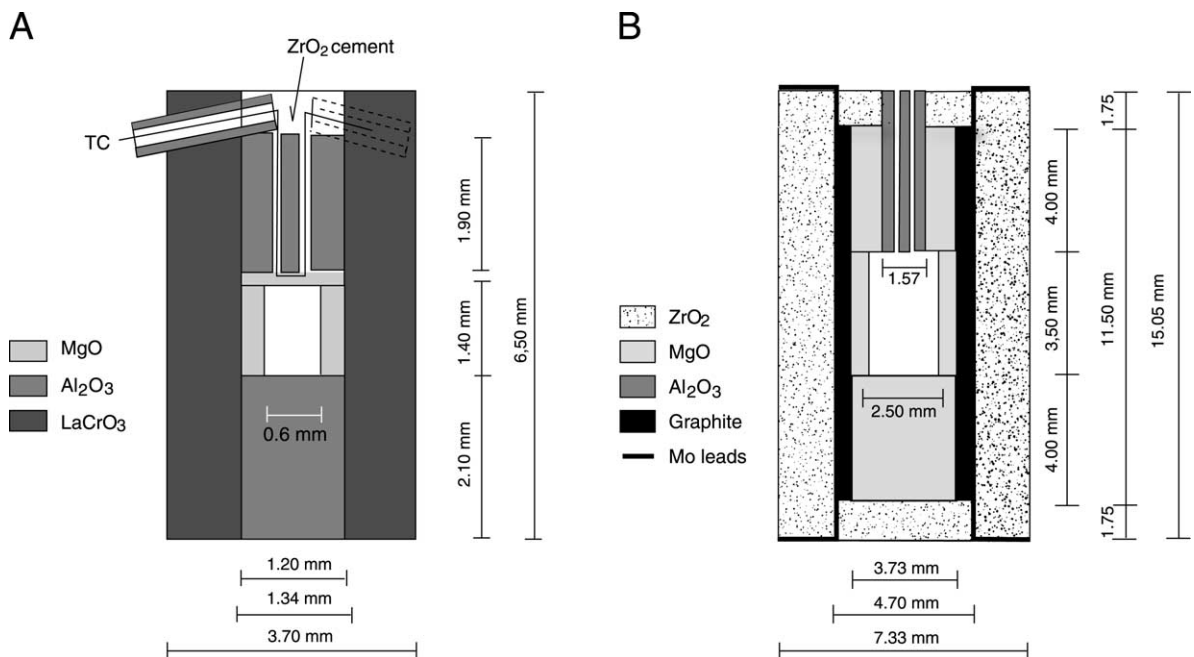


Fig. 4. Assemblies were used in the experiments. (A) Small 8/3 and (B) 18/11 cast.

used for experimental runs of 10 and 15 GPa at 1400°C and ≤ 5 GPa at 1000, 1300 and 1400°C, respectively (Fig. 4). For the small 8/3 assembly, rhenium capsules and rhenium foil heaters were used. Sample temperature was measured with a W5%Re–W26%Re thermocouple. Temperatures were controlled within 1°C of the setting temperature. We limit the sample length to less than 0.5 mm, in order to minimize the temperature gradient. The temperature gradient across the 0.5 mm sample length is about 30°C. For the 18/11 assembly, high temperatures were achieved by graphite furnaces. The sample was loaded into a graphite-lined, 2.5-mm platinum capsule. The temperature gradient in this large assembly is substantially smaller, less than 25°C across the entire sample length. The oxygen fugacity in the charge is partially controlled by the capsule materials. The rhenium capsule may provide more oxidized environment than the graphite-lined platinum capsule. No iron loss was detected in either capsule arrangement. In these experiments, pressure was first increased to the desired value at the rate of 5 GPa/h; subsequently the sample was heated to the desired temperature with a rate of 100°C/min. At the end of each experiment, the charge was quenched in a few seconds to room temperature by shutting off the power to the apparatus. The pressure was then slowly decreased over a period of 5–8 h or longer.

3.3. Experimental results

Most of the runs were carried out at 1400°C and pressure ranges from 5 to 15 GPa; other experiments at low pressures of 4 and 5 GPa were

run at 1000 and 1300°C (Table 2). Several characteristics of these experiments are shown. (1) The reaction rate was significant in these 2–3 days experiments, and compositions of recrystallized phases are rather homogeneous. (2) The size of neoblastic grains in run products is coarse enough for detailed microprobe analysis. (3) The compositions of run products are different from the minerals of starting material, indicating no original phase left in the products. (4) Except for minor melt in experiments at 1300–1400°C and 5 GPa, the run products consist of garnet+clinopyroxene \pm ilmenite (or rutile). These features suggest that the experiments may have nearly reached equilibrium (Fig. 5).

The average compositions (4–15 analyses) of neoblastic garnet, clinopyroxene, ilmenite and melt (Table 3) were analyzed using JEOL JXA-8800L Superprobe at the Geophysical Laboratory, Carnegie Institution of Washington and JEOL 733 Superprobe at Stanford University, both with five spectrometers employing the wavelength dispersive system (WDS). Operating conditions were 15 kV and 12 nA beam current. Uncertainties of these superprobe analyses depend on oxide content, from 0.1, 1, and 10 to 100 wt%, their uncertainties are about 10, 4.5, 2.5 and 1%, respectively. The run product at 15 GPa and 1400°C consists of majoritic garnet ($\sim 46\%$) and clinopyroxene ($\sim 54\%$). The garnet contains 4.44 ± 0.1 wt% TiO₂, 41% majorite component, and is characterized by high Si, Ti, Ca and Na, and a deficiency in octahedral Al. Clinopyroxene is nearly stoichiometric diopside with low Al₂O₃ (~ 0.9 wt%) and TiO₂ (~ 0.2 wt%). The run product of the experiment at 10 GPa and 1400°C is similar

Table 2
Experimental run conditions and products

Run no.	<i>T</i> (°C)	<i>P</i> (GPa)	Time	Assembly	Products (vol%)	TiO ₂ wt% (average)
696	1400	15	48 h	small 8/3	Grt (46), Cpx (54)	4.44 (Grt); 0.20 (Cpx)
698	1400	10	48 h	small 8/3	Grt (30), Cpx (68), Ilm	2.60 (Grt); 0.33 (Cpx)
697	1400	5	48 h	18/11 cast	Cpx (80), melt (20) ^a	0.36 (Cpx)
712	1300	5	48 h	18/11 cast	Grt (22), Cpx (75), Rt/Ilm	1.67 (Grt); 0.53 (Cpx)
701	1000	5	48 h	18/11 cast	Grt (22), Cpx (75), Rt	0.86 (Grt); 0.24 (Cpx)
717	1000	4	72 h	18/11 cast	Grt (20), Cpx (76) Ilm	0.79 (Grt); 0.28 (Cpx)

^a Quenched melt, locally with Fe–Ti-rich, tiny rods (< 1 μ m).

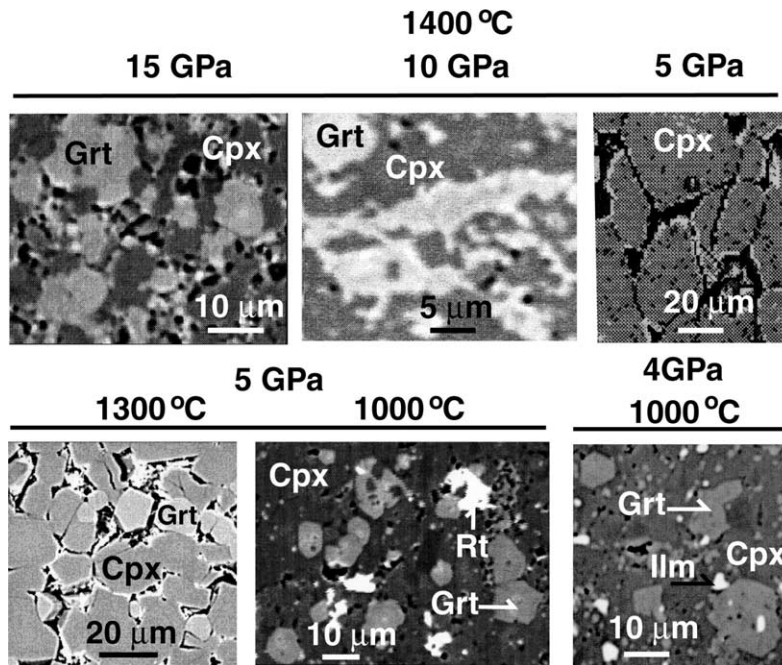


Fig. 5. Back-scattered electron image of experimental products showing grain size and equilibrium texture.

Table 3
Mineral analyses of experimental products

Exp no.	717			701		712		697	698		696		
Mineral	Grt	Cpx	Ilm ^a	Grt	Cpx	Grt	Cpx	Cpx	melt	Grt	Cpx	Grt	Cpx
SiO ₂	39.80	52.84	0.73	41.11	54.04	40.17	53.01	53.09	45.87	40.86	54.73	40.42	54.99
TiO ₂	0.79	0.28	38.74	0.86	0.24	1.67	0.53	0.36	5.28	2.60	0.33	4.44	0.17
Cr ₂ O ₃	0.47	0.14	0.76	0.52	0.13	0.80	0.19	0.32	0.12	0.55	0.32	0.53	0.06
Al ₂ O ₃	19.77	1.87	1.02	21.04	2.23	19.53	3.40	4.25	9.23	16.29	1.50	11.26	0.91
FeO	13.85	4.68	49.22	13.48	4.01	10.32	4.66	3.13	6.96	12.66	4.36	10.33	3.30
MnO	0.31	0.05	0.12	0.36	0.06	0.27	0.07	0.07	0.14	0.25	0.05	0.14	0.02
MgO	10.54	15.36	5.48	11.69	16.12	12.46	15.49	16.15	11.52	11.43	16.44	12.60	17.15
CaO	13.99	22.95	0.91	12.79	23.77	13.23	21.83	22.26	19.65	15.07	22.28	19.29	22.86
Na ₂ O	0.05	0.73	0.03	0.06	0.62	0.04	0.70	0.62	0.60	0.10	0.65	0.15	0.74
K ₂ O	0.04	0.05	0.04	0.03	0.03	0.00	0.05	0.02	0.02	0.01	0.03	0.02	0.06
Total	99.72	98.95	97.05	101.94	101.26	98.48	99.92	100.05	99.40	99.81	100.69	98.89	100.17
Si	3.003	1.959	0.018	3.006	1.953	3.014	1.937	1.921		3.080	1.981	3.101	1.993
Ti	0.045	0.009	0.709	0.047	0.007	0.094	0.014	0.010		0.147	0.009	0.256	0.005
Cr	0.035	0.004	0.015	0.030	0.004	0.047	0.005	0.009		0.033	0.009	0.032	0.002
Al	1.758	0.082	0.029	1.814	0.095	1.726	0.146	0.181		1.448	0.064	1.018	0.039
Fe	0.874	0.145	1.002	0.825	0.121	0.647	0.142	0.095		0.798	0.132	0.663	0.100
Mn	0.020	0.002	0.002	0.022	0.002	0.017	0.002	0.002		0.016	0.001	0.009	0.001
Mg	1.185	0.849	0.199	1.274	0.868	1.394	0.844	0.871		1.284	0.887	1.441	0.927
Ca	1.131	0.912	0.024	1.002	0.920	1.063	0.855	0.863		1.217	0.864	1.586	0.888
Na	0.007	0.052	0.001	0.008	0.043	0.006	0.049	0.043		0.015	0.045	0.022	0.052
K	0.004	0.002	0.001	0.003	0.001	0.000	0.002	0.001		0.001	0.001	0.002	0.003
Total	8.062	4.016	2.000	8.031	4.014	8.009	3.998	3.996		8.040	3.996	8.130	4.009

^a Formula of ilmenite was calculated by two cations, it includes 0.505 Fe³⁺ and 0.497 Fe²⁺. Formula of garnet and clinopyroxene was calculated by O₁₂ and O₆ respectively.

to that of 15 GPa, but contains traces of very fine-grained ilmenite that are difficult to analyze. The majorite component and TiO_2 content of garnet decrease to 24 mol% and 2.6 ± 0.1 wt% respectively (Table 4). Garnet contains higher Cr_2O_3 (~ 0.5 wt%) than coexisting clinopyroxene, but no clear variation from 10 to 15 GPa. Clearly, the TiO_2 , CaO and MgO contents of garnet increase from 10 to 15 GPa at 1400°C, but Al_2O_3 and FeO decrease. This is consistent with Irifune's experiment that with increasing pressure, garnet becomes more calcium-rich and also deviates from normal Al_2O_3 stoichiometry towards the pyroxene join $\text{Ca}(\text{MgFe})\text{Si}_2\text{O}_6$ – $(\text{MgFe})\text{SiO}_3$ [16].

The product of the experiment at 5 GPa and 1400°C consists of mainly clinopyroxene and minor melt (~ 20 vol%), indicating that P – T conditions of the run were slightly higher than the solidus for the bulk composition. Most clinopyroxene grains are 30–50 μm in size, and contain the highest Al_2O_3 (4.25 wt%) among all six runs. Melt is much higher in TiO_2 (5.28 wt%), Al_2O_3 (9.23 wt%), FeO (6.96 wt%) and lower in SiO_2 , MgO, and CaO compared with the coexisting clinopyroxene. Other experiments at 1000 and 1300°C at 5 GPa, and 1000°C at 4 GPa grew a discrete titanian phase (rutile or ilmenite) in addition to Grt+Cpx. Garnet of these experiments contains very minor (5–11 mol%) majorite component, and has lower TiO_2 , CaO and MgO contents in comparison with products of high-pres-

sure experiments at 10 and 15 GPa. The Al content of clinopyroxene decreases with pressure but increases with temperature (Fig. 5). Rutile is present only in the run products of 1000 and 1300°C at 5 GPa; ilmenite appears in the run products of 1000°C and 4 GPa, and contains 5.5 wt% MgO and 1 wt% Al_2O_3 . Minor ilmenite also appears in the run products of 1300°C and 5 GPa in the charge close to the appearance of melt $\leq 1\%$. The presence of the minor Ti-bearing phases is related to the solubility of Ti in garnet and clinopyroxene. The solubilities of Ti in garnet, particularly in clinopyroxene are relatively low at low temperatures. By mass balance, the minor Ti-bearing phases are expected to be present at low temperatures.

4. Discussion

4.1. TiO_2 solubility in garnet and clinopyroxene

Previous experiments on Ti solubility in garnet and clinopyroxene used Fe-rich and Mg-rich eclogites as starting materials and were run at 2.0–5.5 GPa, 1100–1440°C [9]. These experiments yielded garnet, clinopyroxene, rutile and melt in run products; Ti solubility in garnet increased with increasing temperature and pressure, but was mainly pressure dependent. Titanium solubility in clinopyroxene increased with increasing tem-

Table 4
Compositions and end-members of garnets ($\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$)

		1000/4	1000/5	1300/5	1400/10	1400/15
C group	Si	3.00	3.00	3.00	3.00	3.00
	Al					
B group	Si	0.00	0.01	0.01	0.08	0.10
	Al+Cr	1.79	1.84	1.77	1.48	1.05
	Ti	0.05	0.05	0.10	0.15	0.26
	M^{2+}	0.16	0.10	0.12	0.29	0.59
A group	Na	0.01	0.01	0.01	0.02	0.02
	Ca	1.13	1.00	1.06	1.22	1.59
	M^{2+}	1.92	2.02	1.94	1.80	1.52
Total		8.06	8.03	8.01	8.04	8.13
$\text{Ca}_2\text{Na}(\text{SiAl})\text{Si}_3\text{O}_{12}$		0.0	1.0	1.0	2.1	2.3
$\text{M}_3(\text{MTi})\text{Si}_3\text{O}_{12}$		5.3	5.1	10.1	15.6	29.7
$\text{M}_3(\text{MSi})\text{Si}_3\text{O}_{12}$		0.0	0.0	0.0	6.3	9.1
$\text{M}_3\text{Al}_2\text{Si}_3\text{O}_{12}$		94.7	93.9	88.9	76.0	58.9

perature, but decreased with elevated pressure. Titanium partitioning between Grt and Cpx was demonstrated to be a function of P , T , and bulk composition.

Our experimental results show that Ti solubility in garnet is high at high pressure, and Ti content of garnet has a pronounced positive correlation with pressure between 5 and 15 GPa (Fig. 6). TiO₂ contents of garnets increase from 0.79 wt% at 1000°C and 4 GPa to 4.44 wt% at 15 GPa, 1400°C. At a constant pressure of 5 GPa, the Ti content of garnet has a positive temperature dependence; garnet at 1300°C contains higher TiO₂ (1.67 wt%) than that at 1000°C (0.86 wt%). At 15 GPa, about 95 wt% TiO₂ of the starting composition is incorporated in garnet and 5 wt% TiO₂ is contained in clinopyroxene; no discrete Ti phase was found. Minor Ti-bearing phases including ilmenite and rutile are present in most run products except for 15 and 5 GPa at 1400°C. Very minor, tiny grains of FeTiO₃ are present at 10 GPa, 1400°C and of rutile at 1000°C and 5 GPa. In contrast to the garnet, the TiO₂ content of clinopyroxene coexisting with garnet is low, ranging from 0.17 to 0.53 wt%, and has no significant pressure dependence. The TiO₂ content of clinopyroxene decreases from 0.33 to 0.17 wt% from 10 to 15 GPa at 1400°C, and slightly increases with increasing temperature at a constant pressure of 5 GPa. The ratio of Grt_{Ti}/Cpx_{Ti}, however, has a pronounced increase with pressure, from ~6.7 at 5 GPa to 51.2 at 15 GPa. Our results are mostly consistent with Fett's experiments at low pressures of 2.0–5.5 GPa [9].

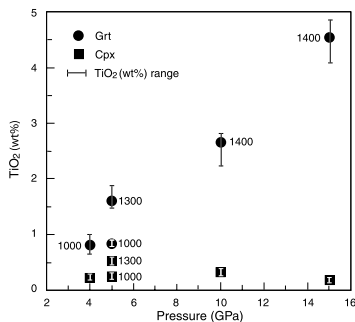


Fig. 6. TiO₂ contents of garnets and clinopyroxenes at various pressures and temperatures.

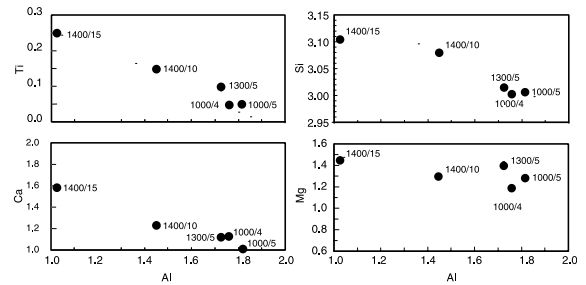


Fig. 7. Plots of Ti, Ca, Si and Mg versus Al of garnet produced at various P - T conditions showing Ti, Ca, Si and Mg positive and Al negative correlation with pressure.

As described above, Ti, Ca, Mg, Si and Na per formula unit (pfu) of garnet increase with decreasing Al, suggesting that the principal substitutions are $\text{Ca}^{2+}\text{Ti}^{4+} \rightarrow 2\text{Al}^{3+}$ and $\text{Si}^{4+}\text{Mg}^{2+} \rightarrow 2\text{Al}^{3+}$ (Table 4; Fig. 7), and only subordinate $\text{Na}^{1+}\text{Si}^{4+} \rightarrow \text{Ca}^{2+}\text{Al}^{3+}$ or $\text{Na}^{1+}\text{Ti}^{4+} \rightarrow \text{Ca}^{2+}\text{Al}^{3+}$. In general terms, the solid solution relationships can be described in $M_3(\text{Al}_{2-2x}\text{Mg}_x\text{Si}_x)\text{Si}_3\text{O}_{12}$, $M_3(\text{Al}_{2-2x}\text{Ca}_x\text{Ti}_x)\text{Si}_3\text{O}_{12}$ ($0 \leq x \leq 1$, $M = \text{Mg, Fe, Ca}$), and $(\text{Na}_x\text{Ca}_{3-x})(\text{Al}_{2-x}\text{Si}_x)\text{Si}_3\text{O}_{12}$ or $(\text{Na}_x\text{Ca}_{3-x})(\text{Al}_{2-x}\text{Ti}_x)\text{Si}_3\text{O}_{12}$ ($0 \leq x \leq 2$), respectively. Sobolev and Lavrentev [22] indicated that garnet contains 0.01–0.22 wt% Na₂O based on 124 analyses of garnets from diamond inclusions, xenoliths of peridotite and eclogite within kimberlitic pipes, and metamorphic complexes. They suggested NaSi rather than NaTi substitution for CaAl to explain the high Na content of garnet from diamond-bearing eclogites and inclusions in diamond. Presence of exsolved apatite rods in garnet suggests that phosphorus enter the garnet structure according to the coupled substitution $\text{Na}^{1+}\text{P}^{5+} \rightarrow \text{Si}^{4+}\text{Ca}^{2+}$.

4.2. Significance of Ti-bearing phase exsolution in garnet and in clinopyroxene

Some garnets in ultramafic xenoliths within diamond-bearing kimberlite contain exsolved pyroxene lamellae along the {111} garnet crystallographic plane [23]. If the original garnet had the composition Grt₇₀Cpx₃₀, such as those in the xenolith JX-25 reported by Haggerty and Sautter [22], it could be stable at pressures of 10–12

GPa, based on experimental phase relations along the join $\text{MgSiO}_3\text{--Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. The precursor of Grt+Cpx intergrowths has been suggested to be a majoritic garnet derived from >300 km.

The investigated garnet pyroxenite and eclogite, in which garnets contain exsolved rutile, formed at least in the coesite stability field. Ultrahigh-*P* metamorphic evidences of these rocks include the following: (1) Apatite and pyroxene together with rutile occur as exsolved rods in garnet, indicating the previous presence of a majoritic garnet precursor [5]. (2) Inclusions of coesite or quartz pseudomorphs after coesite and exsolved rutile are present in a single garnet crystal (Fig. 2a) or in different grains in a single thin section. (3) Ultramafic rocks hosting the eclogite were subjected to UHP metamorphism at 4.0–6.7 GPa and 750–900°C [4] based on Al partitioning in orthopyroxene. Primary garnet, prior to the exsolution of Ti-bearing phase, could contain a considerable amount of TiO_2 . During isothermal decompression, TiO_2 would exsolve from garnet along crystallographically controlled planes, as Ti^{VI} is not stable in garnet crystal structure at low pressures. Most rutile rods orientated along {111} and the rods connect Al^{VI} sites in the garnet structure. A possible reaction responsible for the formation of rutile needle in garnet is $M_3(\text{MTi})\text{Si}_3\text{O}_{12} + \text{CaAl}_2\text{SiO}_6 + \text{SiO}_2 = M_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{TiO}_2 + \text{CaMSi}_2\text{O}_6$. Here $M = \text{Ca}, \text{Mg}, \text{Fe}$.

Our experiments on the ilmenite-rich garnet clinopyroxenite ($\text{CaO--MgO--FeO--TiO}_2\text{--Al}_2\text{O}_3\text{--SiO}_2$) indicate that Ti contents of garnet coexisting with clinopyroxene are strongly pressure dependent. The major coupled substitutions are $\text{Ca}^{2+}\text{Ti}^{4+} \rightarrow 2\text{Al}^{3+}$ and $\text{Si}^{4+}\text{Mg}^{2+} \rightarrow 2\text{Al}^{3+}$. Rutile exsolution in garnet is similar to the pyroxene exsolution in garnet; both are derived from a majoritic garnet. The amount of orientated rutile rods in garnet is highly pressure dependent, although it is also related to bulk composition and temperature.

Ilmenite lamellae or rods in coarse-grained clinopyroxene were found in some clinopyroxenites with or without garnet in the Hujialin and Suoluoshu bodies. Our experiments indicate that TiO_2 mostly dissolved in garnet rather than clinopyroxene, and Ti partitioning between garnet and cli-

nopyroxene has a positive correlation with pressure. Variation of TiO_2 content in clinopyroxene is not as large as garnet with pressure change; therefore, the TiO_2 content of clinopyroxene is not a good indicator of pressure. Ilmenite exsolution would occur during increasing pressure and/or decreasing temperature. However, in a garnet-absent xenolith in kimberlite, an intergrowth of clinopyroxene+ilmenite may have had a precursor homogeneous majoritic garnet solid solution, as documented by experiments of Ringwood and Lovering [24]; at such high-pressure conditions, pyroxene transforms to a majoritic garnet structure that accommodates abundant titanium.

5. Concluding remarks

As exsolved phases, ilmenite in clinopyroxene, and rutile in garnet from eclogite and garnet clinopyroxenite have been commonly identified in the Sulu UHP terrane. The exsolution microstructure, as a record of an early history of UHP metamorphism, is only observed in porphyroblastic (or porphyroclastic) minerals, rather than in the matrix minerals. Experiments using Ilm-rich garnet clinopyroxenite as starting material at a *P–T* range of 4–15 GPa and 1000–1400°C indicate that Ti solubility in coexisting garnet and clinopyroxene depends on bulk composition and *P–T* conditions. Titanium solubility in clinopyroxene has a negative correlation with pressure at constant temperature, and increases with temperature at given pressure, but the variation is limited in a small range of 0.17–0.53 wt% TiO_2 . Titanium solubility in garnet (0.8–4.5 wt%) between 5 and 15 GPa shows a pronounced positive correlation with pressure, according to the principal coupled substitutions of $\text{Ca}^{2+}\text{Ti}^{4+} \rightarrow 2\text{Al}^{3+}$. Minor ilmenite exsolution in clinopyroxene is related to the process of increasing pressure and/or decreasing temperature. In contrast, rutile exsolution is mainly due to decompression, although temperature may have similar effect. The nature of rutile exsolution in garnet is the same as pyroxene exsolution in garnet. Therefore, the amount of such exsolved lamellae is a potential indicator of UHP metamorphism at mantle depths.

Acknowledgements

We thank Willem van Westrenen and K. Haddad of the Geophysical Laboratory, Carnegie Institution of Washington, for their help at experimental study and probe analysis in 2002. We also are grateful to W.G. Ernst for a critical review of the manuscript. This research was supported by NSF EAR 0003355. **[BOYLE]**

References

- [1] L. Dobrzhinetskaya, H.W. Green, S. Wang, Alpe Arami: a peridotite massif from depths of more than 300 kilometers, *Science* 271 (1996) 1841–1846.
- [2] R.Y. Zhang, J.G. Liou, B.L. Cong, Petrogenesis of garnet-bearing ultramafic rocks and associated eclogites in the Su-Lu ultrahigh-*P* metamorphic terrane, eastern China, *J. Metamorph. Geol.* 12 (1994) 169–186.
- [3] R.Y. Zhang, J.G. Liou, Exsolution lamellae in minerals from ultrahigh-*P* rocks, *Int. Geol. Rev.* 41 (1999) 981–993.
- [4] R.Y. Zhang, J.G. Liou, J.S. Yang, T.-F. Yui, Petrochemical constraints for dual origin of garnet peridotites from the Dabie-Sulu UHP terrane, eastern-central China, *J. Metamorph. Geol.* 18 (2000) 149–166.
- [5] K. Ye, B. Cong, D. Ye, The possible subduction of continental material to depths greater than 200 km, *Nature* 407 (2000) 734–736.
- [6] P. Ulmer, V. Trommsdorff, Titanium content of mantle olivine; an experimental study to 10 GPa, *Terra* 9 (1997) 39.
- [7] L. Dobrzhinetskaya, K.N. Bozhilov, H.W. Green, The solubility of TiO₂ in olivine: implications for the mantle wedge environment, *Chem. Geol.* 163 (2000) 325–338.
- [8] D. Tinker, C.E. Leshner, Solubility of TiO₂ in olivine from 1 to 8 GPa, *EOS Trans. AGU* 82 (2001) F1393.
- [9] A. Fett, Partitioning of Ti between garnet and clinopyroxene in high pressure experiments and high pressure rocks – a comparison, Ph.D. thesis, Joh. Gutenberg-Universität Mainz, Germany, 1995.
- [10] R.Y. Zhang, J.G. Liou, Clinopyroxenite from the Sulu ultrahigh-pressure terrane, eastern China: origin, evolution of garnet exsolution in clinopyroxene, *Am. Mineral.* (2003) 1591–1600.
- [11] H.-J. Massonne, H.J. Bartsch, An unusual garnet pyroxenite from the Granulitgebirge, Germany: origin in the transition zone (>400 km Earth's depth) or in a shallower upper mantle region?, *Int. Geol. Rev.* 44 (2002) 779–796.
- [12] M. Akaogi, S. Akimoto, Pyroxene-garnet solid-solution equilibria in the systems Mg₄Si₄O₁₂–Mg₃Al₂Si₃O₁₂ and Fe₄Si₄O₁₂–Fe₃Al₂Si₃O₁₂ at high pressures and temperature, *Phys. Earth Planet. Inter.* 15 (1977) 90–106.
- [13] M. Akaogi, S. Akimoto, High-pressure phase equilibria in a garnet lherzolite, with special reference to Mg²⁺–Fe²⁺ partitioning among constituent minerals, *Phys. Earth Planet. Inter.* 19 (1979) 31–51.
- [14] M. Kanzaki, Ultrahigh-pressure phase relations in the system Mg₄Si₄O₁₂–Mg₃Al₂Si₃O₁₂, *Phys. Earth Planet. Inter.* 49 (1987) 168–175.
- [15] T. Gasparik, Melting experiments on the enstatite–pyrope join at 80–152 kbar, *J. Geophys. Res.* 97 (1992) 15181–15188.
- [16] T. Irifune, T. Sekine, A.E. Ringwood, W.O. Hibberson, The eclogite–garnetite transformation at high pressure and some geophysical implications, *Earth Planet. Sci. Lett.* 7 (1986) 245–256.
- [17] Y. Fei, C.M. Bertka, Phase transitions in the Earth's mantle and mantle mineralogy, in: Y. Fei, C.M. Bertka, B.O. Mysen (Eds.), *Mantle Petrology: Field Observation and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd*, The Geochemical Society Publication 6, 1999, pp. 189–207.
- [18] L. Liu, Y. Sun, P. Xiao, Z. Che, J. Luo, D. Chen, Y. Wang, A. Zhang, L. Cheng, Y.-H. Wang, Discovery of ultrahigh-pressure magnesite-bearing garnet lherzolite (>3.8 GPa) in the Altyn Tagh, northwest China, *Chinese Sci. Bull.* 47 (2002) 881–886.
- [19] R. Kretz, Symbols for rock-forming minerals, *Am. Mineral.* 68 (1983) 277–279.
- [20] R.Y. Zhang, J.G. Liou, Partial transformation of gabbro to coesite-bearing eclogite from Yangkou, the Sulu terrane, eastern China, *J. Metamorph. Geol.* 15 (1997) 183–202.
- [21] C.M. Bertka, Y. Fei, Mineralogy of Martian interior up to core–mantle boundary pressure, *J. Geophys. Res.* 102 (1997) 5251–5264.
- [22] N.V. Sobolev, Y.G. Lavrentev, Isomorphous sodium admixture in garnets formed at high pressures, *Contrib. Mineral. Petrol.* 31 (1971) 1–12.
- [23] S.E. Haggerty, V. Sautter, Ultradeep (greater than 300 kilometers) ultramafic upper mantle xenoliths, *Science* 248 (1990) 993–996.
- [24] A.E. Ringwood, J.F. Lovering, Significance of pyroxene–ilmenite intergrowths among kimberlite xenoliths, *Earth Planet. Sci. Lett.* 7 (1970) 371–375.