



Partitioning of trace elements between Na-bearing majoritic garnet and melt at 8.5 GPa and 1500–1900 °C



Andrey V. Bobrov^{a,b,*}, Yuriy A. Litvin^b, Anastasia V. Kuzyura^b, Anna M. Dymshits^c, Teresa Jeffries^d, Luca Bindi^e

^a Department of Petrology, Geological Faculty, Moscow State University, Leninskie gory, Moscow 119234, Russia

^b Institute of Experimental Mineralogy, Russian Academy of Sciences, Institutskaya Str. 4, Chernogolovka, 142432, Russia

^c Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Ak. Koptuyuga pr. 3, Novosibirsk 630090, Russia

^d Natural History Museum, Cromwell Road, London SW7 5BD, UK

^e Dipartimento di Scienze della Terra, Università di Firenze, I-50121 Firenze, Italy

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ABSTRACT

New experimental data on trace element partitioning between Na-bearing majoritic garnet and melt at $P = 8.5$ GPa and $T = 1500$ – 1900 °C applicable to partial melting of Na-rich eclogite are presented. We have found that Na-bearing garnet is a liquidus phase of the system at 1850–1650 °C being accompanied by enstatitic pyroxene at lower temperatures. With decreasing temperature, Na concentration in garnet increases up to >1 wt.% Na₂O due to progressive incorporation of a Na majorite component (Na₂MgSi₅O₁₂). Most of the studied trace elements are incompatible, except for Er, Tm, Yb (in some runs), Lu, and Sc (in all runs), which are distributed into garnet. The main characteristic of the trace-element partitioning in our experiments is a different behaviour of the LREE (La, Ce, Pr) in comparison with MREE and HREE (Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu). In particular, a significant increase of D values for LREE with the increase of Na₂O concentration in garnet is observed. As predicted from lattice strain, partitioning coefficients for REEs entering the X site of garnet exhibit a near-parabolic dependence on ionic radius. The results of the study are applied to the formation of inclusions of Na-bearing majoritic garnets in diamonds, and equilibrium melts significantly enriched in LREEs.

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1. Introduction

Partitioning of trace and rare-earth elements between mantle minerals and melts at high pressures and temperatures is of key importance for all geochemical models involving melting of the Earth's mantle. Among these minerals, garnet has the most significant influence on trace element signatures of mantle-derived magmas produced by melting of both ultramafic (garnet peridotite) and mafic (MORB-like eclogite) substrates. A large number of previous studies have demonstrated the effects of pressure, temperature, and the composition of garnet (Klemme et al., 2002; Pertermann et al., 2004; van Westrenen et al., 1999, 2000, 2001) and melt (Kuzyura et al., 2010; Prowatke and Klemme, 2005; Salters et al., 2002) on mineral/liquid partitioning coefficients.

Experimental studies performed at low pressures of ~ 3 GPa using magnesium-rich starting materials (Hauri et al., 1994; Johnson, 1998; Salters and Longhi, 1999; Shimizu and Kushiro, 1975; van Westrenen et al., 1999) demonstrated that garnet/melt partitioning coefficients for LREE were much lower than those for HREE (so-called “garnet signature”), and liquids in equilibrium with garnets were complementarily depleted in HREE and enriched in LREE. According to the results of

experiments performed at higher pressures of 5–9 GPa (Draper et al., 2003) and 10–24 GPa (Corgne et al., 2012; Kato et al., 1988; Ohtani et al., 1989; Yurimoto and Ohtani, 1992) corresponding to the conditions of the formation of majoritic garnet in the lowermost upper mantle and transition zone, garnet/melt partition coefficients for HREE decrease substantially with increasing pressure, while those for LREE increase slightly.

Addition of grossular component to garnet structure (increase of Ca content in the X site of garnet) results in an increase of garnet/melt partitioning coefficients for almost all trace elements, but especially LREE (Klemme et al., 2002; Pertermann et al., 2004; van Westrenen et al., 1999). This can be explained by incorporation of the larger cation (calcium, 1.12 Å) instead of magnesium (0.89 Å) in the X site of pyrope garnet. Since Ca-rich garnets in the mantle are often eclogitic and most of majoritic garnets with Si atoms per formula units (pfu) greater than 3.07 also belong to the eclogitic assemblage, these observations are applicable to high-pressure melting of eclogite and pyroxenite. Majoritic garnets of such type demonstrate unusually high Na₂O concentrations ranging up to ~ 1.4 wt.% (Stachel et al., 2000). Recently Harte and Cayzer (2007) documented evidence of exsolution textures involving clinopyroxene and majoritic garnet which suggest original majoritic garnets with up to 2.16 wt.% Na₂O. According to experimental data (Bobrov et al., 2008; Dymshits et al., 2013; Gasparik, 1996, 2002; Ono and Yasuda, 1996), sodium-rich garnets can be stable at P – T conditions near the solidus of eclogite.

* Corresponding author at: Department of Petrology, Geological Faculty, Moscow State University, Leninskie gory, Moscow 119234, Russia.

E-mail address: archi@geol.msu.ru (A.V. Bobrov).

Table 1
Run conditions and products of experiments at 8.5 GPa.

Run	T (°C)	Duration, min	Phase assemblage (vol %)
2321	1900	30	L (100)
2326	1850	40	L (90) + Grt (10)
2323	1800	60	L (75) + Grt (25)
2322	1750	60	L (70) + Grt (30)
2327	1700	60	L (60) + Grt (40)
2325	1650	90	L (50) + Grt (50)
2324	1600	90	L (40) + Grt (50) + En (10)
2328	1550	90	L (25) + Grt (60) + En (15)
2329	1500	90	Grt (70) + En (20) + NaPx (10)

Abbreviations: T, temperature; L, alkaline aluminosilicate melt (products of melt quenching); Grt, Na-bearing majoritic garnet; En, enstatite-rich pyroxene; NaPx, sodium-rich pyroxene close to Na₂MgSi₅O₁₂. Phase proportions were determined on the basis of quantitative analysis of BSE images.

Experimental studies of the model system pyrope Mg₃Al₂Si₃O₁₂ (Prp)–Na-majorite Na₂MgSi₅O₁₂ (NaMaj) under *P*–*T* conditions of diamond formation (7.0 and 8.5 GPa) (Bobrov et al., 2008) provided evidence for significant sodium incorporation in garnet (0.3–0.6 wt.% Na₂O). The highest sodium concentrations of >1.5 wt.% Na₂O (~12 mol% of Na₂MgSi₅O₁₂) were obtained at *P* = 8.5 GPa near the solidus of the system.

Our experiments were aimed at the study of trace element partitioning between Na-bearing majoritic garnet and melt at *P* = 8.5 GPa and *T* = 1500–1900 °C. As the ionic size of sodium (1.18 Å; Shannon, 1981) is larger than those of both magnesium and calcium, it may be expected that Na incorporation in garnet solid solutions may also affect partition coefficients. Experiments were carried out for Prp₅₀NaMaj₅₀ (mol%) starting composition, at which the highest Na concentrations in garnet were obtained (Bobrov et al., 2008). Temperature variations between the runs allowed us to synthesize garnets with different Na₂O concentrations from 0.2 to >1.0 wt.%. The obtained

results were fitted to the lattice-strain model (Blundy and Wood, 1994, 2003) that allows calculation of partition coefficients for trace elements entering the X site of the garnet structure.

2. Experimental and analytical techniques

Homogenized mixtures of pyrope Mg₃Al₂Si₃O₁₂ and Na-majorite Na₂MgSi₅O₁₂ gels prepared by the nitrate gelling method (Hamilton and Henderson, 1968) were used as starting material. Gels were mixed in ethanol in equal mole proportions. The major-element composition of the starting material (wt.%) is SiO₂ 59.65, Al₂O₃ 12.65, MgO 20.01, Na₂O 7.69. A trace-element mixture of 30 mg each of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Hf, Zr, Nb, Sc, Ta, Pb, Zn oxides, RbCl and Sr-, Ba-, and Li-carbonates was prepared and homogenized by prolonged grinding in the presence of ethanol, dried and then added to the aluminosilicate mixture in a weight ratio of 2/98. The starting aluminosilicate and the trace-element mixtures were blended, homogenized thoroughly during 1 h, and then dried for a few days at a temperature of 105 °C and kept in a desiccator.

Experiments were carried out on a toroidal “anvil-with-hole” apparatus with cells made of lithographic stone (limestone) (Litvin, 1991). We used quasi-isothermal cells with a sample volume of 2.5–3 mm³ analogous to those described by Bobrov et al. (2008). Solid-state cells of 30-mm outer diameter were manufactured from lithographic limestone (Algeti Mine, Georgia) and contained an ultra-pure graphite heater of 6-mm outer diameter and 7.2 mm in length. A sleeve 8 mm in outer diameter and 6 mm in inner diameter made of pressed MgO and BN mixture (MgO/BN = 3/1) was placed in the limestone cell as a thermal insulator. The heater had a hole with 2 mm diameter and 2 mm depth in the center of the cell, in which experimental starting materials were loaded. After pressurization the sample volume was reduced to ~1 mm³. The apparatus allows a homogeneous distribution of pressure and temperature (~1 °C/mm⁻¹), which has been estimated by special runs on basalt-liquidus melting (Litvin, 1991).

Table 2
Mean composition of phases produced in experiments at 8.5 GPa and 1600–1900 °C.

Run	2326		2323		2322		2327	
	Grt	L	Grt	L	Grt	L	Grt	L
SiO ₂	45.02(0.31)	70.96(0.47)	45.35(0.35)	72.09(0.41)	46.02(0.33)	71.84(0.39)	46.58(0.40)	70.56(0.48)
Al ₂ O ₃	24.89(0.20)	9.42(0.16)	24.55(0.22)	10.88(0.20)	23.86(0.14)	11.02(0.21)	23.33(0.26)	11.57(0.19)
MgO	29.72(0.29)	10.59(0.20)	28.85(0.25)	9.52(0.15)	28.76(0.19)	9.61(0.13)	28.69(0.30)	10.41(0.15)
Na ₂ O	0.20(0.04)	7.06(0.25)	0.50(0.09)	6.14(0.09)	0.90(0.08)	5.70(0.10)	1.08(0.11)	5.59(0.18)
Total	99.83	98.03	99.25	98.63	99.54	98.17	99.68	98.13
<i>Formula per 12 O for garnet and 6 O for pyroxene</i>								
Si	3.026		3.062		3.104		3.137	
Al	1.972		1.953		1.896		1.852	
Mg	2.976		2.915		2.889		2.878	
Na	0.026		0.065		0.119		0.141	
Total	8.000		7.995		8.008		8.008	
Run	2325		2324			2328		
	Grt	L	Grt	En	L	Grt	En	L
SiO ₂	45.85(0.28)	69.62(0.40)	45.23(0.30)	59.03(0.34)	72.32(0.48)	45.15(0.32)	59.73(0.37)	71.86(0.46)
Al ₂ O ₃	23.88(0.18)	9.82(0.15)	24.30(0.22)	1.31(0.06)	11.06(0.22)	24.47(0.19)	2.53(0.10)	11.43(0.24)
MgO	28.85(0.21)	11.69(0.20)	29.30(0.23)	38.70(0.27)	9.53(0.20)	29.51(0.19)	35.88(0.25)	8.81(0.22)
Na ₂ O	0.75(0.07)	7.01(0.26)	0.49(0.05)	0.83(0.11)	5.28(0.13)	0.42(0.05)	1.67(0.12)	6.01(0.17)
Total	99.33	98.14	99.32	99.87	98.19	99.55	99.81	98.11
<i>Formula per 12 O for garnet and 6 O for clinopyroxene</i>								
Si	3.087		3.057			3.045		
Al	1.895		1.935			1.945		
Mg	2.934		2.950			2.965		
Na	0.098		0.064			0.055		
Total	8.014		8.006			8.010		

Abbreviations: Each analysis is an average of 5–7 individual analyses; standard deviations of phase compositions are given in parentheses. Grt, Na-bearing majoritic garnet; En, enstatite-rich pyroxene; L, products of melt quenching comprising dendritic clinopyroxene, coesite, minor garnet, and interstitial glass; the analyses were obtained using a defocused beam from 10 × 10 μm area.

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