



Trace element partitioning between majoritic garnet and silicate melt at 10–17 GPa: Implications for deep mantle processes

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ABSTRACT

Melting experiments were performed on a silica-rich peridotite composition at 10–17 GPa to determine majoritic garnet–melt partition coefficients (*D*) for major and trace elements. Our results show that *D* for many elements, including Na, Sc, Y and rare earth elements (REE), varies significantly with increasing pressure or proportion of majorite component. Lu and Sc become incompatible at 17 GPa, with *D* decreasing from 1.5 at 10 GPa to 0.9 at 17 GPa. As predicted from lattice strain, log *D* for isovalent cations entering the large site of majoritic garnet exhibits a near-parabolic dependence on ionic radius. Our data are used to refine a previously published predictive model for garnet–melt partitioning of trivalent cations, which suffered from a lack of calibration in the 10–20 GPa range. Our results suggest that Archean Al-depleted komatiites from Barberton (South Africa) may have been generated by partial melting of dry peridotite at depths between 200 and 400 km. We also speculate that transition zone diamonds from Kankan (Guinea), which contain inclusions of majoritic garnet, may have formed from the partial reduction of CO₂-rich magmas that subsequently transported them to the surface. This hypothesis would provide an explanation for the REE patterns of majoritic garnet trapped within these diamonds, including Eu anomalies. Finally, we show that segregation of majoritic garnet-bearing cumulates during crystallisation of a deep Martian magma ocean could lead to a variety of Lu/Hf and Sm/Nd ratios depending on pressure, leading to a range of ε¹⁴³Nd and ε¹⁷⁶Hf isotope signatures for potential mantle sources of Martian rocks.

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1. Introduction

Majoritic garnet is with olivine and its high-pressure polymorphs one of the main constituents of the deep upper mantle and transition zone of both Earth and Mars (e.g. Bertka and Fei, 1997; Ringwood, 1991). To understand the distribution of trace elements in the mantle of these planets, it is therefore crucial to constrain how trace elements dissolve in these minerals. Since fractionation of elements between different planetary reservoirs almost invariably takes place through processes of melting and crystallisation, it is appropriate to consider element distributions in terms of partitioning between minerals and melts. Majoritic garnet is of particular importance because it is the

first mineral to crystallise from a peridotitic silicate melt (i.e. the liquidus phase) at pressures greater than ~14 GPa (e.g., Zhang and Herzberg, 1994). However, to date, limited partitioning data are available to model the geochemical consequences of crystallisation or melting in the stability field of majoritic garnet. Most of published garnet–melt partition coefficients of trace elements have thus far been obtained at pressures less than ~3 GPa (e.g., Fujinawa and Green, 1997; Hauri et al., 1994; Johnson, 1998; Nicholls and Harris, 1980; Salters and Longhi, 1999; Shimizu and Kushiro, 1975; van Westrenen et al., 1999, 2000a). Owing largely to technical issues, there are only a small number of data at higher pressures. Since garnet is progressively more enriched in the majorite component (MgSiO₃) at higher pressures and temperatures (e.g., Irifune, 1987), trace element partitioning patterns in the deep asthenosphere and transition zone are likely to be different from those at lithospheric levels. Therefore, low-pressure garnet–melt partitioning data are potentially unsuitable to model mantle melting or crystallisation at greater depths. Kato et al. (1988) and Ohtani and co-workers (Ohtani et al., 1989; Yurimoto and Ohtani, 1992) reported

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pioneering results for a small number of lithophile trace elements over the 15–24 GPa and 16–20 GPa pressure ranges, respectively. These studies revealed that partition coefficients for heavy rare earth elements (REE) decrease substantially with increasing pressure while those for light REE may increase slightly. However, run durations were extremely short in these early experiments and chemical equilibrium may not have been completely attained, casting doubts on the accuracy of these first results. More recently, Draper et al. (2003) and Dwarzski et al. (2006) presented new data between 3 and 9 GPa, underlining the effect of pressure on garnet–melt partitioning of trace elements, respectively using Martian- and lunar-type compositions. Finally, Walter et al. (2004) and Corgne and Wood (2004) provided partition coefficients for a large number of trace elements at about 23 and 25 GPa, respectively, i.e. approximately at the deepest levels of the garnet stability field in the mantles of Earth and Mars.

The aim of this experimental study was to generate high-quality majoritic garnet–melt partition coefficients for a series of lithophile trace elements at pressures of the deep asthenosphere and transition zone. Experiments were carried out using a silica-rich peridotite starting composition at 10, 15 and 17 GPa to cover a wide range of pressure and generate data complementary to the existing data set. A first objective was to use our new data together with literature data to constrain further the systematics of trace element partitioning as a function of pressure. These new data have also been used to test current predictive partitioning models (Draper and van Westrenen, 2007; van Westrenen and Draper, 2007) and geobarometers based on majoritic garnet composition (e.g., Collerson et al., 2010). A second objective was to use our partition coefficients to model deep mantle processes in the stability field of majoritic garnet and shed light on the origin of Al-depleted komatiites, the formation of diamonds containing inclusions of majoritic garnets, and the chemical differentiation of a putative Martian magma ocean.

2. Experimental and analytical techniques

The starting material used in this study is a silica-rich peridotite composition. The major element composition determined by X-ray fluorescence (XRF) on a split portion of the starting material is given in Table 1. It is characterised by a molar Mg/Si ratio of ~1.1 as in carbonaceous chondrites, and by a molar Mg/[Mg + Fe] ratio (hereafter Mg#) of ~0.88. The reasons for choosing this composition rather than a fertile peridotite composition were two-fold: (1) cosmochemical comparisons suggest that terrestrial planets like Earth and Mars are potentially made of carbonaceous chondrites (e.g. McDonough and Sun, 1995); (2) a relatively low Mg/Si ratio should enhance the crystallisation of majoritic garnet. The starting mixture was prepared by mixing dried analytical grade oxides and carbonates. After grinding under ethanol in an agate mortar, the mixture was slowly decarbonated in air from 600 to 1000 °C and

reground before adding trace elements at ~50–500 ppm level using 1000 ppm atomic absorption standard solutions. The doped powder was then denitrified at 800 °C for about 2 h and was subsequently reduced in a controlled atmosphere furnace at 1000 °C for several hours at an oxygen fugacity about 2 log units below the fayalite–magnetite–quartz oxygen buffer.

Experiments were performed at 10, 15, and 17 GPa using 800- and 1500-ton Walker-type multi-anvil presses at the Geophysical Laboratory. The pressure scale was calibrated against the coesite–stishovite transformation at 1500 °C (Zhang et al., 1996) and the forsterite–wadsleyite transformation in Fo₉₂ at 1600 °C (Katsura et al., 2004). We estimate pressure uncertainties to be ±0.5 GPa. The starting mixture was contained in an unsealed rhenium capsule (~1.5 mm long prior to experiment) surrounded by a magnesia sleeve, a cylindrical rhenium heater and an outer zirconia sleeve as thermal insulator (Fig. 1). The octahedral pressure cell (MgO with 5% Cr₂O₃) with 10 mm edge length was compressed using 25 mm Toshiba tungsten carbide anvils with 5 mm truncations. Temperature was measured using type-C (W₂₆Re–W₅Re) thermocouples and was controlled automatically to within ±2 °C. The effect of pressure on the thermocouple electromotive force was ignored. The thermocouple was inserted axially above the rhenium capsule (Fig. 1). Given the dimensions of the sample chamber during heating (diameter × height = 250 × 150 μm), the temperature gradient across the sample in this set of experiments is estimated to be within 30 °C. This estimation is derived from the studies of Walter et al. (1995) and van Westrenen et al. (2003) on temperature distribution in multi-anvil assemblies. Each experiment was pressurised at room temperature at ~3 GPa/h, then raised at ~100 °C/min to the target temperature and held there for 45–150 min to approach chemical equilibrium. The experiment was quenched rapidly by switching off the power to the rhenium furnace and then decompressed gradually at ~3 GPa/h. The recovered pressure cell was mounted in Petropoxy-154 resin and polished longitudinally for optical and chemical analyses. Table 2 details run conditions and produced phase assemblages. The experimental approach followed here therefore contrasts with a number of previous experimental studies on mantle melting, where a large temperature gradient (>200 °C) existed across the sample and run durations were as short as a few minutes

Table 1
Composition of the starting mixture and comparison with model mantle compositions.

	This study	Pyrolite-model	CI-model
SiO ₂ (wt.%)	47.8	44.9	49.4
TiO ₂	0.21	0.20	0.16
Al ₂ O ₃	4.50	4.44	3.62
Cr ₂ O ₃	0.37	0.38	0.44
FeO*	8.00	8.03	7.93
MgO	35.0	37.7	34.8
CaO	3.50	3.54	2.87
MnO	0.15	0.14	0.13
NiO	0.22	0.25	0.25
Na ₂ O	0.20	0.36	0.34
K ₂ O	0.03	0.03	0.02
Total	100.0	100.2	100.5
Molar Mg/Si	1.09	1.25	1.05
Molar Mg/[Mg + Fe]	0.886	0.893	0.887

Pyrolite- and CI-model from McDonough and Sun (1995).

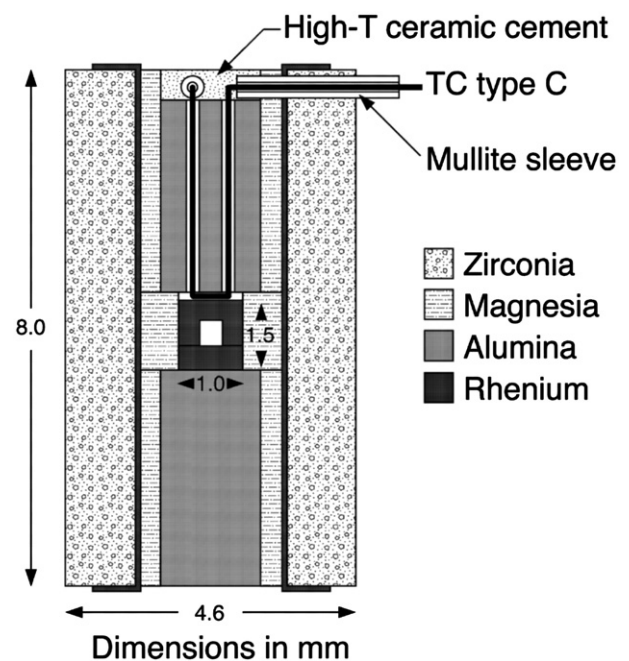


Fig. 1. Schematic cross-section of the 10 mm cell-assembly used in this study.

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