

Stephan Klemme · Hugh StC. O'Neill

## The near-solidus transition from garnet lherzolite to spinel lherzolite

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**Abstract** The position of the transition from spinel lherzolite to garnet lherzolite in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  (CMAS) has been determined experimentally at near-solidus temperatures. In reversed experiments, the transition occurs between 18 and 20 kbar at 1200 °C and between 26 and 27 kbar at 1500 °C, corresponding to higher pressures than previously envisaged. A position for the transition deeper within the Earth further complicates the explanation of the so-called garnet signatures in the trace element and isotope patterns of mid-ocean ridge basalts. If melting during adiabatic upwelling beneath a mid-ocean ridge begins at the depth required for the stability of garnet in peridotitic compositions, simple melting models predict that the amount of melt produced should be much greater than the observed thickness of the oceanic crust. A partial solution to the apparent conflict might be that (1) the rather simplistic melting models are in error, (2) that melting begins in garnet pyroxenite veins that are believed to be stable at lower pressures than garnet lherzolite or (3) that melting does not involve garnet at all, but it is clinopyroxene causing the trace element patterns observed in basalts erupted at mid-ocean ridges. A second set of reversal experiments were conducted to investigate the solubility of alumina in both orthopyroxenes and clinopyroxenes at the high temperatures near the solidus in the system CMAS. The results are compatible with most previous studies, and may be used as a starting point to calibrate thermodynamic

models for pyroxenes in chemical systems, approximating upper mantle chemistry.

### Introduction

With increasing depths, the aluminous phase in the upper mantle changes from plagioclase to spinel to garnet. The transition from spinel lherzolite (olivine + orthopyroxene + clinopyroxene + spinel) to garnet lherzolite (olivine + orthopyroxene + clinopyroxene + garnet) could potentially influence the characteristics of some kinds of basalts, particularly mid-ocean ridge basalts (MORB), since this transition is thought to occur at about the same depths at which MORB may originate. There is evidence from trace element and isotope geochemistry that MORB are generated in the presence of garnet (Klein and Langmuir 1987; Hirschmann and Stolper 1996). The evidence includes the depletion of heavier rare earth elements relative to lighter rare earth elements (Kay and Gast 1973), depletion in  $^{177}\text{Lu}/^{176}\text{Hf}$  (Salters and Hart 1989) and elevated  $^{230}\text{Th}/^{238}\text{U}$  ratios (Beattie 1993a, b; LaTourrette et al. 1993). This is generally referred to as the 'garnet signature' in MORB. However, if melting started in the garnet lherzolite stability field, simple melting models (e.g. Klein and Langmuir 1987; McKenzie and Bickle 1988; Iwamori et al. 1995) predict a thickness of the oceanic crust much greater than the average crust at  $7 \pm 1$  km inferred from seismological studies (e.g. White et al. 1992). Several possible solutions have been put forward to resolve this apparent conflict, including: (1) reduced melt productivity of upwelling peridotite (Asimov et al. 1995); (2) variations in depth of melting on the top of the melting zone beneath ridges (Shen and Forsyth 1995); or (3) partial melting of small amounts of garnet-bearing assemblages in veins such as garnet pyroxenites or eclogites (among others: Wood 1979; Allègre et al. 1984; Hirschmann and Stolper 1996).

However, such speculation is somewhat premature, in that the position of the spinel lherzolite to garnet

S. Klemme (✉)<sup>1</sup> · H.StC. O'Neill  
Research School of Earth Sciences,  
The Australian National University,  
Canberra, ACT 0200, Australia

*Present address:*

<sup>1</sup>Department of Earth Sciences, University of Bristol,  
Wills Memorial Building, Queen's Road, Bristol BS8 1RJ, UK  
e-mail: stephan.klemme@bristol.ac.uk

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lherzolite transition in likely upper mantle compositions is surprisingly poorly constrained at near-solidus temperatures by existing experimental data (see Fig. 1 for a summary of previous work).

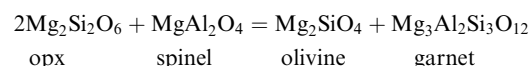
Several studies have investigated the transition from garnet lherzolite to spinel lherzolite in CMAS at lower temperatures, i.e. from 800 to 1100 °C (e.g. O'Hara et al. 1971; Jenkins and Newton 1979; O'Neill 1981). However, there is only little and, unfortunately, controversial information available for the high-temperature part of the univariant reaction close to the solidus, the pressure–temperature (P–T) range where mid-ocean ridge magmas are likely to be generated.

The transition from spinel lherzolite to garnet lherzolite is found to be curved (Jenkins and Newton 1979; O'Neill 1981; Gasparik 1984). The curvature with temperature is caused by increasing disorder in  $\text{MgAl}_2\text{O}_4$  spinel with increasing temperature (e.g. Wood et al. 1986) as well as by a large increase in the amounts of alumina dissolved in both orthopyroxene and clinopyroxene with increasing temperature. The curvature cannot be predicted accurately without very accurate thermodynamic models for the order–disorder in spinel, and the solubility of alumina in pyroxenes. Currently available thermodynamic models are not sufficiently well founded for this purpose, especially for aluminous pyroxenes. Hence the position of the transition in P–T space needs to be determined experimentally. Con-

versely, however, determination of the curvature of the transition will then be valuable in constraining thermodynamic models for aluminous pyroxenes. In turn, such information is needed for the further refinement of the ideas of Asimov et al. (1995) concerning melt productivity, e.g. to calculate accurately the entropy change across the transition.

The approach chosen here is to investigate the transition in a chemical system that contains all relevant mantle phases and closely approximates upper mantle composition. The CMAS system is an excellent starting point because its composition represents more than 90% of the upper mantle's composition and it contains the major mantle minerals olivine, garnet, spinel, orthopyroxene and clinopyroxene. In contrast to experiments in natural, complex compositions, the attainment of equilibrium in simple systems can be rigorously assessed and extraction of thermodynamic data is facilitated.

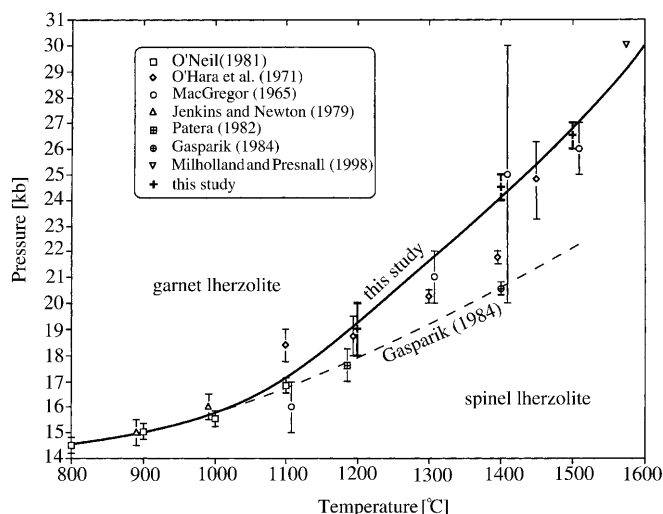
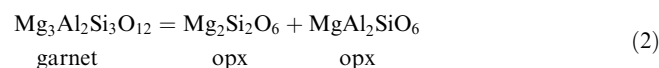
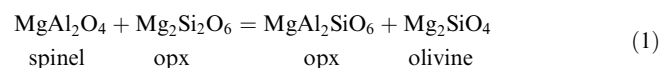
From a phase equilibrium perspective, the reaction that defines the phase transition from spinel to garnet lherzolite in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  (MAS) may in essence be written as follows:



This equilibrium is univariant in the simple MAS system, and remains univariant in the CMAS system if a calcium-containing phase, here clinopyroxene, is present to buffer the chemical potential of  $\text{CaO}$ .

There are, in principle, two ways to investigate the aforementioned univariant equilibrium. The reaction may be investigated *directly* by performing reversal experiments with starting material containing both reactants and products of the reaction. Analysis of coexisting phases with X-ray diffraction or electron microprobe shows which phase assemblage grew and which is consumed. However, for situations, such as here, where some of the phases partaking in the reaction are solid solutions of variable composition (orthopyroxene, clinopyroxene and garnet), this standard approach needs extra care to ensure that the compositions of these phases are appropriate for the P–T conditions. Otherwise there is a danger that growth or loss of garnet or spinel may be proceeding metastably. Ideally, therefore, starting materials should be pre-equilibrated in the divariant fields both above and below the anticipated position of the univariant reaction.

A second, somewhat different approach, investigates the behaviour of the isopleths of alumina in the pyroxenes (i.e. curves in P–T space of constant alumina content in orthopyroxene or clinopyroxene). The solubility of alumina in pyroxenes can be described by the following two equations,



**Fig. 1** A compilation of literature data on the transition from spinel lherzolite to garnet lherzolite in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ . Reversed experiments, analysed with electron microprobe, are from Jenkins and Newton (1979), O'Neill (1981) [corrected for friction, see text for details], Gasparik (1984) and this study. Note that most of the other experiments (within the somewhat large uncertainties) at temperatures above 1200 °C agree well with the present study; only Gasparik's (1984) experiment is in disagreement. For clarity, all experimental results are represented by average values for the transition and error bars. For example, the 1400 °C bracket by MacGregor (1965) represents in fact two experiments at 20 and 30 kbar respectively. The higher pressure experiment indicated that the garnet-bearing mineral assemblage grew, while at 20 kbar the spinel-bearing assemblage grew

The isopleths of alumina in orthopyroxene in equilibrium with garnet (reaction 2) have a positive slope in P-T space, while those in equilibrium with spinel (reaction 1) are almost independent of pressure. The position of the transition from garnet lherzolite to spinel lherzolite can be determined *indirectly* in P-T space, by investigating where the isopleths intersect.

This study investigates the transition of garnet to spinel lherzolite near the solidus using both approaches. The position of the univariant reaction in CMAS was directly reversed and the solubility of  $\text{Al}_2\text{O}_3$  in pyroxenes near the solidus has been investigated.

#### Pyroxene compositional variability in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$

As pyroxene compositions are very sensitive to varying P-T conditions, mineral assemblages containing orthopyroxene and clinopyroxene are widely used as indicators of pressure and temperature in ultramafic rocks such as in orogenic peridotites and mantle-derived xenoliths. Pyroxene compositions in the CMAS system may vary considerably in terms of (1) their Ca/Mg ratios, (2) their alumina contents and (3) deviations from ideal stoichiometry due to excess  $\text{SiO}_2$  content (Wood and Henderson 1978; Fockenberg and Schreyer 1997). However, pyroxenes in equilibrium with  $\text{Mg}_2\text{SiO}_4$  (forsterite) appear to have ideal stoichiometry and hence this latter factor will not be discussed further, as all experiments presented here contain forsterite.

The simplest system containing both orthopyroxene and clinopyroxene is the enstatite–diopside join in the system  $\text{CaO-MgO-SiO}_2$  (CMS). The Ca-Mg exchange between clinopyroxene and orthopyroxene was first suggested for use for geothermometry by Atlas (1952). Since then, numerous experimental studies have shown that the shape of the miscibility gap between enstatite and diopside is mainly a function of temperature and not of pressure. Phase relations and thermodynamic models of the diopside–enstatite system have been reviewed by Lindsley et al. (1981), Nickel and Brey (1984) and Carlson and Lindsley (1988).

The  $\text{Al}_2\text{O}_3$  exchange between orthopyroxene and garnet (reaction 2) is sensitive to pressure as well as temperature and is commonly used for geothermobarometry (e.g. Wood and Banno 1973; Nickel and Green 1985; Brey et al. 1986). The exchange of  $\text{Al}_2\text{O}_3$  between the orthopyroxene solid solution and spinel (reaction 1), however, is believed to be mainly sensitive to temperature and has found application in the geothermometry of ultramafic rocks (e.g. Gasparik and Newton 1984; Witt-Eickschen and Seck 1991). The alumina content of orthopyroxene coexisting with olivine and spinel has proven to be almost independent of pressure in the MAS system (e.g. Dankwerth and Newton 1978; Gasparik and Newton 1984) as well as in the CMAS system (Obata 1976; Fujii 1977). Gasparik (1984)

claimed that the presence of Ca in the CMAS system appears to reduce the amount of  $\text{Al}_2\text{O}_3$  in orthopyroxene, but this suggestion has not been explicitly incorporated into existing geothermometers and geobarometers.

The presence of minor components such as Fe, Cr, Na and Ca can have a substantial effect on the subsolidus equilibria (e.g. O'Neill 1981). In order to extrapolate results from simple system experiments to the more complex compositions of naturally occurring rocks, thermodynamic models are needed to account for the influence of these minor components. For instance, the influence of chromium on thermodynamics of pyroxenes has previously been underestimated and will be discussed in subsequent papers (see also Klemme 1998; Klemme and O'Neill 1998). However, the solubility of alumina in pyroxenes in the simple system CMAS must be understood first and the present experiments are designed to serve as a starting point for extrapolation into more complex compositions.

## Experiments

### Experimental strategy

Reactions in the system CMAS such as the transition from garnet lherzolite to spinel lherzolite are well known for their slow kinetics (O'Neill 1981; Nickel et al. 1985). In order to overcome this problem, lengthy experimental run durations were found to be necessary in our experiments (see Table 2). However, conducting high-pressure experiments at high temperatures for many hours or days leads to another problem: Thermocouples that are used for temperature control in the high-pressure, high-temperature experiments can drift to lower or higher temperatures due to contamination ('thermocouple poisoning'), or due to element migration within the thermocouple material itself. That has been a particular problem in the past with the usual types of thermocouples used in experimental petrology, namely type S (Pt-Pt<sub>90</sub>Rh<sub>10</sub>).

In order to prevent thermocouple contamination in the lengthy experiments of this study, care was taken to prepare a clean assembly, free of grease or other potential contaminants. Most experiments were conducted with two different thermocouples to guard against possible thermocouple drift due to contamination.

The position of the univariant equilibrium was bracketed in P-T space *directly* as follows: starting materials containing reactants (i.e. the low-pressure assemblage spinel, forsterite, clinopyroxene, orthopyroxene) as well as products of the reaction (i.e. the high-pressure assembly garnet, forsterite, clinopyroxene, orthopyroxene) were run at pressures and temperatures near the position of the univariant curve. Analysis of coexisting phases with X-ray and electron microprobe techniques show which phase assembly is consumed and which phases grow.

A second series of experiments has been conducted at a pressure of 23 kbar and temperatures between 1400 and 1500 °C, again with rather lengthy run times. Experiments were duplicated with two different starting mixtures: one starting material contained pyroxenes with high  $\text{Al}_2\text{O}_3$  content, the other with only half of the  $\text{Al}_2\text{O}_3$  content. Equilibrium was, therefore, reversed in terms of the alumina content of the pyroxenes, i.e. approached from different sides. The information derived from these reversal experiments in the spinel lherzolite stability field may be used in conjunction with literature data to determine the position of alumina isopleths of orthopyroxene in P-T space and, therefore, to *indirectly* constrain the position of the boundary between garnet lherzolite and spinel lherzolite.

## Starting materials

All experiments were conducted with mixtures of crystalline starting materials pre-synthesized from oxide mixtures. The choice of crystalline materials in contrast to glass or gel as starting material circumvents nucleation problems of garnets and spinel and also prevents formation of pyroxenes, unrealistically high in  $\text{Al}_2\text{O}_3$ , known from unreversed synthesis experiments (cf. Howells and O'Hara 1978; Nickel et al. 1985).

$\text{MgAl}_2\text{O}_4$  was synthesized at 1200 °C at atmospheric pressure for 24 h. Forsterite ( $\text{Mg}_2\text{SiO}_4$ ) was prepared at 1050 °C at atmospheric pressure using a  $\text{Li}_2\text{WO}_4$  flux with a flux/oxide-mix ratio of 4:1 in a Pt-crucible for 6 days. Laser Ablation ICP-MS analysis of the forsterite showed it contained <300 ppm Li and <10 ppm W. Lattice parameters determined with an internal standard of NBS Si are in exact agreement with those obtained for forsterite synthesized directly from pure chemicals. The orthoenstatite ( $\text{Mg}_2\text{Si}_2\text{O}_6$ ) was synthesized from the oxides at 1150 °C and 20 kbar pressure in a graphite capsule. This synthesis experiment was carried out for 24 h. Aluminous clinopyroxenes and orthopyroxenes were synthesized at 1200 °C and 30 kbar for 12 h. These synthesis runs also contained minor amounts of olivine, whereas no garnet was detected.

All starting materials were checked for composition and homogeneity with the electron microprobe (Ware 1991) and with X-ray diffraction techniques.

Starting materials of the 'direct approach' experiments designed to bracket the position of the garnet–spinel boundary contained synthetic mineral mixtures consisting of all five phases, including minerals on the low-pressure and the high-pressure sides of the reaction. Thus, the starting material contained olivine, clinopyroxene, orthopyroxene, garnet and spinel (Table 1). Mixtures SM 6, 9 and 15 are identical.

The 'direct approach' experiments contained synthesized garnets with two different compositions: SM 3 consisted of garnets with 20 mol% grossular component and SM 4 garnets with 10 mol% grossular component. Five grams of each garnet for the starting mix were synthesized separately at 1400 °C, 30 kbar for 24 h in a large capacity piston-cylinder apparatus at the Research School of Earth Sciences (Australian National University, Canberra).

The starting material of the 'near-solidus solubility' (*indirect approach*) experiments contained pure forsterite and spinel as well as both orthopyroxenes and clinopyroxenes. Experiments were duplicated: one set of experiments was performed with high-alumina starting material orthopyroxenes and clinopyroxenes (approximately 10% [wt] $\text{Al}_2\text{O}_3$  in both pyroxenes) in the starting material (SM 25); a second set of experiments was run with starting material pyroxenes that contained only ~5% (wt)  $\text{Al}_2\text{O}_3$  (SM 28).

## Attainment of equilibrium in the experiments

There are several ways by which the attainment of equilibrium in the present experiments may be tested. Firstly, low standard deviations in analyses indicate homogeneous compositions, which provides direct evidence for chemical equilibration. Secondly, two

different garnet compositions were chosen as starting materials in the 'direct approach' experiments, i.e. garnets with low and high contents of grossular component respectively. Homogeneous garnet compositions throughout the charge were taken as evidence that garnets reached equilibrium in the experiment. Equilibrium in the 'indirect approach' experiments is reversed in terms of the alumina content of the pyroxenes, i.e. the experiments were duplicated with low-alumina and high-alumina start material pyroxene respectively. Although the Ca/Mg exchange between clinopyroxene and orthopyroxene has not been reversed, the attainment of equilibrium can be assessed by comparing the present results with thermometric expressions. Table 3 compares experimental temperatures with calculated temperatures using the geothermometer of Nickel et al. (1985).

In order to obtain further evidence for the attainment of equilibrium in the run products we make use of Fick's second law,  $h = \sqrt{D \cdot t}$  (Spear 1993), where  $D$  is the diffusion coefficient at pressure and temperature,  $h$  the radius of the analysed mineral in an experimental charge and  $t$  the time. Assuming a diffusion coefficient  $D$  for Al diffusion in pyroxene of ca.  $10^{-16} \text{ m}^2/\text{s}$  needed to homogenize a crystal of 10  $\mu\text{m}$  at 1400 °C (Sautter et al. 1988), the equilibration time can be estimated to be in the order of a few days.

## Experimental techniques

High-pressure, high-temperature experiments were carried out in a conventional piston-cylinder apparatus (Boyd and England 1960) using a 0.5 in. diameter assembly. The assembly consists of two inner parts of MgO (66% density) surrounded by three concentric shells: a graphite heater, a glass tube (Pyrex) and an outermost sleeve of NaCl, pressed to >95% of the theoretical density. This low-friction assembly does not require a pressure correction and pressures can therefore be controlled more accurately than in talc–Pyrex assemblies (Green et al. 1966). High temperatures and long run durations should also ensure that any initial friction, if present, decays (Bose and Ganguly 1995). Starting materials were sealed in platinum capsules which were insulated from the graphite heater by a small  $\text{Al}_2\text{O}_3$  sleeve and separated from the thermocouple tip by a 0.5-mm  $\text{Al}_2\text{O}_3$  disc.

All experiments were performed using the 'piston-out' method, where the pressure was first raised to a few kilobars. The temperature was then increased to ca. 450 °C to soften the Pyrex, following which the pressure was increased up to ca. 0.5 kbar higher than the desired pressure and the temperature was increased to the nominal temperature of the run. Finally, the pressure was lowered to the required run pressure.

As a check on pressure calibration, the position of the univariant reaction  $\text{Fe}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{FeSiO}_3$  was reversed, as described by Klemme and O'Neill (1997). No melt could be found in the calibration experiments, indicating perfectly dry conditions. Another important item of evidence for the validity of our pressure calibration of the piston-cylinder apparatus at the Research School of Earth Sciences, is the essentially perfect agreement of thermodynamic data for  $\text{MgCr}_2\text{O}_4$  derived from a high-pressure, high-temperature study (Klemme and O'Neill 1997) and from subsequent calorimetric measurements for  $\text{MgCr}_2\text{O}_4$  (S. Klemme,

**Table 1** Starting materials. SM 6, SM 9 and SM 15 are of identical composition, consisting of  $\text{MgAl}_2\text{O}_4$  (spinel),  $\text{Mg}_2\text{SiO}_4$  (forsterite), SM1 (orthopyroxene and clinopyroxene), and two different garnet

compositions (SM 3 and SM 4, see text). SM 25 and SM 28 consist of  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}_2\text{SiO}_4$  and orthopyroxene and clinopyroxenes

Bulk (wt%)	SM 6/9/15	SM 25	SM 28	SM 4	SM 3
MgO	30.7	36.4	39.6	—	—
CaO	6.9	5.5	6.2	—	—
$\text{SiO}_2$	39.7	36.5	38.1	—	—
$\text{Al}_2\text{O}_3$	22.7	21.4	16.1	—	—
Garnet	—	—	—	$\text{Py}_{90}\text{Gr}_{10}$	$\text{Py}_{80}\text{Gr}_{20}$
Opx	—	10% (wt) $\text{Al}_2\text{O}_3$	5% (wt) $\text{Al}_2\text{O}_3$	—	—
Cpx	—	10% (wt) $\text{Al}_2\text{O}_3$	5% (wt) $\text{Al}_2\text{O}_3$	—	—

H. StC. O'Neill, W. Schnelle, E. Gmelin, unpublished). In particular, the slope of this reaction is constrained by reversal brackets at 100 °C intervals from 1000 to 1500 °C inclusive, using NaCl–Pyrex assemblies identical to those used here. The internal consistency of these results argues against any gross change in the behaviour of the NaCl–Pyrex cells with increasing temperature above the 1050 °C at which we reversed the fayalite–ferrosilite–quartz transition.

Temperatures were measured with Pt<sub>94</sub>Rh<sub>6</sub>–Pt<sub>70</sub>Rh<sub>30</sub> thermocouples (type B) inserted axially into the assembly inside two- or four-bore high-purity Al<sub>2</sub>O<sub>3</sub> tubing. A thermocouple from the same spools of wire as used for the thermocouples in our piston-cylinder experiments was calibrated directly against the melting point of Au at 1 atm pressure, with a result (1065 °C) which is within 1 °C of the accepted temperature. Type B thermocouples are much more resistant to contamination at high temperature than the more commonly used Pt–Pt<sub>90</sub>Rh<sub>10</sub> (type S) or Pt–Pt<sub>87</sub>Rh<sub>13</sub> (type R) thermocouples, although they are somewhat less sensitive. Nevertheless, because thermocouple drift due to contamination is always a potential hazard in piston-cylinder experiments at high temperatures (Holloway and Wood 1988), temperatures in some runs (particularly the higher temperature ones) were additionally monitored with a second thermocouple of W<sub>75</sub>Re<sub>25</sub>–W<sub>97</sub>Re<sub>3</sub> (type C). Temperatures as measured by the two thermocouples differed only by a maximum of 10 °C. The sample was placed in the hot spot of the assembly which was found in previous calibrations in this laboratory (W.O. Hibberson, personal communication). This assembly has also previously been tested for temperature against the melting point of gold (cf. Mirwald and Kennedy 1979). Possible pressure effects on the emf of thermocouple pairs were neglected. The temperature uncertainties are estimated to be less than ±10 °C at lower temperatures, increasing to about ±15 °C at 1500 °C.

In order to minimize contamination of thermocouples in the lengthy runs it was found necessary to use high-purity inner components in the run assemblies. In this study inner parts of the pressure assembly consisted of high-purity Al<sub>2</sub>O<sub>3</sub> thermocouple sleeves, which are chemically more inert than the mullite sleeves previously used in this laboratory.

#### Analytical techniques

Each experimental run product was sectioned longitudinally with a diamond saw, and one half was mounted in epoxy and polished using a series of diamond pastes with a finish of 0.3 µm Al<sub>2</sub>O<sub>3</sub> polishing powder (Linde B). Run products were carbon coated and analysed on a Cameca 'Microbeam' electron microprobe at the Research School of Earth Sciences (ANU) and on a JEOL 6400 scanning electron microprobe (SEM) in energy dispersive mode (EDS) at the Electron Microprobe Unit (EMU) at ANU. Accel-

erating voltage was 15 keV, ZAF correction was applied in all analyses (Ware 1991). Starting material compositions were also analysed using powder X-ray techniques. The standard materials for electron microprobe analyses were natural diopside, garnet and spinel, as well as synthetic corundum crystals. Standards were analysed with both the SEM-EDS as well with the electron microprobe (EDS and WDS). Analytical results obtained with both techniques agree well with each other.

## Results

Table 2 lists experimental conditions, start material information and the phases present in each experiment. Analytical results are presented in Table 3. The position of the univariant reaction is illustrated in Fig. 2.

### Comparison with previous studies and discussion

#### The transition from garnet lherzolite to spinel lherzolite

The transition from garnet lherzolite to spinel lherzolite was first investigated in CMAS by MacGregor (1965) in the temperature range from 1100 to 1500 °C. A similar study by Kushiro and Yoder (1966) (1175–1500 °C) yielded only slightly differing results, probably due to the pressure correction applied. Both MacGregor (1965) and Kushiro and Yoder (1966) proposed a straight line of the univariant reaction in P–T space, in contrast to subsequent work. Studies by Jenkins and Newton (1979) and O'Neill (1981) found, in well-reversed experiments, a curved transition below temperatures of 1300 °C, resulting in a slope of the reaction that was nearly parallel to the temperature axis at temperatures below 1000 °C. In order for these latter results to be compatible with the higher temperature observations, the transition must show strong curvature in P–T space at temperatures between 1000 and 1300 °C. This has the consequence that garnet lherzolite with typical mantle Mg/(Mg + Fe) =

**Table 2** Starting materials, run conditions, results. *T* Temperature in °C, *P* pressure in kbar, *spi* spinel, *cpx* clinopyroxene, *opx* orthopyroxene, *fo* forsterite, *gnt* garnet, *quench* melt. Starting material mixtures are explained in the text

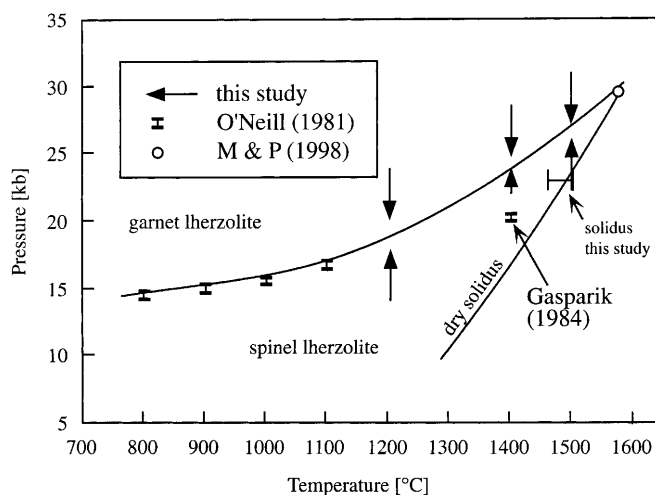
Run no.	Starting material	T (°C)	P (kbar)	Duration (h)	Phases present
C234-S 23	SM 9	1200	18	120	fo opx cpx spi, minor gnt
C276-S 29	SM 15	1200	20	360	fo opx cpx gnt, minor spi
C163-S 10	SM 6	1400	23	72	fo opx cpx spi, minor gnt
C246-S 26	SM 15	1400	24	72	fo opx cpx spi, minor gar
C231-S 21	SM 15	1400	25	72	fo opx cpx gnt, minor spi
C191-S 14	SM 9	1400	27	144	fo opx cpx gnt, minor spi
C418-S 75	SM 15	1475	25	48	opx spi gnt
C332-S 54	SM 15	1500	27	24	fo opx cpx gnt, trace spi
C278-S 30	SM 9	1500	26	15	fo opx cpx spi, minor gnt
C470-S 89	SM 25	1400	23	44	fo opx cpx spi
C467-S 87	SM 25	1450	23	24	fo opx cpx spi
C468-S 88 <sup>a</sup>	SM 25	1475	23	24	fo opx spi quench
C473-S 90 <sup>a</sup>	SM 25	1500	23	12	fo spi quench
C478-S 92	SM 28	1400	23	44	fo opx cpx spi
C485-S 94	SM 28	1425	23	48	fo opx cpx spi
C483-S 93	SM 28	1450	23	24	fo opx cpx spi
C488-S 95	SM 28	1475	23	24	fo opx cpx spi
C477-S 91 <sup>a</sup>	SM 28	1500	23	12	opx spi quench

<sup>a</sup> Contained partial melt

**Table 3** Electron microprobe analyses of experimental run products. All analyses represent averages of numerous analyses (at least ten per mineral per experiment). Numbers show element abundances in oxide components (wt%) as well as recalculated on the basis of six or four oxygens respectively. Numbers in parentheses indicate the analytical uncertainties (e.g. 1.230(3) should be read 1.230 ± 0.003 and 0.564(14) must be read as 0.564 ± 0.014). T (°C) (NBK) quotes temperature estimates (in °C) based on the formulation by Nickel et al. (1985)

	1400 °C 23 kbar S 10 Opx	Cpx	1400 °C 27 kbar S 14 Opx	Cpx	Gar	1200 °C 18 kbar S 23 Opx	Cpx	1400 °C 25 kbar S 21 Opx	Cpx	Gar
SiO <sub>2</sub>	54.4(5)	51.5(2)	54.9(2)	53.4(9)	44.6(7)	54.2(9)	52.3(9)	54.2(3)	52.6(3)	44.8(9)
Al <sub>2</sub> O <sub>3</sub>	9.5(5)	9.5(1)	7.0(3)	6.9(5)	26.4(6)	7.9(11)	7.7(7)	8.8(4)	8.6(5)	25.4(8)
MgO	34.5(4)	22.2(2)	35.6(3)	23.9(3)	26.2(4)	34.6(5)	18.8(7)	34.5(2)	23.2(2)	25.9(3)
CaO	2.4(1)	16.6(3)	2.4(1)	16.6(2)	5.9(4)	2.1(4)	21.8(3)	2.2(1)	16.1(8)	5.6(3)
Total	100.8	99.8	99.9	100.8	103.1	98.8	100.6	99.7	100.5	101.7
Si	1.817(9)	1.811(6)	1.853(8)	1.859(5)	2.953(11)	1.846(22)	1.851(16)	1.830(8)	1.833(17)	3.001(7)
Al	0.373(14)	0.393(2)	0.278(9)	0.283(14)	2.06(7)	0.315(37)	0.321(19)	0.350(12)	0.353(13)	2.005(16)
Mg	1.718(6)	1.164(1)	1.791(0)	1.240(9)	2.586(10)	1.757(24)	0.991(11)	1.736(6)	1.205(7)	2.587(24)
Ca	0.087(4)	0.625(7)	0.087(2)	0.618(3)	0.418(21)	0.077(12)	0.826(9)	0.080(4)	0.600(21)	0.404(14)
Total	3.996(2)	3.993(5)	4.008(3)	4.000(2)	8.017(7)	3.996(3)	3.989(6)	3.995(2)	3.991(10)	7.997(1)
T (°C) (NBK)	1424	1444				1187		1449		
	1400 °C 24 kbar S 26 Opx	Cpx	1200 °C 20 kbar S 29 Opx	Cpx	Gar	1500 °C 27 kbar S 54 Opx	Cpx	1475 °C 25 kbar S 75 Opx	Gar	1500 °C 26 kbar S 30 Opx
SiO <sub>2</sub>	55.3(13)	51.0(6)	54.5(9)	52.7(7)	44.2(9)	54.3(10)	51.8(11)	54.0(13)	43.2(12)	53.9(9)
Al <sub>2</sub> O <sub>3</sub>	9.7(22)	9.8(10)	7.8(11)	7.2(11)	24.8(7)	9.9(15)	9.7(2)	9.9(21)	24.8(10)	10.4(6)
MgO	34.9(9)	21.6(3)	35.4(5)	19.2(3)	25.9(9)	34.6(6)	24.5(6)	34.2(9)	25.7(9)	35.2(8)
CaO	2.3(2)	16.7(0)	1.9(4)	21.2(5)	5.7(3)	1.8(3)	15.0(8)	2.0(2)	5.3(2)	2.2(2)
Total	102.2	99.1	99.5	100.3	100.6	100.6	101.0	100.2	99.0	101.7
Si	1.823(38)	1.807(15)	1.843(22)	1.866(23)	2.998(16)	1.815(24)	1.793(6)	1.814(35)	2.976(17)	1.787(11)
Al	0.373(70)	0.409(32)	0.308(37)	0.301(39)	1.982(1)	0.388(45)	0.396(1)	0.390(66)	2.013(14)	0.406(12)
Mg	1.716(35)	1.138(8)	1.785(24)	1.013(10)	2.618(25)	1.724(27)	1.264(3)	1.713(33)	2.639(8)	1.739(2)
Ca	0.079(4)	0.635(10)	0.067(12)	0.804(4)	0.412(9)	0.064(8)	0.536(17)	0.073(3)	0.389(4)	0.078(7)
Total	3.991(2)	3.989(1)	4.003(3)	3.984(3)	8.011(17)	3.991(2)	4.009(7)	3.991(2)	8.017(10)	4.010(5)
T (°C) (NBK)	1415	1227				1480				1475

	1500 °C			1400 °C			1425 °C			1450 °C		
	26 kbar S30	Cpx	Opx	23 kbar S 89	Cpx	Opx	23 kbar S 92	Cpx	Opx	23 kbar S 94	Cpx	Opx
SiO <sub>2</sub>	51.0(13)		54.3(4)	53.8(5)	51.3(8)	53.6(5)	53.8(5)	51.3(8)	53.6(5)	51.5(4)	50.8(7)	54.0(5)
Al <sub>2</sub> O <sub>3</sub>	10.1(7)		9.6(5)	8.9(8)	8.9(5)	9.3(5)	8.9(8)	8.9(5)	9.3(5)	9.6(1)	10.1(6)	9.6(5)
MgO	23.9(11)		34.6(5)	34.1(4)	22.1(6)	34.1(4)	34.1(4)	22.1(21)	33.5(3)	22.5(6)	23.1(10)	34.0(3)
CaO	15.1(9)		2.2(2)	2.1(1)	17.0(4)	2.1(1)	2.1(1)	16.4(13)	2.2(1)	15.9(10)	15.2(11)	2.3(1)
Total	100.1		100.7	98.9	100.3	98.9	98.9	98.7	98.8	99.5	99.2	99.9
Si	1.783(21)		1.816(13)	1.830(15)	1.820(18)	1.826(6)	1.830(15)	1.826(46)	1.826(6)	1.812(18)	1.792(29)	1.818(7)
Al	0.416(13)		0.376(16)	0.357(26)	0.379(19)	0.371(4)	0.357(26)	0.371(4)	0.375(14)	0.398(1)	0.418(12)	0.381(14)
Mg	1.245(11)		1.725(3)	1.728(11)	1.153(8)	1.728(11)	1.728(11)	1.168(64)	1.706(12)	1.180(13)	1.214(16)	1.707(10)
Ca	0.565(11)		0.079(6)	0.076(2)	0.637(0)	0.082	0.076(2)	0.624(23)	0.082	0.599(26)	0.574(24)	0.084(4)
Total	4.009(14)		3.996(6)	3.991(2)	3.990(9)	3.987(1)	3.991(2)	3.989(44)	3.987(1)	3.989(19)	3.999(23)	3.991(0)
T (°C) (NBK)			1415	1423		1440	1440		1456			1440
	1450 °C			1475 °C			1500 °C					
	23 kbar S 93	Cpx	Opx	23 kbar S 88	Melt	Opx	23 kbar S 91	Cpx	Opx			
SiO <sub>2</sub>	51.5(4)		53.7(9)	53.8(4)	49.3	53.8(4)	53.7(6)	51.7(3)	53.7(6)			
Al <sub>2</sub> O <sub>3</sub>	9.5(6)		10.0(12)	9.6(2)	22.1	9.6(2)	10.5(11)	9.2(6)	10.5(11)			
MgO	21.9(7)		34.1(5)	33.6(2)	15.6	33.6(2)	33.7(5)	23.5(5)	33.7(5)			
CaO	15.9(8)		2.0(2)	2.4(1)	8.0	2.4(1)	2.4(1)	15.0(6)	2.4(1)			
Total	98.9		99.8	99.4	94.9	99.4	100.3	99.4	100.3			
Si	1.822(26)		1.811(19)	1.822(2)		1.816(22)	1.804(20)	1.816(22)	1.804(20)			
Al	0.398(16)		0.396(36)	0.382(3)		0.382(18)	0.414(32)	0.382(18)	0.414(32)			
Mg	1.156(11)		1.712(21)	1.698(3)		1.230(3)	1.687(10)	1.230(3)	1.687(10)			
Ca	0.604(17)		0.072(5)	0.086(2)		0.564(14)	0.085(1)	0.564(14)	0.085(1)			
Total	3.979(18)		3.991(1)	3.987(1)		3.993(13)	3.989(4)	3.993(13)	3.989(4)			
T (°C) (NBK)				1471								



**Fig. 2** The transition from garnet lherzolite to spinel lherzolite in the system CMAS. Experimentally derived brackets from this study (arrows) are compared with results by O'Neill (1981) [corrected for friction; see text], and one datum from Milholland and Presnall (M&P) (1998) and Gasparik (1984) respectively. The present results agree well with brackets (see text) in the low-temperature part of the diagram (800–1200 °C) but for higher temperatures there are considerable differences between the present results and a published datum from Gasparik (1984). A recent datum by Milholland and Presnall (1998), however, is in perfect agreement with the position of the current univariant curve. The transition curve in this diagram is eye-fitted. The dry solidus is taken from Presnall et al. (1979) and Gudfinnsson and Presnall (1996). Our data on the position of the solidus (at 23 kbar) agree well with data from Presnall's laboratory

0.9 is not stable at crustal pressures (but see O'Neill 1981 for a discussion of the effect of  $\text{Fe}^{2+}$  on increasing the stability of garnet plus olivine to lower pressures).

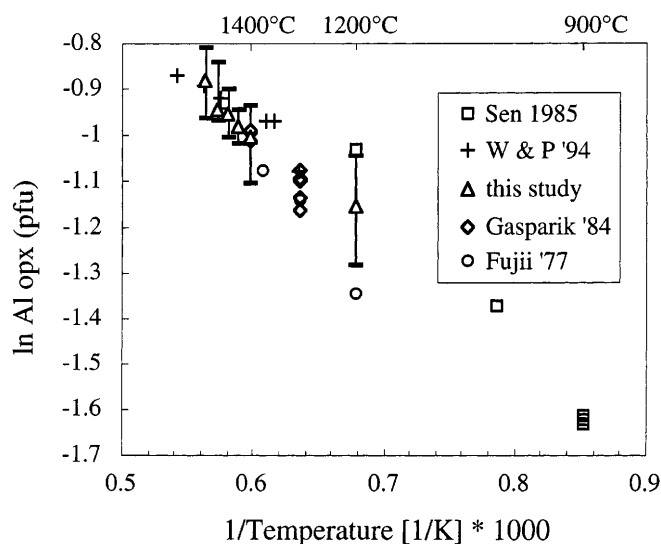
However, the information about the high-temperature part of the univariant reaction in CMAS is, unfortunately, controversial (Fig. 1). MacGregor (1965) and O'Hara et al. (1971) performed bracketing experiments, but microprobe analyses of the experimental charges were not possible so that the attainment of equilibrium could not be assessed. Kushiro and Yoder (1966) determined approximate stability fields of spinel and garnet lherzolite respectively, but their experiments remained unreversed. Besides, uncertain pressure corrections in the different solid-media pressure devices further complicated interlaboratory comparison of early experimental results (Koziol and Newton 1988).

Prior to the commencement of this study, the only experimental datum on the transition from spinel lherzolite to garnet lherzolite in the CMAS system at temperatures higher than 1200 °C, which is both reversed and analysed with electron microprobe, was from Gasparik (1984). Recently, Milholland and Presnall (1998) have reported a experimental datum at 1575 °C and 30 kbar for the transition from garnet to spinel lherzolite exactly on the dry solidus.

The present experimental brackets agree well with a smooth, curved extrapolation of results from the studies of Jenkins and Newton (1979) and O'Neill (1981) at 800 to 1100 °C, and through the reversal bracket of Patera

(1982) at 1200 °C (pressure corrected for friction, cf. Wood and Holloway [1984]), to the results of Milholland and Presnall (1998) on their solidus at 1575 °C. Note that the studies in the low-temperature range from 800 to 1100 °C agree well with each other, provided that a pressure correction of –10% is applied to O'Neill's (1981) data because of the rigid talc–Pyrex assembly he used (Green et al. 1966).

However, our present results disagree considerably with the datum from Gasparik (1984), who determined the equilibrium to lie between 20.3 and 20.8 kbar at 1400 °C, versus our bracket of 24 to 25 kbar at the same temperature. Gasparik's pressures were corrected for friction because of the rigid talc–Pyrex pressure assembly used in his experiments. Although this empirical correction may overestimate the friction at 1400 °C in Gasparik's (1984) experiments, this cannot, however, fully explain the discrepancy between the results of Gasparik (1984) and this study. Apart from pressure, two other possibilities are errors in temperature measurements (the difference in pressure would correspond



**Fig. 3** The solubility of alumina in orthopyroxene ( $\text{Al pfu Al}$  atoms calculated per formula unit of six oxygens) in equilibrium with spinel lherzolite in the system CMAS. Experimental results from reversed studies of Gasparik (1984), Sen (1985) and this study are compared. Also depicted are experimental results of an unreversed study of Walter and Presnall (1994) (W&P '94), from experiments in the system  $\text{Na}_2\text{O-CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ . Walter and Presnall's (1994) results agree well with the present experiments and with those of the other studies, indicating that there is only a minor influence of sodium on the solubility of alumina in orthopyroxene. Sen (1985) presents reversal experiments from 900 to 1200 °C. Good agreement is found between his results and experimental results of this study; one of Sen's data at 1200 °C, however, disagrees with the results presented and with combined results from the other studies. Experiments depicted in this diagram were performed at a range of different pressures, indicating that the alumina solubility in orthopyroxene in the spinel lherzolite stability field does not significantly depend on pressure. For clarity, the uncertainties in the reversed mineral compositions are only indicated in our data. Walter and Presnall (1994) quote analytical uncertainties (of about the same magnitude as in this study) of their unreversed experiments, while Fujii (1977), Gasparik (1984) and Sen (1985) do not quote any uncertainties



to a temperature error of about 150 °C, see Fig. 2) or metastable growth of garnet at the expense of spinel (etc.) in Gasparik's experiment at 20.8 kbar, or of spinel at the expense of garnet in our experiment at 24 kbar. Gasparik's reversals of the alumina content of pyroxenes are in good agreement with the results of our study (Fig. 3), which would tend to argue against errors in temperature measurement as the explanation, although the uncertainties in alumina contents are sufficiently large that this possibility cannot be completely dismissed. As for metastable reactions, the longer run times of our experiments (~72 h at 1400 °C) compared to the ~24 h of those of Gasparik (1984) argues for our results being the more reliable.

### The solubility of alumina in pyroxenes

The '*indirect approach*' as described here was first used by Obata (1976), who deduced the position of reaction (1) using the intersection of the experimentally determined isopleths of  $\text{Al}_2\text{O}_3$  dissolved in orthopyroxene in the MAS system in both the garnet and the spinel lherzolite stability fields. Herzberg (1978) investigated in an analogous study the isopleths of alumina of clinopyroxene, coming to somewhat different conclusions. Both studies suffered from a lack of microprobe analyses of the pyroxenes and the experiments were not reversed.

More recently, Sen (1985) presented reversed experimental data in the spinel stability field that are in good agreement with results presented here. All of his data, but one, compare well with the present results (Fig. 3). An experimental study in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (Walter and Presnall 1994) presents results that are also in good agreement with the results of this study (Fig. 3), indicating that the influence of sodium on the activity of alumina in orthopyroxene can be neglected. However, like most studies of melting equilibria, Walter and Presnall's experiments were unreversed. Of all alumina solubility experiments in the spinel lherzolite stability field, only those of Fujii (1977), Gasparik (1984) and Sen (1985) were both reversed and analysed with electron microprobe, but only those of Sen (1985) report uncertainties in pyroxene compositions.

Run durations in Fujii's (1977) experiments are very short (only a few hours). Comparing his run durations with the present experience with reaction rates in CMAS, a lack of complete equilibrium in his experiments remains possible.

As a further test for consistency, nominal experimental temperatures (this study) were compared to calculated temperatures based on the exchange of Ca and Mg between orthopyroxene and clinopyroxene, using the thermometric formulation of Nickel et al. (1985). Results of the thermometry (Table 3) indicate excellent agreement between the present experiments and Nickel et al.'s (1985) formulation.

### Some notes on two recent abstracts

Longhi (1998) locates the position of the anhydrous solidus in CMAS higher than previously envisaged (by 95 °C at 28 kbar). He explains the temperature differences between his experiments (conducted with a  $\text{BaCO}_3$  pressure medium) and those of Presnall and co-workers (e.g. Walter and Presnall 1994; Gudfinnsson and Presnall 1996) by fluxed melting induced by diffusion of  $\text{H}_2\text{O}$  or boron into the sample from the talc/Pyrex used in Presnall's (University of Texas, Dallas) laboratory.

Although we do not present many data on the position of the solidus, our observations place the solidus below 1500 °C at 23 kbar (Table 2), in good agreement with Walter and Presnall's (1994) and Gudfinnsson and Presnall's (1996) data.

Furthermore, in a recent abstract Longhi and Baker (1999) find the position of the transition between garnet lherzolite and spinel lherzolite in CMAS at 1500 °C between 20 and 22 kbar using  $\text{BaCO}_3$  pressure medium, and 21 and 23 kbar using  $\text{CaF}_2$ . This is considerably lower than our bracket between 26 and 27 kbar (Table 2). Longhi and Baker (1999) compare their results with previous work by Gudfinnsson and Presnall (1996) and others, and again attribute the differences in pressure to talc-breakdown of the talc-Pyrex pressure assemblies used in Presnall's laboratory (Longhi and Baker 1999) or to melting of the Pyrex glass in the talc-Pyrex assemblies (J. Longhi, his review of the present paper). However, the present results may shed some new light on the current debate, as our pressure assembly consists of a dry  $\text{NaCl}$ -Pyrex assembly, which has been calibrated independently (see Klemme and O'Neill 1997). As our data on both the position of the garnet-spinel transition and the solidus agree well with those of Presnall and co-workers, we conclude that talc breakdown is not the correct explanation. As our experiments do not indicate melting of the Pyrex glass either, we also suggest that melting of Pyrex and associated anvil effects in our experiments (J. Longhi, personal communication) cannot account for the large differences between Longhi and Baker's (1999) data and the present results.

We note that the recent observations of Longhi (1998) and Longhi and Baker (1999) could also be accounted for by a systematic error in temperature of about 100 °C. Our experience with long-duration runs at temperatures higher than 1200 °C suggest that thermocouple drift of W-Re thermocouples used by Longhi (personal communication, Longhi's review of this paper) could be the cause for the differing results of Longhi and Baker (1999), especially as the transition is strongly curved at high temperatures. However, this remains only speculation until more details (as thermocouple calibration, pressure calibration, mineral compositions, run durations etc.) of Longhi and Baker's (1999) study are published.

### Conclusions and implications

This study presents new and reversed experimental results on the transition from garnet lherzolite to spinel lherzolite in a simplified system. The transition pressure at temperatures close to the solidus is found to be substantially higher than previously estimated.

Minor elements like Cr and  $\text{Fe}^{2+}$  are known to have a substantial effect on the position of the transition. Cr is known to preferentially stabilize spinel-bearing assemblages (Klemme and O'Neill 1998), while  $\text{Fe}^{2+}$  has the opposite effect, shifting the transition to lower pressures (e.g. MacGregor 1970; O'Neill 1981). Thus, rocks containing coexisting almandine and fayalite ('eulysites') occur in regionally metamorphosed crustal rocks of the amphibolite facies (e.g. Woodland et al. 1995). The effect of  $\text{Fe}^{2+}$  is to shift the transition to about 2 to 3 kbar

lower pressure for the typical mantle  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  of 0.9 (O'Neill 1981). For fertile mantle with high  $\text{Al}/(\text{Al} + \text{Cr})$  ratios, the effect of Cr on the pressure at which garnet appears is only poorly constrained to date, but probably small (Carroll-Webb and Wood 1986; Klemme 1998). The position of the transition in natural compositions is therefore likely to be substantially higher than in some recent estimates (e.g. Hirschmann and Stolper 1996) but consistent with other studies in natural compositions (Green and Falloon 1998; Robinson and Wood 1998; Koga et al. 1999).

The confirmation of a relatively high pressure for the garnet/spinel transition leaves the paradox of the so-called 'garnet signature' in MORB unresolved; indeed, our results worsen the paradox, since we place the transition even higher than earlier studies (e.g. Gasparik 1984). The paradox is that if melting during adiabatic upwelling beneath a mid-ocean ridge begins at the depth required for the stability of garnet in peridotitic compositions, simple melting models (e.g. McKenzie and Bickle 1988) predict that the amount of melt produced should be much greater than the 7 km or so that is observed seismically for the thickness of the oceanic crust.

There are several possible solutions to this paradox. Firstly, the simple melting models presently available may be in error, particularly because of the assumption of a linear increase in melt productivity with temperature above the solidus. For example, Asimov et al. (1995) have argued that melting may cease as upwelling mantle crosses the garnet–spinel transition, due to the entropy of this reaction. It is also possible that C–O–H–silicate fluids, which have much greater segregation velocities than basaltic melts, may scavenge highly incompatible trace elements from regions outside the zones of normal melt productivity, thus imparting a garnet signature, particularly as regards the U–Th disequilibrium series, to aggregated melts that are mostly derived from the spinel lherzolite facies (U. Faul, personal communication). Secondly, the primitive MORB parental magma probably undergoes extensive fractional crystallization of olivine (e.g. Green and Falloon 1998); hence the amount of melt produced is actually much greater than that inferred from seismic imaging of the thickness of the oceanic crust. Melting may also begin in garnet pyroxenite veins that are believed to be stable at lower pressures than garnet lherzolite (e.g. Hirschmann and Stolper 1996). Finally, we note that recent trace element partitioning studies indicate that the melt/crystal partitioning characteristics of clinopyroxene approach those of garnet, both for the heavy rare earth elements (HREE) and for Th versus U, as the clinopyroxene becomes more aluminous and less calcic (Wood and Blundy 1997; Wood et al. 1998). This raises the possibility that the so-called 'garnet signature' in MORB may in fact be due to clinopyroxene of a composition appropriate for near-solidus temperatures in the spinel lherzolite stability field; that is, with  $\text{Ca}/(\text{Ca} + \text{Mg}) < 0.35$ , and alumina contents near 10% (wt), as found in this study.

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