The influence of Cr on the garnet–spinel transition in the Earth's mantle: experiments in the system $MgO–Cr_2O_3–SiO_2$ and thermodynamic modelling

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Abstract

The position of the transition from spinel peridotite to garnet peridotite in a simplified chemical composition has been determined experimentally at high pressures and high temperatures. The univariant reaction $MgCr_2O_4 + 2Mg_2Si_2O_6 = Mg_3Cr_2Si_3O_{12} + Mg_2SiO_4$, has a negative slope in $P–T$ space between 1200 °C and 1600 °C. The experimental results, combined with assessed thermodynamic data for $MgCr_2O_4$, $MgSiO_3$ and Mg_2SiO_4 give the entropy and enthalpy of formation of knorringite garnet ($Mg_3Cr_2Si_3O_{12}$). Thermodynamic calculations in simplified chemical compositions indicate that Cr shifts the garnet-in reaction to much higher pressures than previously anticipated. Moreover, in Cr-bearing systems a pressure–temperature field exists where garnet and spinel coexist. The width of this divariant field strongly depends on the $Cr/(Cr + Al)$ of the system.
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Keywords: Garnet lherzolite; Spinel lherzolite; Experimental petrology; Chromium; Garnet spinel transition; $MgO–Cr_2O_3–SiO_2$; $MgO–Al_2O_3–Cr_2O_3–SiO_2$

1. Introduction

From geophysics and experimental petrology it is well known that the Earth's mantle is stratified. The Earth's uppermost mantle consists of only four main minerals such as olivine, clinopyroxene, orthopyroxene and spinel. At higher pressures, however, the spinel bearing assemblage converts into a garnet bearing mineral assemblage. Among others, the transition from spinel lherzolite to garnet lherzolite is one of the major phase boundaries in the Earth's upper mantle (Asimov et al., 1995; Green and Ringwood, 1967; Hales, 1969; Klemme and O'Neill, 2000a,b; O'Neill, 1981). This transition is of particular petrogenetic relevance as the interpretation of magmatic processes at mid-ocean ridges, for example, requires a sound knowledge of the position of the transition from garnet to spinel lherzolite. For example, geochemists have argued for beginning of melting just within the stability field of garnet lherzolite (e.g. LaTourette et al., 1993; Salters and Hart, 1989), although other interpretation of so-called 'garnet-signatures' have been put forward (Allègre et al., 1984; Asimov et al., 1995; Hirschmann and Stolper, 1996; Klemme and O'Neill, 2000a,b; Shen and Forsyth, 1995; Wood, 1979). To resolve these matters, the garnet–spinel transition needs to be better con-

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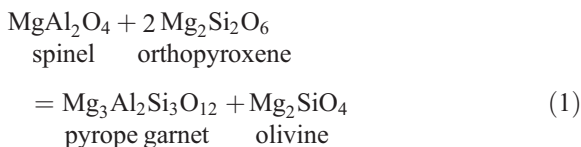[*] Tel.: +49-6221-546039; fax: +49-6221-544805.

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strained as a function of pressure, temperature and, most importantly, composition.

The position of the spinel–garnet transition is well understood in simple chemical systems (e.g. CaO–MgO–Al_2O_3–SiO_2) and in complex, fertile compositions (Gasparik and Newton, 1984; Green and Ringwood, 1967; Hales, 1969; Klemme and O'Neill, 2000a,b; MacGregor, 1965; O'Hara et al., 1971; O'Neill, 1981; Robinson and Wood, 1998). However, a strong influence of minor components such as chromium on the garnet–spinel transition has long been suggested (Brey et al., 1999; MacGregor, 1970; Nickel, 1986; O'Neill, 1981; Webb and Wood, 1986; Wood, 1978) but there is scant experimental data in Cr-rich compositions (Brey et al., 1999; Doroshev et al., 1997; Girnis et al., 2003; Nickel, 1986; Webb and Wood, 1986). This may be of relevance to the deeper continental mantle which is clearly depleted in Al and more or less constant in Cr when compared to normal fertile mantle (e.g. Liang and Elthon, 1990). This trend is believed to be caused by melting events (e.g. Falloon and Green, 1988; Walter et al., 2002) and it seems that the mantle shows increasing Cr/Cr + Al with depth as extremely Cr-rich garnets are commonly found in diamond inclusions (e.g. Stachel and Harris, 1997; Stachel et al., 1998, 2000).

Moreover, rigorous thermodynamic modelling of spinel–garnet reactions in the upper mantle over a range of temperatures, pressures and compositions requires reliable thermodynamic data for Cr-bearing minerals such as Cr-spinels (Klemme and O'Neill, 1997; Klemme et al., 2000; Klemme and van Miltenburg, 2002), Cr-bearing pyroxenes (Klemme and O'Neill, 2000a,b) and Cr-bearing garnets, the latter of which are, unfortunately, rather unconstrained (Doroshev et al., 1997; Irifune et al., 1982; Turkin et al., 1983). The present study tries to fill this gap.

The simplest reaction describing the transition from spinel-bearing peridotite to garnet peridotite may be written as follows

$$MgAl_2O_4 + 2\,Mg_2Si_2O_6$$
$$\text{spinel} \qquad \text{orthopyroxene}$$

$$= Mg_3Al_2Si_3O_{12} + Mg_2SiO_4 \qquad (1)$$
$$\text{pyrope garnet} \qquad \text{olivine}$$

This reaction has been studied previously in the systems MgO–Al_2O_3–SiO_2 and CaO–MgO–Al_2O_3–SiO_2 which are excellent proxies for fertile mantle compositions, i.e. undepleted and poor in Cr (e.g. Danckwerth and Newton, 1978; Gasparik and Newton, 1984; Klemme and O'Neill, 2000a,b; MacGregor, 1965; O'Neill, 1981). Although there was some recent debate about the transition at higher temperature (Klemme and O'Neill, 2000a,b; Longhi, 2002; Walter et al., 2002) there is general agreement, however, that in both these simple systems the garnet–spinel transition is univariant and has a positive slope in pressure–temperature space (Fig. 1). From previous experimental results (Doroshev et al., 1997; Nickel, 1986) and early thermodynamic calculations (O'Neill, 1981; Wood, 1978) it is well known that addition of Cr to the system dramatically increases the stability of the spinel phase assemblage relative to the garnet assemblage (or the plagioclase stability field at lower pressures). But thermodynamic modelling in realistic mantle compositions was unreliable (e.g. Asimov et al., 1995) as thermodynamic data for Cr-spinels were subsequently shown to be in error (Klemme and O'Neill, 1997; Klemme et al., 2000) and reliable thermodynamic data for Cr-bearing garnets were unavailable.

1.1. The stability of knorringite garnet

Three previous studies investigated experimentally the following knorringite forming reaction (Iri-
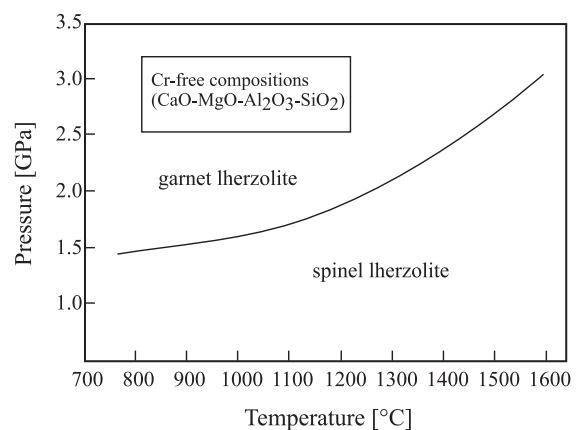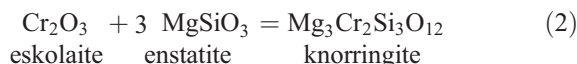

Fig. 1. The transition from garnet lherzolite to spinel lherzolite in Cr-free (fertile) mantle. The curve shown is based on experimental data in the system CaO–MgO–Al_2O_3–SiO_2 as given in Klemme and O'Neill (2000a,b).

fune et al., 1982; Ringwood, 1977; Turkin et al., 1983).

$$Cr_2O_3 + 3\ MgSiO_3 = Mg_3Cr_2Si_3O_{12} \qquad (2)$$
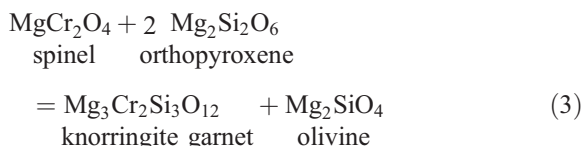$$\text{eskolaite}\quad\text{enstatite}\qquad\text{knorringite}$$

All these previous experimental studies on the stability of knorringite disagree considerably with each other (Fig. 2). This may be due to experimental uncertainties such as pressure calibration or temperature measurements. Moreover, it is well known that garnets tend to nucleate very sluggishly in high pressure experiments. The fact that Irifune et al. (1982) describe large garnets (mm size) in their experiments may indicate a rather large overstepping of the true position of the reaction. Summarising, the stability of knorringite garnet and, consequently, the thermodynamic properties of knorringite garnet were rather unconstrained.

1.2. Experimental strategy

To both investigate the influence of chromium on the garnet–spinel transition in a Cr-rich bulk composition and to derive thermodynamic properties of

3 MgSiO₃ + Cr₂O₃ = Mg₃Cr₂Si₃O₁₂
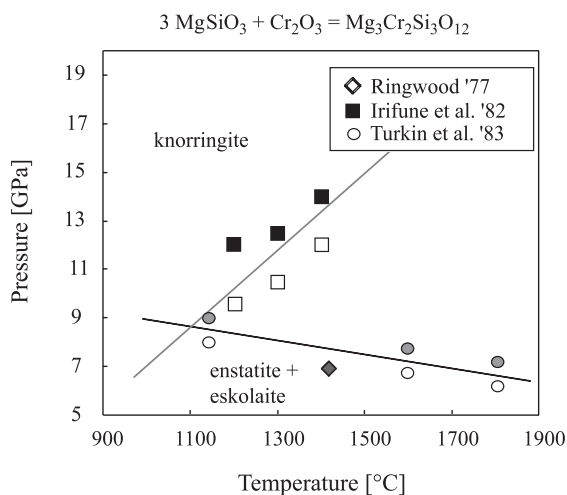
Fig. 2. Previous experimental results on the stability of knorringite ($Mg_3Cr_2Si_3O_{12}$) garnet (Irifune et al., 1982; Ringwood, 1977; Turkin et al., 1983). Filled symbols represent garnet stability. Note considerable differences between the individual studies that are probably due to experimental problems (see text for further information).

knorringite garnet, the analogue reaction to (1) was studied experimentally:

$$MgCr_2O_4 + 2\ Mg_2Si_2O_6$$
$$\text{spinel}\qquad\text{orthopyroxene}$$

$$= Mg_3Cr_2Si_3O_{12}\qquad + Mg_2SiO_4 \qquad (3)$$
$$\text{knorringite garnet}\qquad\text{olivine}$$

This reaction, which has hitherto not been investigated experimentally, describes the maximum stability of spinel in the Earth's mantle. Extraction of thermodynamic data for knorringite garnet is facilitated because reaction (3) is univariant and thermodynamic properties of $MgCr_2O_4$, $Mg_2Si_2O_6$ and Mg_2SiO_4 are well understood (Klemme, 1998; Klemme and O'Neill, 2000a,b) and solid solutions are not significant.

2. Experimental and analytical techniques

Reversal high-pressure high-temperature experiments on reaction (3) were performed between 4.5 and 16 GPa and at temperatures between 1200 and 1600 °C in a multi-anvil apparatus at the Bayerisches Geoinstitut, Germany. Analysis of run products with X-ray diffraction and electron microprobe indicated which phase assemblage grew and which was consumed. The starting material consisted of all four phases partaking in the reaction. Enstatite ($MgSiO_3$), magnesiochromite ($MgCr_2O_4$) and forsterite (Mg_2SiO_4) were synthesised previously and details were described elsewhere (Klemme, 1998; Klemme and O'Neill, 1997; Klemme and O'Neill, 2000a,b). Knorringite ($Mg_3Cr_2Si_3O_{12}$) starting material was synthesised from stoichiometric mixtures of MgO, Cr_2O_3 and SiO_2 in a multi-anvil press in two runs at 16 GPa and 1600 °C for 4 h. X-ray diffraction indicated knorringite only with only very minor peaks of unreacted eskolaite. The experiments were performed in 14/8 and 18/11 (octahedral edge length/truncation edge length) octahedral sample assemblies made from Cr-doped MgO. Starting material were tightly contained in capsules made of thin Re foil. $LaCrO_3$ heaters surrounded by zirconia sleeves were employed with $W_3Re/W_{25}Re$ thermocouples. Experi-

mental run conditions and run times are given in Table 1.

Electron microprobe analyses were done at Heidelberg University using a five spectrometer Cameca SX 51 electron microprobe. Several mineral standards were used (garnets, spinels, orthopyroxene and synthetic eskolaite). Microprobe analyses (Table 2) of the phases indicate essentially pure $MgCr_2O_4$, whereas enstatites contained about 1 wt.% Cr_2O_3. The Cr content of enstatite does not vary significantly with pressure or temperature. The olivines contain very little chromium ($<0.3\%$ (wt.) Cr_2O_3). This may be taken as evidence that almost all chromium is present in the trivalent state as significant amounts of Cr^{2+} in the charge would stabilize the Cr_2SiO_4 component in olivines (Li et al., 1995; Schreiber and Haskin, 1976;

Table 2

Mineral	Kn	For	Sp	En
SiO_2	39.7 (2)	42.4 (3)	0.1 (1)	59.3 (4)
MgO	26.9 (3)	56.9 (4)	21.2 (2)	40.4 (2)
Cr_2O_3	33.6 (2)	0.15 (15)	78.8 (3)	1.1 (3)
Total	100.2 (3)	99.5 (4)	100.1 (2)	100.7 (3)
Si	2.990	0.998	0.003	1.975
Mg	3.020	1.998	1.009	2.006
Cr	2.000	0.004	1.989	0.029
Total	8.010	3.000	3.001	4.010

Representative electron microprobe analyses of experimental run products. Mineral compositions are virtually identical in all runs. Note that most minerals are very close to their ideal composition. Numbers show element abundances in oxide components (wt.%) as well as recalculated on the basis of 4, 6 and 12 oxygens, respectively. Numbers in parenthesis indicate the analytical uncertainties. Kn = knorringite ($Mg_3Cr_2Si_3O_{12}$), For = forsterite (Mg_2SiO_4), Sp = magnesiochromite ($MgCr_2O_4$), En = enstatite ($MgSiO_3$).

Table 1
Experimental run conditions and results

Run #	T (°C)	P (GPa)	Duration (h)	Result
S2685	1600	16	4	Kn (very minor eskolaite)
S2686	1600	16	4	Kn (very minor eskolaite)
S2688	1600	11	4	Kn + For (minor Sp + En)
S2689	1400	11	5	Kn + For (minor Sp + En)
S2690	1200	11	12	Kn + For (minor Sp + En)
S2691	1600	9	4	Kn + For (minor Sp + En)
S2692	1400	9	10	Kn + For (minor Sp + En)
S2693	1600	7	5 h 20 min	Kn + For (minor Sp + En)
S2806	1200	6.4	12	Sp + En (minor Kn + For)
S2807	1600	4.5	1 h 10 min	Sp + En (minor Kn + For)
S2808	1600	5.5	1 h 40 min	Sp + En (minor Kn + For)
S2809	1200	6	11	Sp + En (minor Kn + For)
S2812	1600	6.7	1 h 35 min	Kn + For (minor Sp + En)
S2815	1400	8	6	Kn + For (minor Sp + En)
S2904	1200	7.75	10	Sp + En (minor Kn + For)
S2905	1200	9	12	Kn + For (minor Sp + En)
S2906	1500	6.7	5 h 20 min	Kn + For (minor Sp + En)
S2907	1400	6.4	5 h 20 min	Sp + En (minor Kn + For)

Individual experimental run conditions, experimental results and starting materials. T is temperature in °C, P is calculated run pressure using a number of different calibration runs. Kn = knorringite ($Mg_3Cr_2Si_3O_{12}$), For = forsterite (Mg_2SiO_4), Sp = magnesiochromite ($MgCr_2O_4$), En = enstatite ($MgSiO_3$). All experiments were run with starting material GS2 which contained all four phases that were synthesised prior to the commencement of the study (see text for details). S2685 and S2686 were knorringite synthesis runs and contained $MgCr_2O_4$, MgO and SiO_2 as starting material. Estimated pressure uncertainties are in the order of 0.2 GPa and temperature uncertainties are estimated to be ±15 °C. Note that for runs S2906 and S2907 the thermocouples were dysfunctional, therefore the estimated temperature uncertainties are probably in the order of ±50 °C.

Seifert and Ringwood, 1988). The knorringite garnets were stoichiometric and showed no majorite component. It should be noted that almost all experiments contain coexisting enstatite and knorringite garnets. It is rather surprising that no majorite component was found even at pressures as high as 16 GPa, as significant majorite substitution was reported in pyrope garnets at much lower pressures (Ito and Taka-
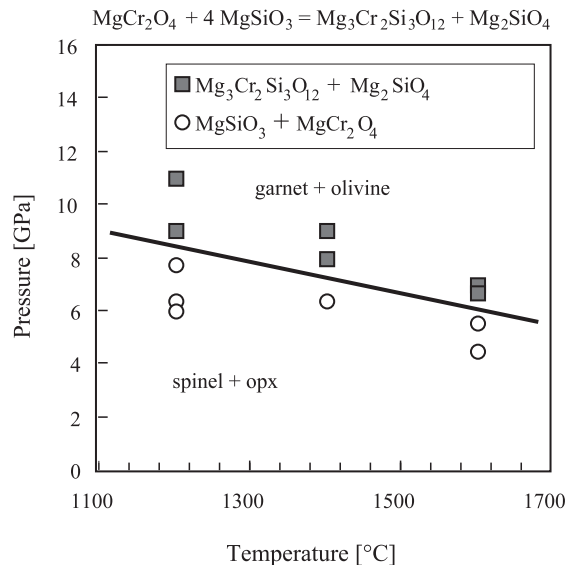
$$MgCr_2O_4 + 4\,MgSiO_3 = Mg_3Cr_2Si_3O_{12} + Mg_2SiO_4$$

Fig. 3. Experimental results on the garnet–spinel transition in the system $MgO–Cr_2O_3–SiO_2$. Filled squares represent garnet stability, whereas circles represent spinel stability.
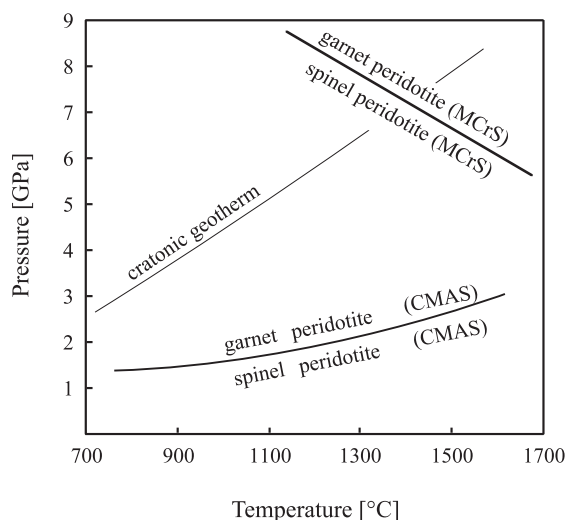
Fig. 4. The garnet–spinel transition in both Cr-free (CMAS: CaO–MgO–Al_2O_3–SiO_2) and Al-free (MCrS: MgO–Cr_2O_3–SiO_2) mantle. A cratonic geotherm ($40 mW/m^2$) intersects the garnet–spinel transition in Al-free mantle at around 7 GPa and 1400 °C.

hashi, 1987; Liu, 1977; Ringwood, 1967; Ringwood and Major, 1971). The present experiments seem to indicate that knorringite is far less susceptible to the majorite substitution than pyrope garnets which would be an interesting subject for further research.

3. Experimental results and discussion

The experimental results on the garnet–spinel transition in the system MgO–Cr_2O_3–SiO_2 (reaction (2)) are given in Table 1 and depicted in Fig. 3. The experiments that closely bracket the reaction are highlighted in the diagram. The garnet–spinel transi-

tion in Al-free compositions (i.e. MgO–Cr_2O_3–SiO_2) exhibits a negative slope in pressure–temperature space which is in stark contrast to the analogue reaction in a Cr-free or fertile compositions (Fig. 4). Note that Doroshev et al. (1997) and Girnis and Brey (1999) proposed a roughly similar position of reaction (3) based on thermodynamic extrapolations. Thermodynamic evaluation of the experimental data yields $S°_{298} = 377$ J mol^{-1} K^{-1} and $\Delta_f°H = -5542$ kJ mol^{-1} for knorringite garnet ($Mg_3Cr_2Si_3O_{12}$), given the thermodynamic data for $MgCr_2O_4$, $MgSiO_3$ and Mg_2SiO_4 (Table 3) and neglecting the effects of possible solid solutions (Klemme and O'Neill, 1997, 2000a,b).

The present experiments define the maximum stability of spinel in the Earth's upper mantle. It may be concluded that no Cr-rich spinel, commonly found in diamond inclusions and in mantle xenoliths has originated at pressures higher than 7.5 GPa assuming a normal cratonic mantle geotherm (Griffin et al., 1999; Kopylova et al., 1999; Russell and Kopylova, 1999). This implies that Cr-rich spinels, commonly transported to the Earth's surface in mantle xenoliths in kimberlites and frequently reported as diamond inclusions, cannot have originated from depths greater than about 240 km.

Moreover, new thermodynamic data for knorringite (this study), Cr-bearing spinels (Klemme et al., 2000) and Cr-bearing pyroxenes (Klemme and O'Neill, 2000a,b) enable thermodynamic calculations to investigate the influence of Cr on phase equilibria with mantle minerals (see Table 3). The thermodynamics of Cr–Al spinel solid solutions, and Cr–Al pyroxene solid solutions are reasonably well understood (Klemme and O'Neill, 2000a,b; Oka et al., 1984),

Table 3
Thermodynamic data

	$\Delta_f H°$ [J mol^{-1}]	Source	$S°$ [J mol^{-1} K^{-1}]	Source	$V°_{298}$ [J bar^{-1} mol^{-1}]	Source
$MgCr_2O_4$	− 1762000	K00	119.6	K00	4.356	R79
Mg_2SiO_4	− 2171870	HP90	94.01	HP90	4.366	HP90
$Mg_3Cr_2Si_3O_{12}$	− 5542310	this study	376.7	this study	11.738	IRI82
$Mg_3Al_2Si_3O_{12}$	− 6282900	K98	266.4	K98	11.318	HP90
$Mg_2Si_2O_6$	− 3089400	HP90	132.5	HP90	6.262	HP90
$MgAl_2SiO_6$	− 3201000	K98	115.7	K98	5.892	K98
$MgCr_2SiO_6$	− 2637800	K98	169.3	K98	6.116	K98

References: K00 = (Klemme et al., 2000), HP90 = (Holland and Powell, 1990), IRI82 = (Irifune et al., 1982), R79 = (Robie et al., 1979). K98 = (Klemme, 1998), Solid solutions used for modelling: $MgAl_2O_4$–$MgCr_2O_4$ (Oka et al., 1984), $Mg_2Si_2O_6$–$MgCr_2SiO_6$ (Klemme, 1998; Klemme and O'Neill, 2000a,b), $Mg_3Al_2Si_3O_{12}$–$Mg_3Cr_2Si_3O_{12}$ (ideal).

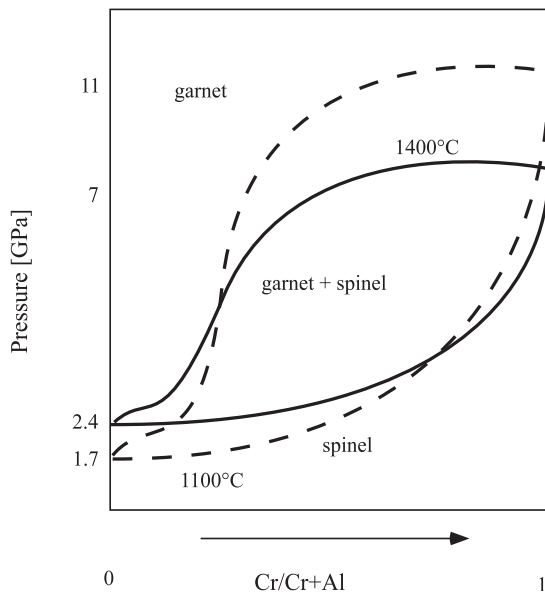Fig. 5. The effect of Cr on the stability of garnet and spinel, based on thermodynamic models in the system $MgO-Al_2O_3-Cr_2O_3-SiO_2$. The garnet–spinel transition is univariant in compositions with $Cr/(Cr+Al)=0$ and $Cr/(Cr+Al)=1$. At intermediate compositions a divariant field exists where garnet and spinel coexist. The width of this garnet + spinel stability field is strongly dependent on $Cr/(Cr+Al)$. In relatively fertile compositions ($Cr/(Cr+Al) \approx 0.1$) the garnet + spinel stability field is relatively narrow. If the bulk composition has $Cr/(Cr+Al) \geq 0.2$ the garnet + spinel stability field expands quite dramatically and spinel is stable to pressures of 7 GPa and higher. The solid lines show coexisting garnet and spinel compositions at 1400 °C, whereas the dashed lines depict their compositions at 1100 °C.

thermodynamics of the pyrope-knorringite solid solution, however, remain somewhat uncertain. As data is lacking, ideal solution was assumed, based on near-ideal chromium-aluminium mixing along the join $Ca_3Al_2Si_3O_{12}-Ca_3Cr_2Si_3O_{12}$ (Wood and Kleppa, 1984). Using free energy minimisation techniques (Klemme, 1998), results from thermodynamic modelling indicate that the divariant field where garnet and spinel coexist, is strongly dependent on bulk composition (Fig. 5). Previous studies reported a strong influence of Cr on the spinel stability relative to garnet stability (Brey et al., 1999; Doroshev et al., 1997; Girnis et al., 2003; O'Neill, 1981; Webb and Wood, 1986). However, the present results from thermodynamic modelling (Fig. 5) extend to much more Cr-rich compositions. In fertile compositions ($0 < Cr/$ (Cr + Al) < 0.2), the divariant garnet + spinel stability field is only fairly narrow, in agreement with experiments in simple and complex fertile bulk compositions (e.g. Green and Ringwood, 1967; Nickel, 1986). The effect of Cr on spinel stability is only small in such relatively Cr-poor compositions. In compositions with higher $Cr/(Cr+Al)$, however, the garnet + spinel stability field expands extraordinarily when the bulk composition exceeds a $Cr/(Cr+Al)$ ratio of about 0.2 (Fig. 5).

The experiments and the results from thermodynamic modelling show that the influence of Cr on the garnet–spinel transition is extraordinary. Therefore, phase equilibria calculations in realistic mantle compositions must account for the influence of Cr (Asimov et al., 1995). Although the present thermodynamic calculations were performed in a simplified chemical composition ($MgO-Al_2O_3-Cr_2O_3-SiO_2$) and other components such as Ca or Fe may influence calculated phase equilibria, it is believed that it is Cr that exerts the major control on phase relations and that the proposed trends should also hold for more complex compositions.

Acknowledgements

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