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Garnet-spinel-olivine-orthopyroxene equilibria in the FeO-MgO-Al₂O₃-SiO₂-Cr₂O₃ system: II. Thermodynamic analysis

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Abstract: Experimental results for the four-phase assemblage in the MASCr (Doroshev *et al.*, 1997) and FMASCr (Brey *et al.*, 1999) systems are evaluated with respect to exchange (Fe-Mg and Cr-Al) and displaced equilibrium reactions (Al solubility in orthopyroxene and spinel-orthopyroxene to garnet-olivine transition). These equilibria are considered on the basis of the thermodynamic data of Berman (1988). The effects of non-ideal mixing in solid solutions is approximated by a subregular Margules formulation, independent for each site of spinel, garnet, and orthopyroxene solid solutions. Mixing parameters were calculated by linear programming considering each experimental point as an independent half-bracket for the concentration term in the respective equilibrium. Cr-Al mixing in all phases is not ideal, but the magnitudes of excess mixing energies are not large. Spinel solid solution shows asymmetric Cr-Al and Mg-Fe excess mixing energy. Cr-Al mixing in garnet is close to an ideal model with a symmetric Margules parameter of 0 to 6 kJ/mol. Standard state properties of knorringite, Mg₃Cr₂Si₃O₁₂ and orthopyroxene end-member MgCrAlSiO₆ are estimated. The major factor determining concentration dependencies of equilibrium constants is the Gibbs free energy changes of reciprocal reactions FeCr + MgAl = FeAl + MgCr in spinel and garnet. The derived thermodynamic parameters are used to calculate phase relationships in the four-mineral region of the FMASCr system, which models depleted mantle harzburgite. The Cr/(Cr+Al) ratio of garnet increases with both pressure and temperature, while that of spinel depends mainly on pressure. The distribution of Cr and Al between spinel and garnet in equilibrium with orthopyroxene and olivine may be used as a thermobarometer for deep mantle xenoliths and inclusions in diamonds.

Key-words: phase equilibrium, peridotite, linear programming, thermobarometry, FeO-MgO-Al₂O₃-SiO₂-Cr₂O₃ system.

Introduction

Phase equilibria in the Earth's mantle may be quite successfully modelled by simple systems, such as MgO-Al₂O₃-SiO₂ (MAS) (Lane & Ganguly, 1980; Gasparik & Newton, 1984), FeO-MgO-Al₂O₃-SiO₂ (FMAS) (Harley & Green, 1982; Harley, 1984a), or CaO-MgO-Al₂O₃-SiO₂ (CMAS) (Herzberg, 1978; Perkins & Newton, 1980; Brey *et al.*, 1986). The addition of Cr to such simple systems greatly affects phase relationships (O'Neill, 1981; Chatterjee & Terhart, 1985)

especially equilibria including spinel and garnet. However, few experimental data were published on the Cr-bearing systems under conditions relevant to the Earth's mantle (Webb & Wood, 1986; Nickel, 1986). The experimental results presented in the first part of this study (Brey *et al.*, 1999, hereafter Part I) provide a basis for estimating the role of chromium on the equilibria between peridotite minerals and on element partitioning between coexisting phases. The system FMASCr is a close approximation to a depleted mantle harzburgite, which is generally very poor in Ca and in-

compatible elements. Moreover, the effect of minor Ca on the FMASCr system may be estimated from experimental work on Ca behaviour in garnet and pyroxene (e.g. Akella, 1976; Ellis & Green, 1979; Harley & Green, 1982; Harley, 1984a, b; Brey *et al.*, 1986).

Doroshev *et al.* (1997) presented results for the MASCr system and calculated phase equilibria including chromium-rich garnet for a range of pressures and temperatures. The present study models phase relations in mantle peridotite using the experimental data from the MASCr (Doroshev *et al.*, 1997) and FMASCr systems (Part I) at pressures from 30 to 60 kbar and temperatures from 1200 to 1500°C. The stability limits and compositions of minerals in the four-phase harzburgite assemblage (olivine, orthorhombic pyroxene, spinel, and garnet) are controlled by Fe-Mg and Cr-Al exchange equilibria and the enstatite + spinel = garnet + olivine reaction. The latter reaction as well as Fe-Mg exchange equilibria have been repeatedly studied (e.g. McGregor, 1974; Danckwerth & Newton, 1978; Sack, 1982; Engi, 1983; Sack & Ghiorso, 1989; von Seckendorff & O'Neill, 1993; Harley, 1984a; Lee & Ganguly, 1988; Kawasaki & Matsui, 1977; O'Neill & Wood, 1979). Our main concern is with Cr-Al partitioning and its influence on the stability fields of garnet and spinel peridotites. The comparison with the results on Cr-free systems is indirect through application of the internally consistent thermodynamic database of Berman (1988) extended by Sack & Ghiorso (1991, 1994a) and mixing parameters consistent with this database (Sack & Ghiorso, 1991, 1994b; Berman *et al.*, 1995). The thermodynamic data derived in the present study and those taken from the internally consistent data sets cited represent the new experimental data set without mutual conflict.

Thermodynamic formulation

Equilibrium for any chemical reaction is described by:

$$\Delta_r G^{T,P} + RT \ln K_D + \Delta_r G_{ex} = 0 \quad (1)$$

where K_D is the concentration equilibrium constant and ${}_r G_{ex}$ is the change in excess Gibbs free energy. ${}_r G^{T,P}$ is the change of Gibbs free energy of pure species at P and T , which can be calculated from the thermodynamic properties (enthalpy H , entropy S , heat capacity C_p , and volume V) of

phases at reference temperature and pressure (T_0 and P_0):

$$\Delta_r G^{T,P} = \Delta_r H^{P_0,T_0} - T \Delta_r S^{T_0,P_0} + \int_{T_0}^T \Delta_r C_p dT - T \int_{T_0}^T \frac{\Delta_r C_p}{T} dT + \int_{P_0}^P \Delta_r V dP \quad (2)$$

The formulation of both K_D and ${}_r G_{ex}$ depends on the accepted model of solid solutions, which are discussed below. Standard state properties for the majority of species considered in this work are given by Berman (1988) and Sack & Ghiorso (1991, 1994b). The more recent thermodynamic parameters provided by Berman & Aranovich (1996) were not used for two reasons. First, unlike the Berman (1988) data, the standard properties of end-members were optimized together with mixing properties (Berman & Aranovich, 1996). Any changes in mixing parameters would destroy the consistency of the Berman & Aranovich (1996) data and can be justified only if all the relevant experimental observations were taken into account. The revision of the whole data set was beyond the scope of the present work, although the incorporation of Cr-Al substitution required certain changes in other mixing parameters. Second, the data of Sack & Ghiorso (1991, 1994b) on Cr-bearing species and aluminous pyroxene are based on Berman (1988) and the compatibility with Berman & Aranovich (1996) is not evident.

Olivine

Olivine from both MASCr and FMASCr experiments always contains substantial amounts of Cr (mostly between 0.5 and 1.2, sometimes up to 2.4 wt.% Cr_2O_3), probably as Cr^{2+} (Part I). Li *et al.* (1995) obtained a Margules mixing parameter of 8600 J/mol for the Mg_2SiO_4 - Cr_2SiO_4 solid solution. Such non-ideality contributes no more than 200 J/mol (in most cases <100 J/mol) to the total excess mixing energy of the experimental olivine. The lack of correlation between Cr content in olivine and experimental conditions does not allow quantitative treatment of Cr_2SiO_4 solution properties. Thus, composition of olivine is described only by $X_{Mg}Ol = Mg/(Mg+Fe)$. Positive deviation from ideal mixing was inferred for $(Fe,Mg)_2SiO_4$ olivines by Sack & Ghiorso (1989), Wisser & Wood (1991), von Seckendorff & O'Neill (1993). Hirschmann (1991) proposed a model to describe ordering of Fe and Mg between two non-equival-

ent sites but at high temperatures (> 1000°C) and low iron contents it is very small and may be ignored. For a symmetrical Margules model the chemical potentials of forsterite and fayalite and Mg-Fe exchange potential are as follows:

$$\mu_{\text{Mg}_2\text{SiO}_4} = \Delta G_{\text{fo}}^0 + 2RT \ln X_{\text{Mg}}^{\text{Ol}} + 2W_{\text{FeMg}}^{\text{Ol}}(1 - X_{\text{Mg}}^{\text{Ol}})^2 \quad (3)$$

$$\mu_{\text{Fe}_2\text{SiO}_4} = \Delta G_{\text{fa}}^0 + 2RT \ln(1 - X_{\text{Mg}}^{\text{Ol}}) + 2W_{\text{FeMg}}^{\text{Ol}}(X_{\text{Mg}}^{\text{Ol}})^2 \quad (4)$$

$$\begin{aligned} \mu_{\text{Mg(Fe)}_{-1}} &= 1/2(\mu_{\text{Mg}_2\text{SiO}_4} - \mu_{\text{Fe}_2\text{SiO}_4}) = 1/2(\Delta G_{\text{fo}}^0 - \Delta G_{\text{fa}}^0) \\ &+ RT \ln \left[\frac{S_{\text{Mg}}^{\text{Ol}}}{(1 - X_{\text{Mg}}^{\text{Ol}})} \right] + W_{\text{FeMg}}^{\text{Ol}}(1 - 2X_{\text{Mg}}^{\text{Ol}}) \end{aligned} \quad (5)$$

All Margules mixing parameters were assumed to be linear in pressure and temperature *i.e.* $W = W^{\text{H}} - TW^{\text{S}} + PW^{\text{V}}$ (Thompson, 1967). The value of $W_{\text{FeMg}}^{\text{Ol}} = 7137.2 + 1.26T + 0.01(P-1)$ [J/mol] was adopted from Berman & Aranovich (1996).

Spinel

Spinel in our experimental products are close to the plane $\text{MgAl}_2\text{O}_4 - \text{FeAl}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{FeCr}_2\text{O}_4$. A model including such spinel solid solutions and compatible with the standard state properties by Berman (1988) was developed by Sack & Ghiorso (1991). This model utilises the second-degree Taylor expansion of Gibbs free energy in composition and ordering parameters and suggests symmetrical deviation from ideal mixing in binary joins independent of temperature and pressure. The ordering parameters calculated by the Sack & Ghiorso (1991) model ($s_1 = X_{\text{Al}}^{\text{Oct}} - X_{\text{Al}}^{\text{Tet}}/2$) and $s_2 = X_{\text{Mg}}^{\text{Tet}} - 2X_{\text{Mg}}^{\text{Oct}}$ for (Fe, Mg)(Cr, Al) O_4 spinels may be successfully approximated by the second-degree Taylor series in composition and temperature within a temperature range of 800–1600°C. Substitution of such expansions into the expression for the Gibbs free energy given by Sack & Ghiorso (1991) results in a third-degree expression in compositional variables (fourth-degree terms are very small and may be ignored). This is equivalent to a model which assumes asymmetric, temperature-dependent non-ideality in binary joins and does not account for cation ordering. It means that it is very difficult to separate the energy effects of cation ordering and deviation from symmetrical regular behaviour in binary sections. Crucial for the correct formulation of thermodynamic properties of spinel are direct measure-

ments of spinel ordering state at different temperatures and compositions. Such data are scarce and sometimes contradictory (Wood *et al.*, 1986; Millard *et al.*, 1992). There are no data on the influence of pressure on the ordering state of spinel, and the model of Sack & Ghiorso (1991) does not account for pressure influence on mixing properties, whereas the molar volume data (Part I) indicate non-zero excess mixing volumes of Cr-Al spinels.

We adopted a simplified model for spinel solid solutions neglecting cation ordering and assuming non-ideal asymmetric mixing of Fe-Mg and Cr-Al on independent sites. This is equivalent to assuming all spinels to be normal. Such a simplification is reasonable for Cr-rich varieties but could be unsatisfactory for aluminous spinel at high temperature (*e.g.* Sack & Ghiorso, 1991). However, the latter does not occur in high-pressure mantle assemblages with khorringite-rich garnet. The composition of spinel is defined by two variables, $X_{\text{Mg}}^{\text{Sp}} = \text{Mg}/(\text{Mg}+\text{Fe})$ and $X_{\text{Cr}}^{\text{Sp}} = \text{Cr}/(\text{Cr}+\text{Al})$. Choosing chromite (*chr*, FeCr_2O_4), spinel (*sp*, MgAl_2O_4) and picrochromite (*pc*, MgCr_2O_4) as independent end-members, we obtain the following expression for the excess free energy of mixing:

$$\begin{aligned} G_{\text{Sp}}^{\text{ex}} &= (1 - X_{\text{Mg}}^{\text{Sp}})(1 - X_{\text{Cr}}^{\text{Sp}})\Delta G_{\text{I}} \\ &+ X_{\text{Mg}}^{\text{Sp}}(1 - X_{\text{Mg}}^{\text{Sp}}) \left[W_{\text{MgFe}}^{\text{Fe}}(1 - X_{\text{Mg}}^{\text{Sp}}) + W_{\text{FeMg}}^{\text{Sp}} X_{\text{Mg}}^{\text{Sp}} \right] \\ &+ 2X_{\text{Cr}}^{\text{Sp}}(1 - X_{\text{Cr}}^{\text{Sp}}) \left[W_{\text{CrAl}}^{\text{Sp}}(1 - X_{\text{Cr}}^{\text{Sp}}) + W_{\text{AlCr}}^{\text{Sp}} X_{\text{Cr}}^{\text{Sp}} \right], \end{aligned} \quad (6)$$

where ΔG_{I} is the Gibbs free energy change of the reciprocal reaction



Differentiation of Eq. 6 with respect to compositional variables yields the chemical potentials of MgAl_2O_4 , Mg(Fe)_{-1} and Al(Cr)_{-1} :

$$\begin{aligned} \mu_{\text{MgAl}_2\text{O}_4} &= \Delta G_{\text{sp}}^0 + RT \ln X_{\text{Mg}}^{\text{Sp}} (X_{\text{Al}}^{\text{Sp}})^2 + (1 - X_{\text{Mg}}^{\text{Sp}}) X_{\text{Cr}}^{\text{Sp}} \Delta G_{\text{I}} \\ &+ (1 - X_{\text{Mg}}^{\text{Sp}})^2 \left[W_{\text{MgFe}} + 2X_{\text{Mg}}^{\text{Sp}} (W_{\text{FeMg}}^{\text{Sp}} - W_{\text{MgFe}}^{\text{Sp}}) \right] \\ &+ 2(X_{\text{Cr}}^{\text{Sp}})^2 \left[W_{\text{CrAl}}^{\text{Sp}} + 2X_{\text{Cr}}^{\text{Sp}} (W_{\text{AlCr}}^{\text{Sp}} - W_{\text{CrAl}}^{\text{Sp}}) \right] \end{aligned} \quad (7)$$

$$\begin{aligned} \mu_{\text{Mg(Fe)}_{-1}} &= \Delta G_{\text{sp}}^0 - \Delta G_{\text{hc}}^0 + RT \ln \left[\frac{X_{\text{Mg}}^{\text{Sp}}}{(1 - X_{\text{Mg}}^{\text{Sp}})} \right] + X_{\text{Cr}}^{\text{Sp}} \Delta G_{\text{I}} \\ &- W_{\text{MgFe}}^{\text{Sp}} (1 - X_{\text{Mg}}^{\text{Sp}}) (3X_{\text{Mg}}^{\text{Sp}} - 1) \\ &- W_{\text{FeMg}}^{\text{Sp}} X_{\text{Mg}}^{\text{Sp}} (3X_{\text{Mg}}^{\text{Sp}} - 2) \end{aligned} \quad (8)$$

$$\mu_{\text{Al(Cr)}_{-1}} = 1/2(\Delta G_{\text{sp}}^0 - \Delta G_{\text{pc}}^0) + RT \ln \left[(1 - X_{\text{Cr}}^{\text{Sp}}) / X_{\text{Cr}}^{\text{Sp}} \right]$$

$$\begin{aligned}
 & + \frac{1}{2}(1 - X_{Mg}^{Sp})\Delta G_I + W_{AlCr}^{Sp} X_{Cr}^{Sp} (3X_{Cr}^{Sp} - 2) \\
 & + W_{CrAl}^{Sp} (1 - X_{Cr}^{Sp}) (3X_{Cr}^{Sp} - 1)
 \end{aligned} \quad (9)$$

Garnet

Garnet in experimental products from one of our starting materials contains up to 2 wt.% CaO (Part I). Thus, garnet must be described as $(Ca, Fe, Mg)_3(Cr, Al)_2Si_3O_{12}$ solid solution. The composition of garnet is then fully described by $X_{Ca}^{Grt} = Ca/(Ca+Mg+Fe)$, $X_{Mg}^{Grt} = Mg/(Ca+Mg+Fe)$, and $X_{Cr}^{Grt} = Cr/(Cr+Al)$. Pyrope (*pyr*, $Mg_3Al_2Si_3O_{12}$), almandine (*alm*, $Fe_3Al_2Si_3O_{12}$), grossular (*gr*, $Ca_3Al_2Si_3O_{12}$) and knorringite (*kn*, $Mg_3Cr_2Si_3O_{12}$) were used as independent end-members. The relative stability of two other possible end-members ($Fe_3Cr_2Si_3O_{12}$ and $Ca_3Cr_2Si_3O_{12}$) is accounted for by the changes of Gibbs free energies of reciprocal reactions describing formation of these species (ΔG_{II} and ΔG_{III} , respectively). Assuming independent mixing of (Fe, Mg, Ca) and (Cr, Al) we obtain:

$$\begin{aligned}
 G_{Grt}^{ex} = & (1 - X_{Mg}^{Grt} - X_{Ca}^{Grt})X_{Cr}^{Grt}\Delta G_{II} + X_{Ca}^{Grt}X_{Cr}^{Grt}\Delta G_{III} \\
 & + G_{Ca-Mg-Fe}^{ex} + G_{Cr-Al}^{ex}
 \end{aligned} \quad (10)$$

where the excess energies are distinguished on each site. The mixing of Ca, Mg and Fe in aluminous garnet has been extensively studied (*e.g.* Geiger *et al.*, 1987; Wood, 1988; Koziol & Newton, 1989; Koziol, 1990). Berman (1990) proposed a model for such garnet using the generalised regular solution equation (Berman & Brown, 1984):

$$\begin{aligned}
 G_{Ca-Mg-Fe}^{ex} = & W_{112}X_1^2X_2 + W_{122}X_1X_2^2 + W_{113}X_1^2X_3 \\
 & + W_{133}X_1X_3^2 + W_{223}X_2^2X_3 + W_{233}X_2X_3^2 \\
 & + W_{123}X_1X_2X_3
 \end{aligned} \quad (11)$$

where indices 1, 2 and 3 denote Ca, Mg, and Fe, respectively. To account for the mixing of divalent cations, we use the parameters given by Berman *et al.* (1995). Cr-Al mixing in garnets is not well known. Existing thermochemical and experimental data suggest that W_{Cr-Al} is rather small (Mattioli & Bishop, 1984; Wood & Kleppa, 1984). Our volume measurements (Part I) indicate non-zero excess mixing volume and a possible asymmetry in

the Cr-Al join. Because of this we started from the asymmetric model

$$G_{Cr-Al}^{ex} = 2X_{Cr}^{Grt}(1 - X_{Cr}^{Grt}) \left[W_{AlCr}^{Grt}X_{Cr}^{Grt} + W_{CrAl}^{Grt}(1 - X_{Cr}^{Grt}) \right] \quad (12)$$

From Eqs. 10–12 we have for the chemical potential of $Mg_3Al_2Si_3O_{12}$, $Mg(Fe)_{-1}$ and $Al(Cr)_{-1}$:

$$\begin{aligned}
 \mu_{Mg_3Al_2Si_3O_{12}} = & \Delta G_{pyr}^0 + RT \ln (X_{Mg}^{Grt})^3 (X_{Al}^{Grt})^2 \\
 & - (1 - X_{Mg}^{Grt} - X_{Ca}^{Grt})X_{Cr}^{Grt}\Delta G_{II} - X_{Ca}^{Grt}X_{Cr}^{Grt}\Delta G_{III} \\
 & + W_{112}(X_{Ca}^{Grt})^2(1 - 3X_{Mg}^{Grt}) \\
 & - 3W_{113}(X_{Ca}^{Grt})^2(1 - X_{Ca}^{Grt} - X_{Mg}^{Grt}) \\
 & + W_{122}X_{Ca}^{Grt}X_{Mg}^{Grt}(2 - 3X_{Mg}^{Grt}) - 3W_{133}X_{Ca}^{Grt} \\
 & (1 - X_{Mg}^{Grt} - X_{Mg}^{Grt})^2 + W_{123}X_{Ca}^{Grt}(1 - X_{Ca}^{Grt} - X_{Mg}^{Grt}) \\
 & + W_{223}X_{Mg}^{Grt}(1 - X_{Mg}^{Grt} - X_{Ca}^{Grt})(2 - 3X_{Mg}^{Grt}) \\
 & + W_{233}(1 - X_{Mg}^{Grt} - X_{Ca}^{Grt})(1 - 3X_{Mg}^{Grt}) \\
 & + 2(X_{Cr}^{Grt})^2 [W_{AlCr}^{Grt} \\
 & + 2(1 - X_{Cr}^{Grt})(W_{CrAl}^{Grt} - W_{AlCr}^{Grt})]
 \end{aligned} \quad (13)$$

$$\begin{aligned}
 \mu_{Mg(Fe)_{-1}} = & \frac{1}{3}(\Delta G_{pyr}^0 - \Delta G_{alm}^0) + RT \ln \left[X_{Mg}^{Grt}(1 - X_{Mg}^{Grt} - X_{Ca}^{Grt}) \right] \\
 & + \frac{1}{3} [W_{112}(X_{Ca}^{Grt})^2 + 2W_{122}X_{Ca}^{Grt}X_{Mg}^{Grt} \\
 & - W_{113}(X_{Ca}^{Grt})^2 - W_{133}X_{Ca}^{Grt}X_{Fe}^{Grt} \\
 & + W_{223}X_{Mg}^{Grt}(2X_{Fe}^{Grt} - X_{Mg}^{Grt}) \\
 & + W_{233}X_{Fe}^{Grt}(X_{Fe}^{Grt} - 2X_{Mg}^{Grt}) \\
 & + W_{123}X_{Ca}^{Grt}(X_{Fe}^{Grt} - X_{Mg}^{Grt}) - X_{Cr}^{Grt}\Delta G_{II}]
 \end{aligned} \quad (14)$$

$$\begin{aligned}
 \mu_{Al(Cr)_{-1}} = & \frac{1}{2}(\Delta G_{pyr}^0 - \Delta G_{kn}^0) + RT \ln \left[(1 - X_{Cr}^{Grt})/X_{Cr}^{Grt} \right] \\
 & - \frac{1}{2}(1 - X_{Mg}^{Grt} - X_{Ca}^{Grt})\Delta G_{II} - \frac{1}{2}X_{Ca}^{Grt}\Delta G_{III} \\
 & + W_{AlCr}^{Grt}X_{Cr}^{Grt} - (3X_{Cr}^{Grt} - 2) \\
 & + W_{CrAl}^{Grt}(1 - X_{Cr}^{Grt})(3X_{Cr}^{Grt} - 1)
 \end{aligned} \quad (15)$$

Orthopyroxene

Orthopyroxene in the FMASCr system may be considered as a three-site solid solution with Si and Al mixing on tetrahedral sites, Mg-Fe on octahedral M2, and Mg, Fe, Cr, and Al on octahedral M1 sites. Site occupancy data demonstrate ordering with Fe partitioning into M2 site (*e.g.* Virgo

& Hafner, 1969; Domeneghetti *et al.*, 1995). Sack & Ghiorso (1994a) proposed a comprehensive model for orthopyroxene solid solutions, which takes into account ordering and non-ideal mixing of end-members. It does not consider Cr in orthopyroxene and is based on the available site partitioning data (Sack & Ghiorso, 1989) which are scattered and restricted to temperatures below 1000°C and atmospheric pressure. The effect of Al and Cr on site occupancies is also not clear. We therefore used a simplified model with random distribution of Fe and Mg between M1 and M2 sites. Three independent compositional parameters are sufficient to specify orthopyroxene composition: $X_{Mg}^{Opx} = Mg/(Mg+Fe)$; $X_{Al}^{M1} = (Al-Cr)/2$; and $X_{Cr}^{M1} = Cr$. We also assumed that Si and Al mix ideally on the tetrahedral position, that mixing on the M1 and M2 sites is independent and that a simple symmetric regular model could be applied for each site (*cf.* Berman *et al.*, 1995). Calibration of more complex models is not justified by the quality of available experimental data (especially, the scatter of Cr and Al contents in orthopyroxenes). Furthermore, possible deviation from a simple regular model for Mg-Fe-Cr-Al mixing may be significant only at high concentrations of Cr and Al; these do not occur in mantle peridotites. At high pressures Al in orthopyroxene is very low and nonideal mixing behaviour becomes almost negligible which allows reliable extrapolation to higher pressure where experimental data are lacking.

With these assumptions we selected enstatite (*en*, $Mg_2Si_2O_6$), ferrosilite (*fs*, $Fe_2Si_2O_6$), $MgAlAlSiO_6$ (*ts*) and $MgCrAlSiO_6$ (*Crts*) as independent end-members. Two other possible end-members ($FeAlAlSiO_6$ and $FeCrAlSiO_6$) are taken into account by two reciprocal terms (G_{IV} and G_V , respectively):

$$G_{Opx}^{ex} = (1-X_{Mg}^{Opx})X_{Al}^{M1}\Delta G_{IV} + (1-X_{Mg}^{Opx})X_{Cr}^{M1}\Delta G_V + X_{Mg}^{Opx}(1-X_{Mg}^{Opx})W_{FeMg}^{M2} + W_{FeMg}^{M1}X_{Mg}^{Opx}(1-X_{Mg}^{Opx})(1-X_{Al}^{M1}-X_{Cr}^{M1})^2 + W_{MgAl}^{M1}X_{Mg}^{Opx}X_{Al}^{M1}(1-X_{Al}^{M1}-X_{Cr}^{M1}) + W_{MgCr}^{M1}X_{Mg}^{Opx}X_{Cr}^{M1}(1-X_{Al}^{M1}-X_{Cr}^{M1}) + W_{FeAl}^{M1}X_{Al}^{M1}(1-X_{Mg}^{Opx})(1-X_{Al}^{M1}-X_{Cr}^{M1}) + W_{FeCr}^{M1}X_{Cr}^{M1}(1-X_{Mg}^{Opx})(1-X_{Al}^{M1}-X_{Cr}^{M1}) + W_{AlCr}^{M1}X_{Al}^{M1}X_{Cr}^{M1} \quad (16)$$

The chemical potentials for enstatite, $MgAlAlSiO_6$ and the Mg-Fe and Al-Cr exchange potentials are then:

$$\mu_{Mg_2Si_2O_6} = \Delta G_{en}^0 + RT \ln \left[(X_{Mg}^{Opx})^2 (1-X_{Al}^{M1}-X_{Cr}^{M1}) + (1-X_{Mg}^{Opx})^2 W_{FeMg}^{M2} + (1-2X_{Mg}^{M1})(X_{Fe}^{M1} W_{FeMg}^{M1} + X_{Al}^{M1} + W_{MgAl}^{M1} + X_{Cr}^{M1} W_{MgCr}^{M1}) - 2(X_{Al}^{M1} X_{Cr}^{M1} W_{AlCr}^{M1} + X_{Al}^{M1} X_{Fe}^{M1} W_{FeAl}^{M1} + X_{Cr}^{M1} X_{Fe}^{M1} W_{FeCr}^{M1}) - (1-X_{Mg}^{Opx}) X_{Al}^{M1} \Delta G_{IV} - (1-X_{Mg}^{Opx}) X_{Cr}^{M1} \Delta G_V \right] \quad (17)$$

$$\mu_{MgAlAlSiO_6} = \Delta G_{ts}^0 + RT \ln \left[X_{Mg}^{Opx} X_{Al}^{M1} + (1-X_{Mg}^{Opx})^2 W_{MgFe}^{M2} + (1-2X_{Al}^{M1})(X_{Mg}^{M1} W_{MgAl}^{M1} + X_{Fe}^{M1} W_{FeAl}^{M1} + X_{Cr}^{M1} W_{AlCr}^{M1}) - 2(X_{Mg}^{M1} W_{FeMg}^{M1} + X_{Mg}^{M1} X_{Cr}^{M1} W_{MgCr}^{M1} + X_{Cr}^{M1} X_{Fe}^{M1} W_{FeCr}^{M1}) - (1-X_{Mg}^{Opx}) X_{Cr}^{M1} \Delta G_V + (1-X_{Mg}^{Opx})(1-X_{Al}^{M1}) \Delta G_{IV} \right] \quad (18)$$

$$\mu_{Mg(Fe)_{-1}} = \Delta G_{MgSiO_3}^0 - \Delta G_{FeSiO_3}^0 + RT \ln \left[X_{Mg}^{Opx} / (1-X_{Mg}^{Opx}) + 1/2 \left[(1-2X_{Mg}^{Opx}) W_{FeMg}^{M2} + (1-2X_{Mg}^{Opx})(1-X_{Al}^{M1}-X_{Cr}^{M1}) W_{FeMg}^{M1} + X_{Al}^{M1} (W_{MgAl}^{M1} - W_{FeAl}^{M1}) \Delta G_{IV} + X_{Cr}^{M1} (W_{MgCr}^{M1} - W_{FeCr}^{M1}) \Delta G_V \right] \right] \quad (19)$$

$$\mu_{Al(Cr)_{-1}} = \Delta G_{MgAlAlSiO_6}^0 - \Delta G_{MgCrAlSiO_6}^0 + RT \ln \left[X_{Al}^{M1} / X_{Cr}^{M1} + (1-X_{Mg}^{Opx})(\Delta G_{IV} - \Delta G_V) + (X_{Cr}^{M1} - X_{Al}^{M1}) W_{CrAl}^{M1} + X_{Mg}^{M1} (W_{MgAl}^{M1} - W_{MgCr}^{M1}) + X_{Fe}^{M1} (W_{FeAl}^{M1} - W_{FeCr}^{M1}) \right] \quad (20)$$

Phase equilibria

For a given pressure, temperature, bulk $Mg/(Mg+Fe)$ ratio, Ca in garnet and Cr in olivine, the equilibrium compositions of all four phases are fully determined by 7 independent reactions. The choice of independent reactions is arbitrary in principle, they may however be selected such that calibration of mixing parameters is facilitated. Since in our experiments spinel is the phase with minimum scatter in both X_{Mg} and X_{Cr} (Part I), it is best to consider $Fe(Mg)_{-1}$ and $Al(Cr)_{-1}$ exchange

equilibria of spinel with all other phases. The first 5 equilibria are then:

1. Mg(Fe)₋₁ exchange between spinel and olivine
2. Mg(Fe)₋₁ exchange between spinel and orthopyroxene
3. Mg(Fe)₋₁ exchange between spinel and garnet
4. Al(Cr)₋₁ exchange between spinel and orthopyroxene
5. Al(Cr)₋₁ exchange between spinel and garnet

In addition we must specify the magnitude of Al or Cr solubility in orthopyroxene and the conditions of the equilibrium between all four phases. For this we choose two reactions from the MAS system which have been experimentally investigated over a wide range of P, T conditions:

6. $\text{Mg}_2\text{Si}_2\text{O}_6^{\text{Opx}} + \text{MgAlAlSiO}_6^{\text{Opx}} = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}^{\text{Grt}}$
7. $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}^{\text{Grt}} + \text{Mg}_2\text{SiO}_4^{\text{Ol}} = 2\text{Mg}_2\text{Si}_2\text{O}_6^{\text{Opx}} + \text{MgAl}_2\text{O}_4^{\text{Sp}}$

Using the above expressions for the chemical potentials of components (Eqs. 3-20), we obtain the following conditions of equilibrium:

$$\begin{aligned} \Delta_r G_1 &= 0 = (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Ol}} - (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Sp}}) \\ &= \Delta_r G_1^0 + \text{RT} \ln \left[\frac{X_{\text{Mg}}^{\text{Ol}} (1 - X_{\text{Mg}}^{\text{Sp}})}{X_{\text{Mg}}^{\text{Sp}} (1 - X_{\text{Mg}}^{\text{Ol}})} \right] \\ &+ \Delta_r G_1^{\text{ex}}, \end{aligned} \quad (21)$$

$$\begin{aligned} \Delta_r G_2 &= 0 = (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Opx}} - (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Sp}}) \\ &= \Delta_r G_2^0 + \text{RT} \ln \left[\frac{X_{\text{Mg}}^{\text{Opx}} (1 - X_{\text{Mg}}^{\text{Sp}})}{X_{\text{Mg}}^{\text{Sp}} (1 - X_{\text{Mg}}^{\text{Opx}})} \right] \\ &+ \Delta_r G_2^{\text{ex}}, \end{aligned} \quad (22)$$

$$\begin{aligned} \Delta_r G_3 &= 0 = (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Grt}} - (\mu_{\text{Mg}(\text{Fe})_{-1}}^{\text{Sp}}) \\ &= \Delta_r G_3^0 + \text{RT} \ln \left[\frac{X_{\text{Mg}}^{\text{Grt}} (1 - X_{\text{Mg}}^{\text{Sp}})}{X_{\text{Mg}}^{\text{Sp}} (1 - X_{\text{Mg}}^{\text{Grt}})} \right] \\ &+ \Delta_r G_3^{\text{ex}}, \end{aligned} \quad (23)$$

$$\begin{aligned} \Delta_r G_4 &= 0 = (\mu_{\text{Al}(\text{Cr})_{-1}}^{\text{Opx}} - (\mu_{\text{Al}(\text{Cr})_{-1}}^{\text{Sp}}) \\ &= \Delta_r G_4^0 + \text{RT} \ln \left[\frac{X_{\text{Al}}^{\text{Opx}} X_{\text{Cr}}^{\text{Sp}}}{(1 - X_{\text{Cr}}^{\text{Sp}}) X_{\text{Cr}}^{\text{Al}}} \right] + \Delta_r G_4^{\text{ex}}, \end{aligned} \quad (24)$$

$$\begin{aligned} \Delta_r G_5 &= 0 = (\mu_{\text{Al}(\text{Cr})_{-1}}^{\text{Grt}} - (\mu_{\text{Al}(\text{Cr})_{-1}}^{\text{Sp}}) \\ &= \Delta_r G_5^0 + \text{RT} \ln \left[\frac{(1 - X_{\text{Cr}}^{\text{Grt}}) X_{\text{Cr}}^{\text{Sp}}}{(1 - X_{\text{Cr}}^{\text{Sp}}) X_{\text{Cr}}^{\text{Grt}}} \right] \\ &+ \Delta_r G_5^{\text{ex}}, \end{aligned} \quad (25)$$

$$\begin{aligned} \Delta_r G_6 &= 0 = (\mu_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Grt}} - (\mu_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{Opx}}) \\ &- (\mu_{\text{MgAlAlSiO}_6}^{\text{Opx}}) \\ &= \Delta_r G_6^0 + \text{RT} \ln \left[\frac{(X_{\text{Mg}}^{\text{Grt}})^3 (1 - X_{\text{Cr}}^{\text{Grt}})^2}{(X_{\text{Mg}}^{\text{Opx}})^3} \right. \\ &\left. (1 - X_{\text{Al}}^{\text{Ml}} - X_{\text{Cr}}^{\text{Ml}}) (X_{\text{Al}}^{\text{Ml}}) \right] + \Delta_r G_6^{\text{ex}}, \end{aligned} \quad (26)$$

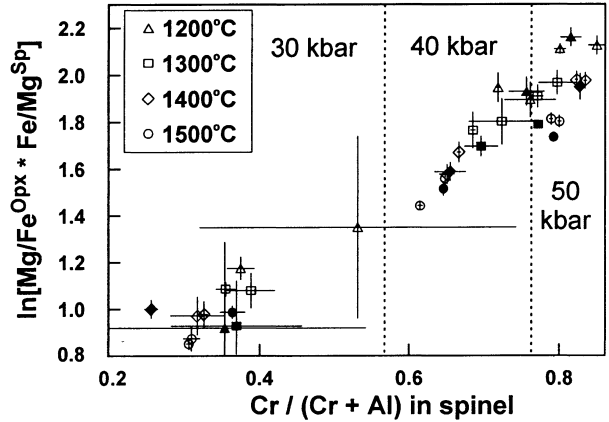
$$\begin{aligned} \Delta_r G_7 &= 0 = (\mu_{\text{MgAl}_2\text{O}_4}^{\text{Sp}} + 2(\mu_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{Opx}}) \\ &- (\mu_{\text{Mg}_2\text{SiO}_4}^{\text{Ol}}) - (\mu_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Grt}}) \\ &= \Delta_r G_7^0 + \text{RT} \ln \left[\frac{(X_{\text{Mg}}^{\text{Ml}} X_{\text{Mg}}^{\text{Ml}_2})^2 X_{\text{Mg}}^{\text{Sp}} (1 - X_{\text{Cr}}^{\text{Sp}})^2}{(X_{\text{Mg}}^{\text{Ol}})^2 (X_{\text{Mg}}^{\text{Grt}})^3 (1 - X_{\text{Cr}}^{\text{Grt}})^2} \right] + \Delta_r G_7^{\text{ex}}. \end{aligned} \quad (27)$$

Calibration of model parameters

Composition of phases

The standard state thermodynamic properties of all species participating in equilibria 1–7 except for knorringite and MgCrAlSiO₆ orthopyroxene are tabulated by Berman (1988) and Sack & Ghiorso (1991, 1994b). Most parameters related to $\Delta_r G^{\text{ex}}$ have to be determined from our experimental results. In general, the main difficulty in the interpretation of experimental data is heterogeneity of mineral compositions and lack of stringent criteria for equilibrium. As in a number of other studies, we attempted to overcome these problems by using different starting materials in order to reverse mineral reactions. This method is very successful in simple systems, whereas in more complex systems many possible exchange vectors are more difficult to account for. The brackets for equilibrium compositions with respect to Cr-Al exchange in garnet and orthopyroxene are generally not very tight both in MASCr (Doroshv *et al.*, 1997) and FMASCr (Part I) and the choice of ‘true’ equilibrium compositions was not unambiguous. Also, in the FMASCr system, compositions of minerals are not co-linear in compositional space, and the results of ‘reversal’ experiments cannot be considered as brackets defining the range within which the equilibrium composition is located. This may be exemplified for garnet compositions. We used either pure pyrope or knorringite-rich garnet in the starting mixes (Part I) to approach equilibrium composition from either the Al or Cr side. In general, newly formed garnets with a range of Cr/(Cr+Al) ratios together with relic garnets were found in each charge. The most reacted garnets in these reversals overlap for the same P and T with re-

Fig. 1. Fe/Mg distribution coefficient between orthopyroxene and spinel vs. spinel composition at various pressures and temperatures for the experiments in the FMASCr system. Average values of parameters and standard deviations are shown. Filled symbols are experiments with FeAl_2O_4 in the starting mixture, and unfilled symbols are those with MgAl_2O_4 or MgCr_2O_4 .



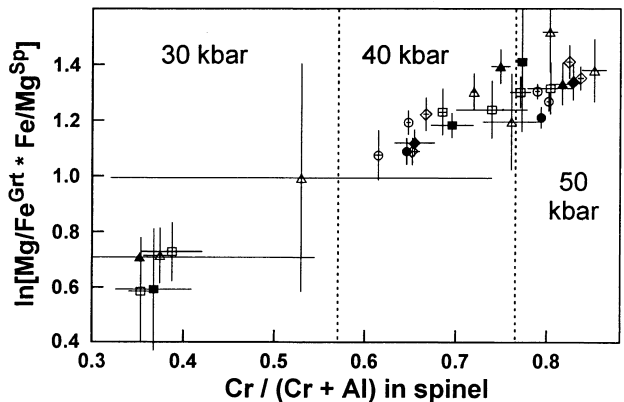
spect to $X_{\text{Cr}}^{\text{Grt}}$. In binary systems such overlap characterizes the minimum uncertainty for equilibrium composition (e.g. Berman *et al.*, 1995). In more complex systems this is not necessarily so. Garnets from the two experimental series differ in their $\text{Mg}/(\text{Mg}+\text{Fe})$ values as well, which also influence the equilibrium value of $X_{\text{Cr}}^{\text{Grt}}$.

We did not attempt to define equilibrium compositions of minerals but considered each charge independently as posing some constraints on equilibrium composition at a given P and T. These constraints are determined by the following assumptions:

1. Fe-Mg exchange is relatively fast and the range of $X_{\text{Mg}}^{\text{Grt}}$ determined for each phase contains the equilibrium value. This is supported by rather small intervals of $X_{\text{Mg}}^{\text{Grt}}$ independent of the type of starting material which had Fe either in spinel or in garnet.

2. Spinel also shows a small range in X_{Cr} and no relic spinels are found. Thus the equilibrium spinel composition should be located within this range of X_{Cr} .
3. Garnet from the experiments starting with pure pyrope [mixtures (A) and (D)] is always less chromian than garnet from the experiments starting with khorringite-rich garnet and enstatite [starting mixtures (B) and (E)]. Garnet in experimental products starting with Al-Cr orthopyroxene [starting mixtures (C) and (E)] is too inhomogeneous to pose constraints on the equilibrium with respect to Cr-Al exchange.
4. Experiments with mixtures (C) and (F) with starting Al-Cr-rich orthopyroxene were not used to constrain equilibrium orthopyroxene compositions. In all other experiments at 50 kbar and 1400–1500°C and also in experiments at lower pressure and temperature with

Fig. 2. Fe/Mg distribution coefficient between garnet and spinel vs. spinel composition at various pressures and temperatures for the experiments in the FMASCr system. Symbols show average values and error bars – one standard deviation. Filled symbols are experiments with FeAl_2O_4 in the starting mixture, and unfilled symbols are those with MgAl_2O_4 or MgCr_2O_4 .



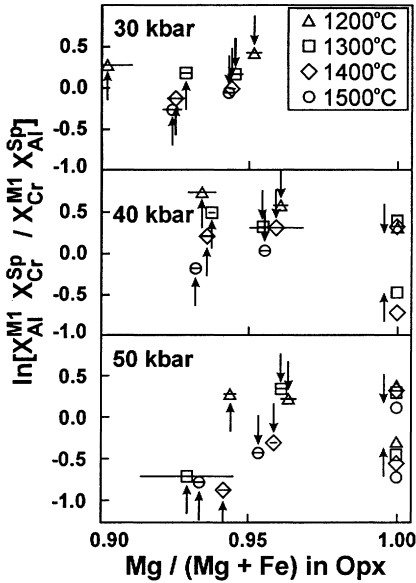


Fig. 3. Experimental constraints on the equilibrium values of Al/Cr distribution coefficient between orthopyroxene and spinel at various pressures and temperatures from experiments in MASCr (Doroshev *et al.*, 1997) and FMASCr systems. Shown are maximum or minimum values of $\ln K$ deduced from experimental results. Arrows show the direction of approach to equilibrium. Horizontal error bars are uncertainties in the Mg/(Mg + Fe) ratio of experimental phases.

pyrope in the starting mixes (A and D) orthopyroxene approached equilibrium by increasing its X_{Cr}^{M1} and X_{Al}^{M1} values. In these experiments orthopyroxene was assumed to be lower in Cr and Al than the equilibrium composition. Knorringite-rich garnet from the starting mixtures (B) and (E) decomposed at the onset of the experiments at P 50 kbar to form Al- and Cr-rich orthopyroxene. In these experiments the orthopyroxene was considered to constrain the maximum possible Cr and Al contents.

Taking these assumption we calculated minimum and maximum constraints for equilibrium constants ($K_D^<$ and $K_D^>$, respectively). Each sample provided two constraints on the Fe-Mg equilibrium between phases and one (or no) constraint with respect to Cr-Al exchange and displaced equilibrium reactions (6) and (7). Figs. 1–4 summarize experimental results on exchange equilibria between phases. Both garnet-orthopyroxene and spinel-orthopyroxene Fe-Mg exchange reac-

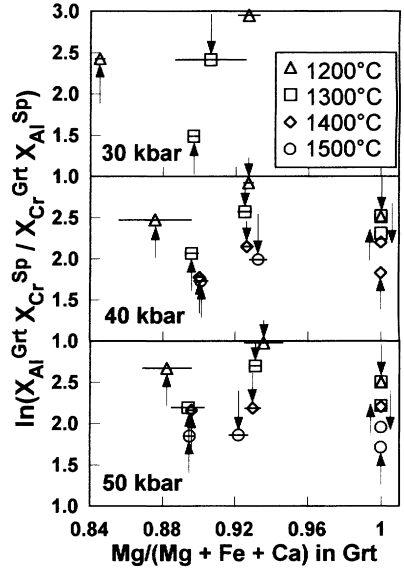


Fig. 4. Experimental constraints on the equilibrium values of Al/Cr distribution coefficient between garnet and spinel at various pressures and temperatures from experiments in the MASCr (Doroshev *et al.*, 1997) and FMASCr systems. Shown are maximum or minimum values of $\ln K$ deduced from experimental results. Arrows show the direction of approach to the equilibrium. Horizontal error bars are uncertainties in the Mg/(Mg + Fe) ratio of experimental phases.

tions depend primarily on x_{Cr}^{Sp} (Fig. 1, 2), whereas the pressure effect is smaller. This means that the Gibbs free energy change of reciprocal reaction I, ΔG_1 is the main controlling factor. The values of $\ln(K)$ for both orthopyroxene-spinel and garnet-spinel Cr-Al exchange reactions decrease with temperature (Fig. 3, 4). There is no distinct correlation of $\ln(K_4)$ and $\ln(K_5)$ with pressure and Mg/(Mg + Fe) ratio of phases.

Fig. 1–4 illustrate the main problems with the interpretation of our experimental data. Experiments at high pressures and temperatures provide narrow ranges of equilibrium constants for both Fe-Mg and Cr-Al exchange reactions suggesting close approach to equilibrium. Experiments at low temperatures (1200–1300°C) and a pressure of 30 kbar show very large variations of K_D and compositional parameters, which makes these results less valuable for the derivation of thermodynamic properties. Some of the reversals show an apparent overlap in equilibrium constants of Cr-Al exchange reactions, *i.e.* $K_D^> > K_D^<$. Note that these

discrepancies could stem from analytical uncertainties or dependence of K values on $Mg/(Mg + Fe)$ ratio, and do not necessarily imply incompatibility of experimental data.

Computation technique

The system of equations (21-27) was transformed into the system of inequalities of the form:

$$\Delta_r G^{T,P} + RT \ln K_D^< + \Delta G_{ex} < 0 \quad \text{and} \quad (28)$$

$$\Delta_r G^{T,P} + RT \ln K_D^> + \Delta G_{ex} > 0 \quad (29)$$

which were solved by linear programming to obtain the unknown mixing parameters and thermodynamic properties of some end-members.

Since the work of Gordon (1973), linear programming has been successfully used in determining thermodynamic parameters of minerals from phase equilibrium data (*e.g.* Berman *et al.*, 1986; Berman, 1988). The use of linear programming as opposed to the least squares technique in calculating thermodynamic properties of solid phases has been actively discussed in the literature (Berman *et al.*, 1986; Powell & Holland, 1993). It is evident that for very precise experimental data both methods should yield compatible results. However, if experimental brackets are much wider than analytical uncertainty there is no statistical basis to select a specific value of the compositional parameter as an estimate for the 'true' equilibrium value (Demarest & Haselton, 1981), and more adequate results may be obtained by linear programming which considers each half-bracket independently. The choice of linear programming for evaluating our experimental data was guided by two facts: (i) Our experimental compositions are characterised by rather large uncertainties so that, in general, only a range of concentrations may be defined that constrains the equilibrium composition. The resulting brackets are in many cases much wider than the standard deviation of compositional parameters. (ii) The complexity of mineral compositions with 3-4 independent end-members does not allow us to consider experimental points as compositional brackets at fixed P and T . Each experiment has to be considered as an independent half-bracket which defines a minimum or maximum limit of the equilibrium constant.

A linear programming problem includes an objective function and a set of linear equality or

inequality constraints. The solution of the problem (if any) provides an extreme value for the objective function, which is compatible with all constraints. There is no general method to define an objective function in phase equilibrium problems. Several approaches were proposed among which are linear (Halbach & Chatterjee, 1982) or non-linear (Berman *et al.*, 1986) functions characterising the deviation of some unknown parameters from the values that were measured independently with high precision, such as thermochemical or volume data for minerals. If such data are missing the objective function may be not defined, and the linear programming technique allows then the calculation of a set of feasible solutions. This set may be empty, contain only one or an infinite number of solutions. In the absence of an objective function all feasible solutions are assumed to have the same probability, whereas the values outside the feasible region are considered to be impossible. Because of this we calculated not a unique value but a range for each of the unknown thermodynamic parameters and relationships between them which are compatible with all experimental constraints.

A problem arises with linear programming if the set of feasible solutions is empty *i.e.*, not all constraints are compatible with each other. This occurs commonly in the interpretation of phase equilibrium data (*i.e.* Halbach & Chatterjee, 1982) because of the experimental errors and complex reaction mechanisms resulting in 'overlapping' of compositions in reversal experiments. The latter was observed in the present study. This dilemma may be solved by changing the measured values (compositions, pressure and temperature) within certain limits, for example one standard deviation (Berman *et al.*, 1995). We suggest that experiments with a larger scatter of microprobe analyses are more likely to lead to incompatibility for a set of inequality constraints. With this assumption, the system (28)-(29) was transformed into:

$$\Delta_r G^{T,P} + RT \ln K_D^< + \Delta G_{ex} < \alpha \sigma (RT \ln K_D) \quad \text{and} \quad (30)$$

$$\Delta_r G^{T,P} + RT \ln K_D^> + \Delta G_{ex} > -\alpha \sigma (RT \ln K_D), \quad (31)$$

where $\sigma (RT \ln K_D)$ is the standard deviation of the quantity $RT \ln K_D$ calculated from the standard deviation of measured compositional parameters [$\sigma(X_i)$] using the general expression for error propagation:

$$\sigma^2 (RT \ln K_D) = \sum \sigma^2 (X_i) (dRT \ln K_D / dX_i)^2 \quad (32)$$

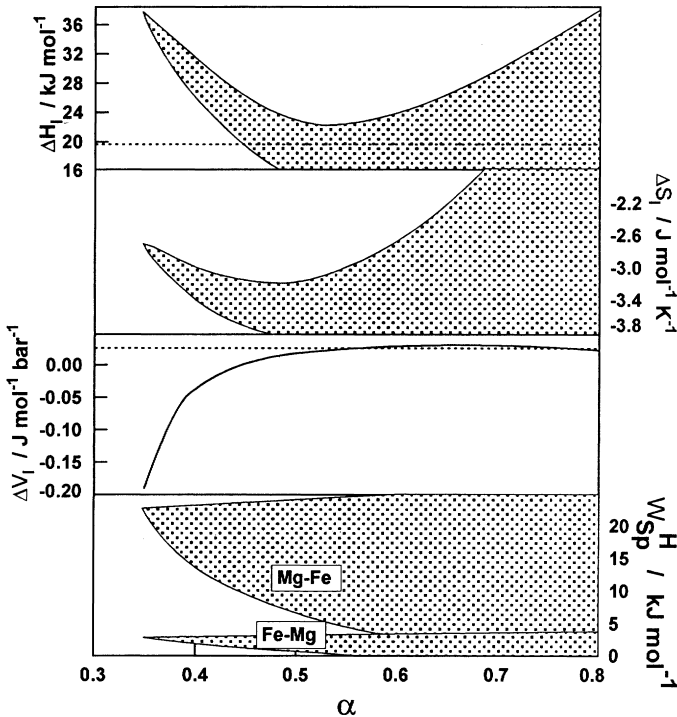


Fig. 5. Thermodynamic parameters derived by linear programming from the experimental data on Fe-Mg exchange between phases as a function of parameter α (Eqs. 30, 31). Shaded areas show the feasible region, and dashed lines are the values of ΔH_1 and ΔV_1 obtained from the database of Berman (1988) and Sack & Ghiorso (1991).

The unknown values were computed as a function of parameter α which was allowed to change from 0 to 1. Normally feasible solutions for all equilibria appeared at $\alpha = 0$ to 0.4. However, the set of parameters corresponding to the lowest possible values of α included frequently physically unrealistic values (*i.e.* very large Margules mixing parameters). This results from the fact that the points which are characterised by the highest error could exert the strongest influence on the solution, especially if the solution is unique or lies within a very narrow interval. Similar problems arise in least squares analysis, as discussed by Wood & Crerar (1985) who suggested to use ridge regression in order to obtain solutions with parameters of physically realistic signs and magnitudes. The idea of ridge regression is to introduce small changes into the best fit which would result in higher residues but more stable and realistic parameters. We used a similar approach, noting that increasing α initially affects the values of calculated parameters strongly, while at a certain level this dependency becomes less definite and further increase of α results only in wider intervals of feasible solutions (Fig. 5). It is difficult to determine rigorous criteria for choosing the final value of α , because our

approach is based on the suggestion that the data set contains an unknown source of internal incompatibility. The only reasonable criterion is compatibility with independent data. We used a solution obtained at α which was below 1.0 but higher than the minimum possible value in order to obtain the range, which would include ΔH_1 and ΔV_1 values for reciprocal reaction I calculated using the thermodynamic data of Berman (1988) and Sack & Ghiorso (1991) (Fig. 5).

Results

All expressions describing the equilibrium state in the system (Eqs. 21–27) may be solved simultaneously, but it is apparent that many parameters occur only in one equation (standard state properties of khorringite and MgCrAlSiO_6) or have significant influence only in part of the equations. For this reason, we separated the problem into two blocks and determined initially the values of ΔG_1 and Fe-Mg mixing parameters from the Fe-Mg exchange equilibria. Then we analysed other parameters from Cr-Al and displaced equilibrium reactions.

All standard state properties were taken from Berman (1988) and Sack & Ghiorso (1991, 1994b). The free energy change of the reciprocal reaction $\text{CaAl} + \text{MgCr} = \text{CaCr} + \text{MgAl}$ for garnet (ΔG_{III}) was estimated by Wood & Nicholls (1978) to be on the order of -50 kJ/mol. Similar values but with strong temperature and pressure dependencies were obtained by Brey & Koehler (1990). Since the exact value is not well constrained, we assumed $\Delta G_{\text{III}} = -50$ kJ/mol. The excess mixing volumes of minerals were taken from our measurements of unit-cell parameters of minerals (Part I). Our data do not show any statistically significant temperature dependencies of the Margules parameters for Fe-Mg exchange in spinel and orthopyroxene and the respective values of W^{S} were set to zero.

The compositional dependence of Fe-Mg distribution coefficients is determined mainly by the change in the Gibbs free energy of reciprocal reaction I. From the three equilibria a temperature and pressure dependence of ΔG_{I} may be estimated: $\Delta G_{\text{I}} = \Delta H_{\text{I}} - \Delta S_{\text{I}} T + \Delta V_{\text{I}} (P-1)$ together with excess Fe-Mg mixing parameters for spinel solid solution. The derived values are compatible for all experimental compositions at $\alpha = 0.34$ but are unrealistically high (Fig. 5). More realistic lower values of $W_{\text{FeMg}}^{\text{Sp}}$ and $W_{\text{MgFe}}^{\text{Sp}}$ are derived at $\alpha > 0.5$, which also allow consistency with ΔH_{I} and ΔV_{I} calculated from the Berman (1988) and Sack & Ghiorso (1991) data. A constraint is provided from our X-ray data (Part I) which yield a very small value of ΔV_{I} at around zero. The resulting hercynite molar volume is 4.062 J/bar, within the range of direct measurements from 4.055 to 4.086 J/bar (Lindsley, 1976; Bohlen *et al.*, 1986). This corresponds to ΔV_{I} from -0.007 to 0.024 J/bar. Within this interval we obtain feasible solutions for ΔG_{I} , ΔG_{II} , and $W_{\text{FeMg}}^{\text{Sp}}$ and $W_{\text{MgFe}}^{\text{Sp}}$. These parameters are mutually correlated, such that at any definite value of ΔH_{I} the feasible interval for other parameters is much narrower, especially for ΔS_{I} . The results require an asymmetric mixing model for Fe-Mg spinel solid solution with $W_{\text{MgFe}}^{\text{H}} = 9270$ to 10890 and $W_{\text{FeMg}}^{\text{H}} = 1540$ to 2140 J/mol. Similar values of $W_{\text{MgFe}}^{\text{H}}$ and $W_{\text{FeMg}}^{\text{H}}$ for spinel solid solution (9140 and 0 J/mol, respectively) were obtained by Chatterjee (1987) on the basis of thermochemical and phase equilibrium data.

Equilibrium between garnet and spinel depends also on the Gibbs free energy change (ΔG_{II}) of the reciprocal reaction specifying the formation of $\text{Fe}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$. The experimental results do not

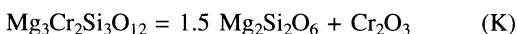
allow us to determine the temperature dependence of ΔG_{II} so that it was approximated by $\Delta H_{\text{II}} + \Delta V_{\text{II}}(P-1)$, where $\Delta V_{\text{II}} = 0.035$ J/bar was taken from our unit-cell measurements (Part I). Feasible value of ΔH_{II} range from -15 to -20 kJ/mol and depend on the values for ΔH_{I} (Table 1).

Sack & Ghiorso (1989) separated ordering and excess mixing energies for Fe-Mg orthopyroxene solid solutions and proposed a large value of $W_{\text{FeMg}}^{\text{H}} = 8.4$ kJ/mol counterbalanced to some extent by negative ordering energy. Von Seckendorff & O'Neill (1993) argued that $W_{\text{FeMg}}^{\text{H}}$ is much smaller and depends strongly on the thermodynamic mixing properties of other minerals. Our data on the Fe-Mg exchange equilibrium between spinel and orthopyroxene are consistent with the zero contribution of Fe-Mg non-ideality in orthopyroxene, so that both $W_{\text{MgFe}}^{\text{M2}}$ and $W_{\text{MgFe}}^{\text{M1}}$ may be neglected (*cf.* Chatterjee, 1987) and

$$W_{\text{MgAl}}^{\text{M1}} - W_{\text{FeAl}} - \Delta H_{\text{IV}} = W_{\text{MgCr}}^{\text{M1}} - W_{\text{FeCr}}^{\text{M1}} - \Delta H_{\text{V}} = 0.$$

The Cr-Al exchange equilibrium between garnet and spinel determines the relationships between Cr-Al mixing in garnet and standard state properties of knorringite. To extrapolate thermodynamic properties of knorringite to the reference conditions (298 K, 1 bar) we assumed its compressibility and thermal expansion to be equal to those of pyrope (Berman, 1988), while heat capacity (C_p) was calculated as $C_{\text{kn}} = C_{\text{pyr}} + C_{\text{pc}} - C_{\text{sp}}$ using the values from Berman (1988) and Sack & Ghiorso (1991). Our experimental results on garnet-spinel equilibrium are compatible with values for $\Delta H_{\text{kn}}^{\text{o}}$ from -5590 to -5670 kJ/mol, S_{kn}^{o} from 325 to 360 J/mol K and a symmetric Cr-Al mixing model for garnet with $W_{\text{CrAl}}^{\text{Grt}} = W_{\text{AlCr}}^{\text{Grt}} = -10$ to 6 kJ/mol. These values are strongly correlated (Fig. 6) and the Gibbs free energy of knorringite determined from these values has much lower uncertainties (no more than 3 kJ at the pressure and temperature of interest). Feasible values of $W_{\text{CrAl}}^{\text{Grt}}$ also depend on the accepted entropy value of knorringite (Fig. 6).

The standard state properties of knorringite may be additionally constrained by the reaction:



We accepted the approximate limit of knorringite stability as determined by Turkin *et al.* (1983) at 80–100 kbar at 1200°C and 75.5–82.5 kbar at

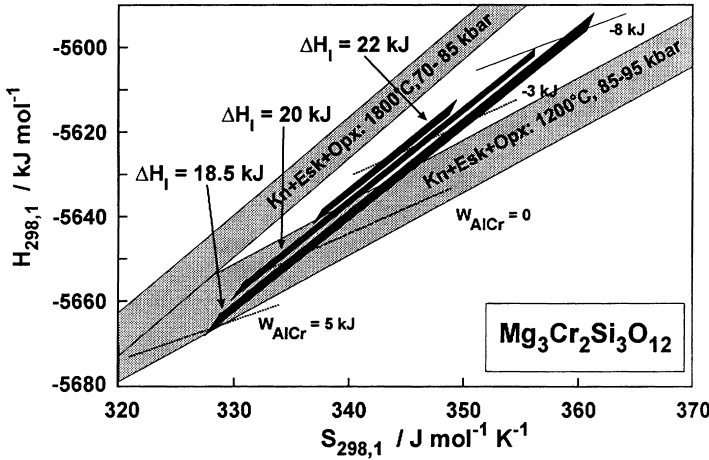
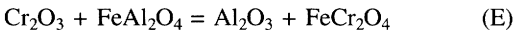


Fig. 6. Constraints on the standard state thermodynamic properties of knorringite. Narrow diagonal quadrilaterals show the values of ΔH_{kn} and S_{kn} at different values of ΔH_1 compatible with the experimental data on Cr and Al distribution between garnet and spinel (Part I; Doroshev *et al.*, 1997). Thin solid lines illustrate the approximate change of W_{AlCr}^{Grt} along the feasible region of ΔH_{kn} and S_{kn} . Shaded bands are the relationships between ΔH_{kn} and S_{kn} consistent with the conditions of decomposition of pure knorringite $kn = Opx + esk$ as determined by Turkin *et al.* (1983).

1800 °C. To keep consistency with the thermodynamic data of Sack & Ghiorso (1991) we proceed by summing reaction (K) with the exchange reaction (Petric & Jacob, 1982)



which, according to Sack & Ghiorso (1991), has a Gibbs free energy change between -15 and -24 kJ over a wide range of pressure and temperature. Using thermodynamic parameters for enstatite and corundum from Berman (1988) (noting that at very high pressure orthopyroxene is almost pure enstatite) and chromite and hercynite from Sack & Ghiorso (1991) we obtain a relationship between S_{kn}^o and ΔH_{kn}^o for the conditions of knorringite equilibrium with orthopyroxene and eskolaite at 1200 and 1800 °C (Fig. 6). These dependencies intersect at $S_{kn}^o < 330$ J/mol, close to the lower limit obtained from the present experiments in the FMASCr system. The most probable values of S_{kn}^o are about 325–340 J/mol K, close to the exchange entropy: $S_{kn}^o \approx S_{pyr}^o + S_{pc}^o - S_{sp}^o = 324.5$ J/mol K. This constrains the range of feasible values for W_{CrAl}^{Grt} between 6000 and 0 J/mol. Such low values of W_{CrAl}^{Grt} are consistent with thermochemical and phase equilibrium data on Cr-Al mixing in garnet (Mattioli & Bishop, 1984; Wood & Kleppa, 1984).

Non-ideality for Cr-Al mixing in spinel appears to be much larger. Oka *et al.* (1984) calculated: $W_{CrAl}^{Sp} \approx 14$ kJ/mol and $W_{CrAl}^{Sp} \approx 10.5$ kJ/mol for single-site Cr-Al mixing. Sack & Ghiorso (1991) reported a higher symmetric Margules pa-

rameter of 25 kJ/mol for Cr-Al mixing on the octahedral site, which is compensated by a large negative ordering energy (-36 kJ/mol) for the transition of Al from octahedral to tetrahedral site. In our model this ordering energy is included into mixing parameters, so we obtained lower W_{CrAl} and W_{AlCr} (< 10 kJ/mol).

The excess mixing parameters for orthopyroxene solid solution are least constrained because of the low and restricted range in Al, Cr, and Fe contents. This is not critical for the calculation of phase equilibrium and thermobarometry of deep-seated xenoliths because of the equally narrow ranges of Al, Cr and X_{Fe} in natural orthopyroxenes. We took the heat capacity of $MgCrAl-SiO_6$ as $C_{MgCrAlSiO_6} = C_{MgAlAlSiO_6} + \frac{1}{2}C_{MgCr_2O_4} - \frac{1}{2}C_{MgAl_2O_4}$ (values from Berman (1988) and Sack & Ghiorso (1994b)) and the thermal expansion and compressibility as equal to those of $MgAlAl-SiO_6$ (Sack & Ghiorso, 1994b). This yielded ΔH_{Crt}^o between -2857 and -2898 kJ/mol, S_{Crt}^o between 157 and 179 J/mol K and an asymmetrical Cr-Al mixing model ($W_{AlCr}^{Sp} = -1500$ to +5300 and $W_{CrAl}^{Sp} = 200$ to 11900 J/mol with strong negative correlation between these two values).

To restrict our model further we searched for a tentative solution close to the point of the minimum deviation from ideality in orthopyroxene solid solution minimising the objective function:

$$Z = \Sigma (W_{ij}^{Ml})^2 \quad (33)$$

and then allowing all W_{ij}^{Ml} parameters to vary within ± 5 kJ near the optimised values. Thus, we obtained ranges of thermodynamic parameters

Table 1. Thermodynamic parameters derived from the experimental results on the garnet-spinel-olivine-orthopyroxene equilibria in the MASCr (Doroshev *et al.*, 1997) and FMASCr (Brey *et al.*, 1999) systems.

Parameter	Feasible range		Relations with other values	Used for Fig. 8-10
	Min	Max		
Spinel				
ΔH_i , kJ mol ⁻¹	18.5	21.0		19.1
ΔS_i , J mol ⁻¹ K ⁻¹	-4.28	-3.05	= -13.36 + 4.91 10 ⁻⁴ ΔH_i	-3.99
ΔV_i , J mol ⁻¹ bar ⁻¹	-0.007	0.024		0.024*
W_{MgFe}^H , kJ mol ⁻¹	9.2	10.9		10.0
W_{MgFe}^V , J mol ⁻¹ bar ⁻¹	-0.022	-0.008		-0.015*
W_{FeMg}^H , kJ mol ⁻¹	1.55	2.14		1.8
W_{FeMg}^V , J mol ⁻¹ bar ⁻¹	-0.008	-0.022		-0.015*
W_{AlCr}^H , kJ mol ⁻¹	-0.59	1.84		0.6
W_{AlCr}^V , J mol ⁻¹ bar ⁻¹	-0.013	-0.001		-0.007*
W_{CrAl}^H , kJ mol ⁻¹	5.18	9.70		8.0
W_{CrAl}^V , J mol ⁻¹ bar ⁻¹	-0.007	-0.027		0.017*
Garnet				
ΔH_{II} , kJ mol ⁻¹	-18.6	-15.6	= -40.7 + 1.194 ΔH_i	-17.9
ΔS_{II}	0			0
ΔV_{II} , J mol ⁻¹ bar ⁻¹	0.02	0.05		0.035*
$\Delta H_{kn}^{298,1}$, kJ mol ⁻¹	-5668.2	-5637.5	= -6333.8 + 2048 S_{kn}	-5658.0
$S_{kn}^{298,1}$, J mol ⁻¹ bar ⁻¹	325	340		330
$W_{AlCr}^H = W_{CrAl}^H$, kJ mol ⁻¹	0	6.0		3.0
$W_{AlCr}^V = W_{CrAl}^V$, J mol ⁻¹ bar ⁻¹	0.008	0.028		0.018*
Orthopyroxene				
$\Delta H_{CrtS}^{298,1}$, kJ mol ⁻¹	-2884.3	-2867.8	= -3159.65 + 1667 S_{CrtS}	-2881.3
$S_{CrtS}^{298,1}$, J mol ⁻¹ K ⁻¹	165.2	175.1		167
$W_{MgFe}^{M1} = W_{MgFe}^{M2}$	0			0
W_{CrAl}^{M1} , kJ mol ⁻¹	6.5	16.5		15.0
W_{MgAl}^{M1} , kJ mol ⁻¹	-12.9	-7.4		-9.4
W_{MgCr}^{M1} , kJ mol ⁻¹	-24.3	-16.5		-20.0
W_{FeAl}^{M1} , kJ mol ⁻¹	-9.2	0.9		-4.2
W_{FeCr}^{M1} , kJ mol ⁻¹	-1.9	8.1		3.1
ΔG_{IV} , kJ mol ⁻¹	-12.0	-5.0	= $W_{MgAl}^{M1} -$ W_{FeAl}^{M1}	-8.5
ΔG_V , kJ mol ⁻¹	-14.5	-32.0	= $W_{MgCr}^{M1} -$ W_{FeCr}^{M1}	-23.0

*Values from X-ray diffraction data (Brey *et al.*, 1999).

which are compatible with our experimental results and do not require strong non-ideality of orthopyroxene solid solution. Correlation between some of these parameters (Fig. 7) decreases the uncertainties in values that may be derived from the model (Eqs. 21–27).

Discussion and conclusions

Table 1 shows the range of thermodynamic parameters compatible with our experimental results for the systems MASCr and FMASCr and with the thermodynamic database of Berman (1988).

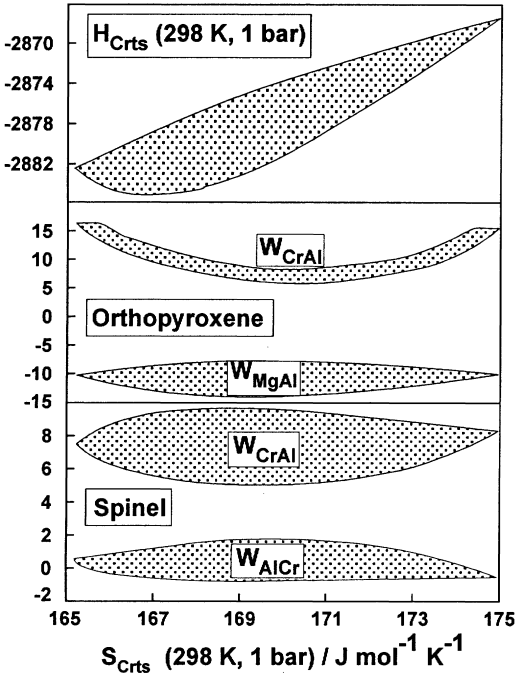


Fig. 7. Feasible values of MgCrAlSiO_6 (Crts) standard state properties and orthopyroxene and spinel mixing parameters derived from the results on Cr-Al exchange and displaced equilibrium reactions in the MASCr (Doroshv *et al.*, 1997) and FMASCr systems. Only the lower limit of the feasible region is shown for $W_{\text{CrAl}}^{\text{Opx}}$.

They may be used to calculate phase relations in peridotite assemblage or to determine pressure and temperature of equilibration from natural mineral compositions. These possibilities are discussed briefly in the following, including the accuracy of extrapolation to pressures and temperatures outside the experimental range.

In the system FMASCr, the four-phase assemblage garnet-spinel-olivine-orthopyroxene has three degrees of freedom, *i.e.* at a given pressure and temperature only one compositional parameter is independent. It is convenient to choose $X_{\text{Mg}}^{\text{Ol}}$ because it changes only slightly in mantle peridotite and may be set to 0.95 for strongly depleted harzburgite. Simultaneous solution of equations 21–27 at the pressure and temperature of interest yields all other compositional parameters. The influence of small Ca contents in garnet is also accounted for in these equations, provided that the bulk Ca content of peridotite is low enough to allow ignoring Ca in orthopyroxene

(*i.e.* <0.5 wt.% CaO). We also restricted our calculations to $P < 80$ kbar because at higher pressures orthopyroxene is transformed to clinopyroxene (Pacalo & Gasparik, 1990; Woodland & Angel, 1996).

We then calculated the compositions of phases in the pressure and temperature ranges of 30–80 kbar and 800–1800°C with the preferred values of mixing parameters of Table 1. The results are shown as Cr/(Cr+Al) isopleths of coexisting garnet and spinel (Fig. 8). Garnet isopleths have a negative slope on the P-T diagram with khorringite increasing with both pressure and temperature, as in the iron-free system (Doroshv *et al.*, 1997). The Cr/(Cr+Al) isopleths of spinel have positive slopes at low pressures and temperatures and negative at higher P and T where garnet becomes very rich in chromium. The change of slope occurs between 900–1300°C and 40–70 kbar, parameters typical of deep-seated mantle xenoliths and inclusions in diamonds (Boyd & Finnerty, 1980). At these conditions the Cr/(Cr+Al) ratio of spinel is insensitive to temperature and changes only with pressure (Fig. 8). Thus, approximate pressure estimates are possible on the basis of Cr/(Cr+Al) ratio of spinel alone. Indeed, in another projection, $X_{\text{Cr}}^{\text{Sp}}$ vs. $X_{\text{Cr}}^{\text{Grt}}$ (Fig. 9) isobars are almost horizontal at pressures above 45 kbar. Fig. 9 may be used to determine pressure and temperature simultaneously from the composition of coexisting spinel and garnet from harzburgites.

The uncertainty in the positions of the isolines stems mainly from two sources. Firstly, the uncertainty in the model parameters determined in this work. By assigning an equal probability to any set of parameters from the calculated ranges, the isopleths in Fig. 8 may be regarded as reference lines close to the central parts of bands. The width of these bands is defined by the feasible ranges of thermodynamic parameters (Table 1). Shaded rhombi in Fig. 8 indicate the errors at selected P, T conditions due to variations of model parameters within their feasible ranges. The resulting uncertainties in temperature and pressure are approximately ± 10 –20°C and ± 1 –2.5 kbar, which correspond to the range of X_{Cr} in both garnet and spinel from ± 0.01 to ± 0.05 (Fig. 8).

In Fig. 10 the calculated isopleths are compared with the experimentally determined compositions. There is good agreement but the model predicts a more rapid increase of $X_{\text{Cr}}^{\text{Grt}}$ at pressures and temperatures above the experimentally studied conditions than is apparent from our ex-

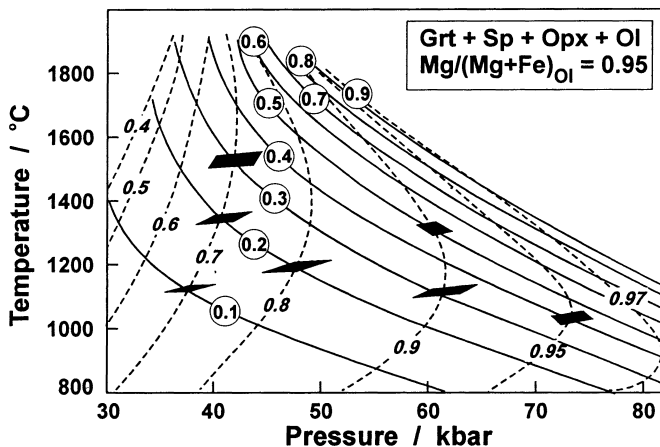


Fig. 8. P-T projection of Cr/(Cr + Al) isopleths for garnet (solid lines, numerals in circles) and spinel (dashed lines). The isopleths are calculated with thermodynamic parameters from Table 1. Shaded rectangles demonstrate possible changes in the position of isopleths consistent with the whole feasible region of the derived mixing parameters.

perimental results. This is required by the compatibility with the thermodynamic database of Berman (1988). The uncertainties in thermodynamic properties of minerals are thus the second possible source of errors. For enthalpies obtained from thermochemical data on the mineral end-members considered in the present work a standard error of 2–4 kJ may be assumed (Berman, 1988). The uncertainty is probably lower for the Gibbs free energy change of the reactions because the procedure of deriving an internally consistent set of thermodynamic properties should result in more accurate values. Errors of *ca.* 3 kJ in the standard state values of $\Delta_r G^{T,P}$ result in uncertainties in the position of the isopleths, different for different reactions. Errors in the Fe-Mg exchange reactions (1–3) do not influence the calculated Cr-Al relationships much, especially at high

pressures and temperatures. Reaction (6) is also of minor importance especially at high X_{Cr}^{Grt} , when orthopyroxene is very poor in alumina. Errors related to the Cr-Al exchange equilibria (4–6) and reaction (7) could result in an error of pressure and temperature estimates of ± 2.5 kbar and ± 50 °C. Thus, the accuracy of calculated phase equilibria as well as estimates of pressure and temperature from spinel and garnet Cr-Al relationships outside the experimental range critically depends on the reliability of extrapolation of Berman's (1988) data for the MAS system and the accuracy of our results on Cr/Al distribution between spinel and garnet.

The two sources of error are not independent, because the range of mixing parameters (Table 1) was calculated for the values of thermodynamic properties tabulated by Berman (1988). A change

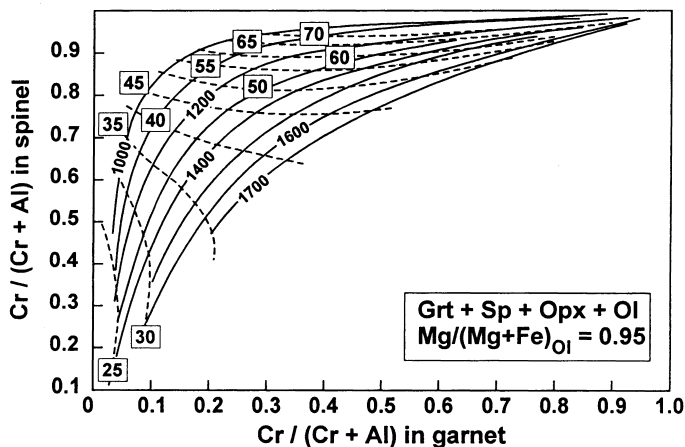


Fig. 9. Calculated isotherms (°C, solid lines) and isobars (kbar, dashed lines) for the four-phase mineral assemblage in the FMASCr system in the $X_{Cr}^{Sp} - X_{Cr}^{Grt}$ plane.

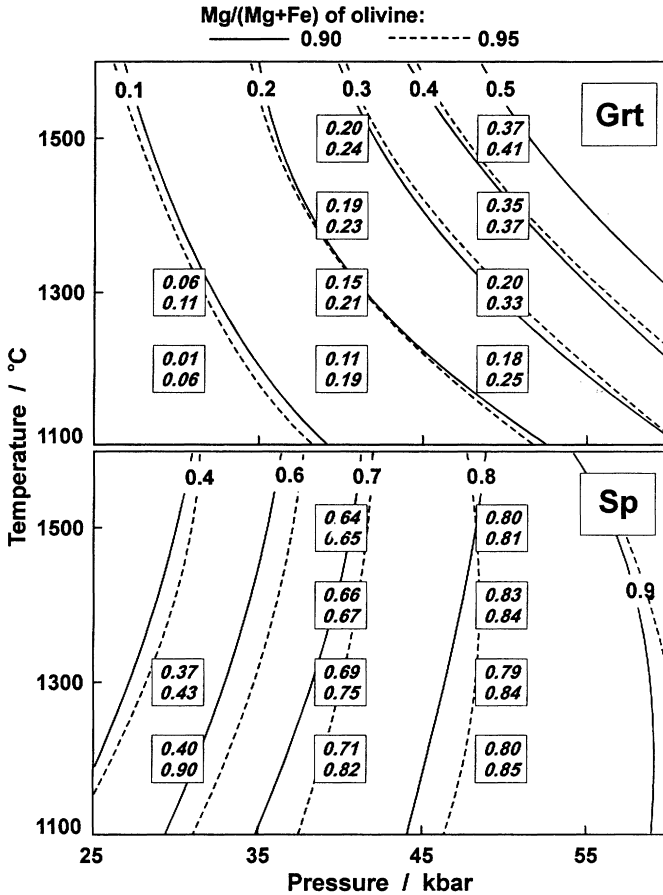


Fig. 10. Comparison of calculated garnet and spinel $\text{Cr}/(\text{Cr}+\text{Al})$ isopleths with the composition ranges for the minerals from the experiments. Numbers in rectangles are maximum and minimum $\text{Cr}/(\text{Cr}+\text{Al})$ ratio constrained by the experiments in the MASCr (Doroshchev *et al.*, 1997) and FMASCr systems.

in these values will inevitably result in a different feasible range of mixing parameters, which will compensate to some extent the variation of calculated parameters. Thus, the overall precision of pressure and temperature estimates with the derived relations is better than the sum of uncertainties from these two sources and probably no more than ± 4 kbar and $\pm 50^\circ\text{C}$.

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