THE INFLUENCE OF Cr_2O_3 ON THE RELATIONSHIPS BETWEEN SPINEL- AND GARNET-PERIDOTITES

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Introduction

The main object of this study has been to determine the stability fields of spinel- and garnet-peridotites in the system $MgO-Al_2O_3-Cr_2O_3-SiO_2$ as a function of the (Cr/Cr+Al) ratio of the spinel. Extrapolation of these experimental data to natural systems is, to some extent, complicated by interactions in high-Ca, high-Cr garnets. The magnitudes of these interactions and their influence on relevant equilibria have been estimated from partitioning in natural assemblages.

Experimental

All experiments were performed in an 0.5" piston-cylinder apparatus using crystalline starting materials. Forsterite, pyrope and orthopyroxene (with 2% and 11% Al_2O_3) were separately prepared by crystallising gel starting materials under appropriate P-T conditions. $MgAl_2O_4$ spinel and $MgCr_2O_4$ spinel were synthesized from oxides at 1 atmosphere and 1400°C. Sealed Pt capsules and either an H_2O or a CO_2 vapour phase were used.
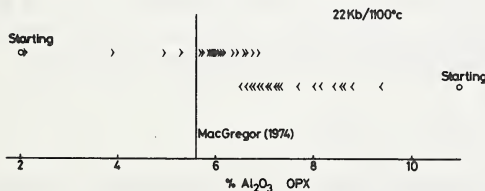
$MgO-Al_2O_3-SiO_2$ system :

The reaction :

$$\text{Orthopyroxene + spinel = garnet + olivine} \qquad (1)$$
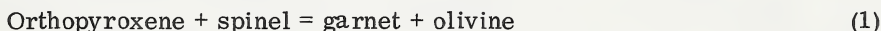
was found to lie between 23.5 and 24 kb at 1100°C and 22 and 23.2 kb at 1000°C. These results are reversals with crystalline starting material using piston-out procedure and CO_2 vapour.

The Al_2O_3 content of orthopyroxene coexisting with garnet has been determined at 22 kb/1100°C using the crystallised gel starting materials. Results starting with $(MgSiO_3)_{0.98}$ $(Al_2O_3)_{0.02}$ opx and $(MgSiO_3)_{0.89}$ $(Al_2O_3)_{0.11}$ opx are shown in figure 1. Despite the considerable scatter, agreement with the experiments of MacGregor (1974) is reasonably good. These results do not support the contention that the "primary" starting material, gel in this case, glass in the earlier cases, affects the Al_2O_3 content of the product orthopyroxene.


$MgO-Al_2O_3-SiO_2-Cr_2O_3$ system :

Experiments were performed with two starting materials :

(a)   Forsterite + pyrope + orthopyroxene (All Cr-free) + $MgCr_2O_4$ spinel

(b)   Forsterite + pyrope + orthopyroxene (all Cr-free) + $MgAl_2O_4$ spinel

+ Cr_2O_3. Results are shown in figure 2 as ΔP (run pressure minus equilibrium pressure in MAS system) versus $Cr/(Cr+Al)$ in the spinel. Arrow pointing to the left denotes olivine absent from products. Arrow pointing right denotes orthopyroxene absent.   Labelled curves were calculated (at the temperature indicated) by assuming that the spinel behaves as an ideal solution.
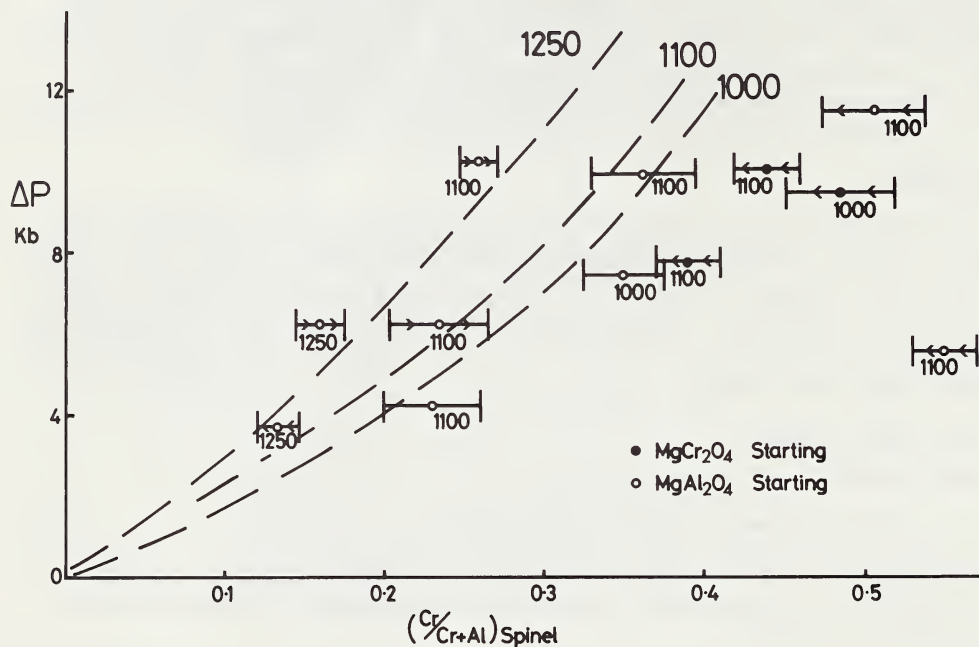

The compositions of product spinels were determined by microprobe and with EMMA-IV.   They are, in general, closely grouped in any one experiment and results from starting material (b) are consistent with those from starting material (a). It may be seen from figure 2 that stabilisation of spinel + olivine due to a given $(Cr/Cr+Al)$ of the spinel is close to that which would be predicted on the basis of ideal two-site $MgAl_2O_4$-$MgCr_{2.}O_4$ solution.

<u>Extension to natural systems</u> :

In order to extrapolate these results to natural systems it is necessary to take account, in particular, of the presence of Fe^{2+} in all phases and of Ca in garnet. If we make the common assumption of ideal Mg-Fe mixing, then the main non-ideal terms will involve Ca in a garnet, the composition of which may be approximated by $(Mg_xFe_y$ $Ca_{(1-x-y)})_3$ $(Al_zCr_{(1-z)})_2$ Si_3O_{12}. Treating double site garnet using the reciprocal salt approach   the principal contribution to the activity coefficient of

$Mg_3Al_2Si_3O_{12}$ component arises from the standard state free energy change of the exchange reaction :

$$Mg_3Cr_2Si_3O_{12} + Ca_3Al_2Si_3O_{12} \rightleftharpoons Mg_3Al_2Si_3O_{12} + Ca_3Cr_2Si_3O_{12} \quad \Delta G_2^o = -ve \quad (2)$$
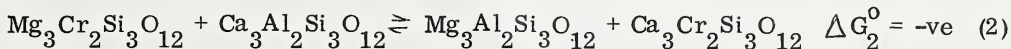
Note that for the garnet solid solution to be ideal, ΔG_2^o must be zero. ΔG_2^o may be estimated from the magnitude of the well-known coupling between Ca and Cr in the garnet. A plot of $\ln$ $(Cr/Al)_{garnet} \cdot (Al/Cr)_{spinel}$ versus X_{Ca}^{gt} in spinel + garnet lherzolites (figure 3) yields ΔG_2^o of about -50 kcals.
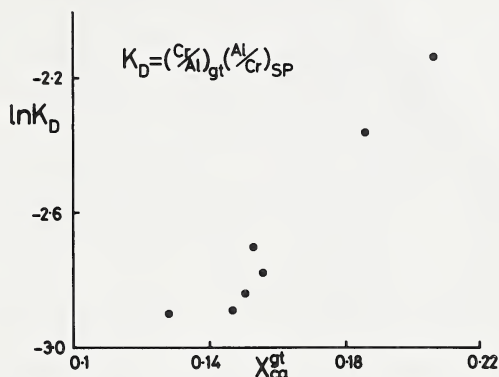
From this we have :

$$RT \ln \gamma^{gt}_{Mg_3Al_2Si_3O_{12}} \simeq X_{Ca}^c \cdot X_{Cr} \ (50\ 000) \tag{3}$$

$$RT \ln a^{gt}_{Mg_3Al_2Si_3O_{12}} \simeq RT \ln\left(X_{Mg}^{c3} \cdot X_{Al}^{o2}\right) + X_{Ca}^c X_{Cr}^o \ (50\ 000)$$

Where X_{Mg}^c, X_{Al}^o refer to the atomic fractions of Mg and Al in cubic and octahedral sites respectively.

The P-T curve for a natural garnet-spinel-olivine-clinopyroxene assemblage can thus be represented by (from reaction 1) :

$$RT \ln K = 1.987 \ln \left(\frac{a_{Mg_3Al_2Si_3O_{12}} \cdot X_{Fo}^{ol^2}}{\left(X_{Mg}^t\right)_{sp}^2 \left(X_{Al}^o\right)_{sp}^2 \cdot X_{Mg}^{M1^2} \cdot X_{Mg}^{M2^2}} \right) \tag{4}$$

$$= -4420 + 0.54\,T + 0.1895\,P$$

In equation (4) t and o refer to tetrahedral and octahedral sites in the spinel phase and the P term appropriate for low Al_2O_3 contents of the orthopyroxene (4 wt % or less).