

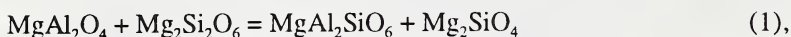
# The partitioning of Chromium between orthopyroxene and spinel in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ : implications for geothermobarometry for Upper Mantle rocks

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## Introduction

The solubility of alumina in orthopyroxene co-existing with forsterite and spinel in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  (MAS) may be formulated as follows (Gasparik & Newton, 1984):



while the solubility of alumina in orthopyroxene co-existing with garnet is given by:



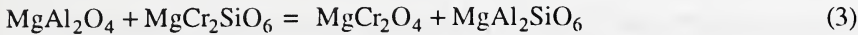
Equilibrium (1) is widely used as a geothermometer in the spinel lherzolite facies, while equation (2) is the main geothermobarometer for garnet lherzolites. However, the application of these equilibria to the multicomponent compositions of natural rocks is presently somewhat uncertain due to our lack of knowledge of the effects of minor components. In particular, the replacement of Al by Cr in orthopyroxene probably exerts a large influence. However, this study investigates the influence of Cr on reaction (1) and derives thermodynamic properties for Cr-bearing orthopyroxene.

## Experiments

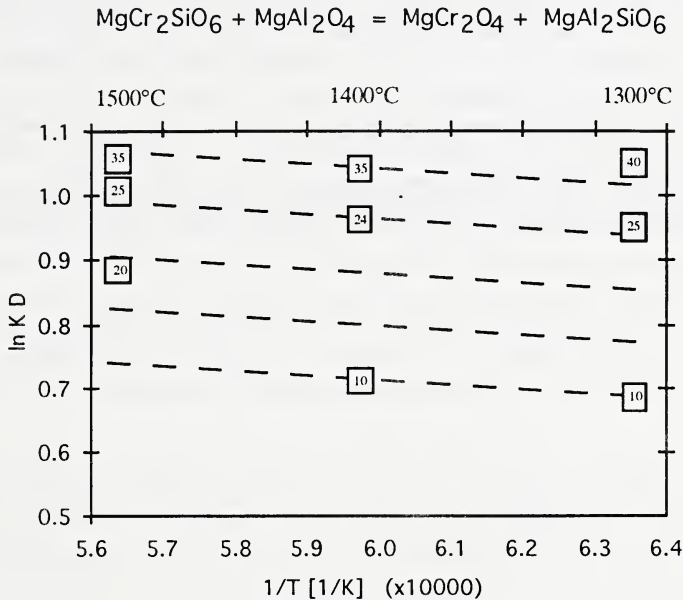
We have equilibrated spinels with orthopyroxenes and forsterite in a series of high-pressure high-temperature experiments with three different bulk compositions in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ . Experiments were performed in a conventional piston-cylinder apparatus at temperatures from 1300-1500°C and pressures ranging from 1 to 4 GPa. Because Cr-bearing mineral assemblages are known to react sluggishly under experimental conditions, lengthy run times were used to ensure attainment of equilibrium. Two thermocouples were employed in our experiments to check for possible thermocouple drift due to contamination. So far we have failed to produce satisfactory results at run temperatures below 1300°C.

Preliminary results

In addition to reaction (1), the equation between spinel and orthopyroxene in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$  (MASCr) may be described by the exchange reaction of Cr and Al between orthopyroxene and spinel.



Preliminary results show that the exchange reaction (3) is found to be pressure and temperature dependent, as illustrated in Fig.1. Experiments with a high Cr/Cr+Al bulk composition yielded orthopyroxenes that contained more Cr than Al, therefore we chose the  $\text{MgCr}_2\text{SiO}_6$  component rather than the more conventional  $\text{MgCrAlSiO}_6$  component to describe the exchange reaction.



**Fig.1** The  $\ln K_D$  of the exchange reaction between orthopyroxene and spinel in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ , as a function of reciprocal temperature and of pressure (shown inside squares [kb]).

In order to develop a thermodynamic model for Cr-bearing orthopyroxenes, we combine reactions (1) and (3) in both the chromium free (MAS) and the MASCr systems. Inserting the correct thermodynamic endmember properties (Klemme and O'Neill, 1997) and the appropriate activity models for the spinel solid solution, we are able to extract thermodynamic endmember properties for the  $\text{MgCr}_2\text{SiO}_6$  (CrTs) endmember and develop an appropriate activity model for the orthopyroxene solid solution. Initial modelling results show that an ideal mixing model for orthopyroxene

combined with a regular solution for spinel is in good agreement with our experiments and with experiments in the system MAS (Gasparik and Newton, 1984).

## Conclusions

The influence of Chromium on Upper Mantle phase relations must not be underestimated: Cr partitions mainly into the spinel phase but pyroxenes can contain up to 2% (wt.) of  $\text{Cr}_2\text{O}_3$ . However, the modal amount of pyroxenes is much higher than that of spinels in normal lherzolites so that pyroxenes accommodate a quite substantial amount of the bulk Cr of the whole rock. When modelling phase relations of the Upper Mantle, neglecting the Cr content of pyroxenes has the effect of overestimating the stability field of spinel relative to garnet or plagioclase. This latter transition exerts an important influence on the major and trace element composition of partial melts of peridotite.

## References

- Gasparik, T. & Newton, R.C., 1984, The reversed alumina contents of orthopyroxene in equilibrium with spinel and forsterite in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ : Contributions to Mineralogy and Petrology, 85, p. 186-196.
- Klemme, S. & O'Neill, H.St.C., 1997, The reaction  $\text{MgCr}_2\text{O}_4 + \text{SiO}_2 = \text{Cr}_2\text{O}_3 + \text{MgSiO}_3$  and the free energy of formation of magnesiochromite ( $\text{MgCr}_2\text{O}_4$ ): Contributions to Mineralogy and Petrology, 130, p. 59-65.