

The partitioning of chromium between orthopyroxene and spinel in the system MgO-Al₂O₃-SiO₂-Cr₂O₃

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The solubility of alumina in orthopyroxene co-existing with forsterite and spinel is widely used as a geothermometer in the spinel lherzolite facies. In the simple system MgO-Al₂O₃-SiO₂ (MAS) the relevant reaction may be formulated as follows (Gasparik and Newton, 1984):



The application of this equilibrium to the multi-component 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.

In this paper we present results of a series of high-pressure high-temperature experiments intended to investigate the influence of chromium on the solubility of alumina in orthopyroxene in equilibrium with spinel and olivine in the system MgO-Al₂O₃-SiO₂-Cr₂O₃. We also derive thermodynamic properties for Cr-bearing orthopyroxene and present a thermodynamic model of subsolidus equilibria in Cr-bearing systems.

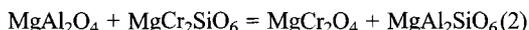
Experiments

We have equilibrated spinels with orthopyroxenes and forsterite in a series of high-pressure high-temperature experiments at different Cr/Al ratios in the system MgO-Al₂O₃-SiO₂-Cr₂O₃. Most experiments were performed in a conventional piston-cylinder apparatus at temperatures from 1300–1500°C and pressures ranging from 0.5 to 5.4 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 most of our experiments to check for possible thermocouple drift due to contamination. All charges were examined with electron microprobe techniques. To check for the presence of Cr²⁺ in the experiments we have conducted a few runs with a Re-ReO₂ buffer to generate a high oxygen fugacity

environment. No evidence for the presence of Cr²⁺ was found. Another item of evidence against the presence of significant Cr²⁺ in our experiments is the lack of detectable Cr in olivine analyses. To check the attainment of equilibrium in our experiments we have conducted a time series of experiments with different run durations. At 1400°C we found a run duration of >120 hours to be sufficient. However, experiments at 1300°C had to be run for several weeks. So far we have failed to produce satisfactory results at run temperatures below 1300°C. Several fluxes (PbO, BaO-B₂O₃, H₂O, H₂O-CO₂) were considered to promote equilibration in our experiments but none was found to be appropriate. A few reversal experiments, especially at 10 kb, were performed as further confirmation of the achievement of equilibrium. The reversal experiments contain two different starting materials, one consists of pyroxenes with high Al₂O₃ and Cr₂O₃ contents, while the other consists of pure Mg₂Si₂O₆ as the starting pyroxene composition.

Results

The solubility of Al and Cr in orthopyroxene in equilibrium with olivine and spinel in this Cr-containing system is described by two reactions, reaction (1) and also the exchange reaction that may be written as follows:



The addition of Cr to equilibrium (1) substantially lowers the amount of alumina in pyroxenes, as depicted in Fig. 1. The magnitude of this effect also seems to depend on pressure (Fig. 2). However, a satisfactory solution model for the Cr/Al-containing orthopyroxenes still needs to be developed.

To explain this pressure and temperature effect on the partitioning of Cr and Al between orthopyroxene solid solution and coexisting spinel solid solution, we have regressed the experiments employing a non-ideal symmetric solid solution for spinels and a symmetric ternary solid solution for orthopyroxenes.

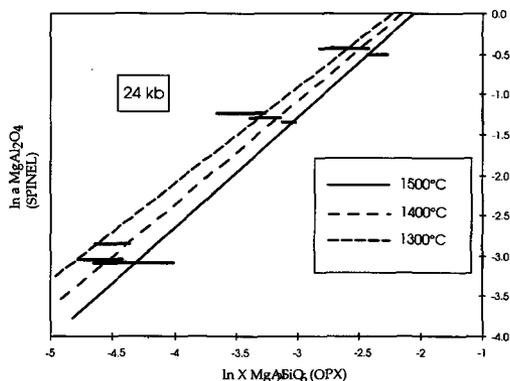


FIG. 1. The activity of the MgAl_2O_4 component in spinel as a function of the molar fraction of the $\text{MgAl}_2\text{SiO}_6$ component (MgTs) in orthopyroxene in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Cr}_2\text{O}_3$. Only experiments at 24 kb are depicted, although similar trends are observed at other pressures. The equilibrium between spinel and orthopyroxene is found to be temperature dependent. Bars represent uncertainties in the experiments.

Preliminary results of the regression of the exchange reaction (2) show that our data yield consistent mixing parameters for the spinel solid solution as predicted by Oka *et al.* (1984), if the mixing of Al and Cr in orthopyroxene is assumed to be ideal with mixing on a 2-site basis. The consistency of our data with the reversal experi-

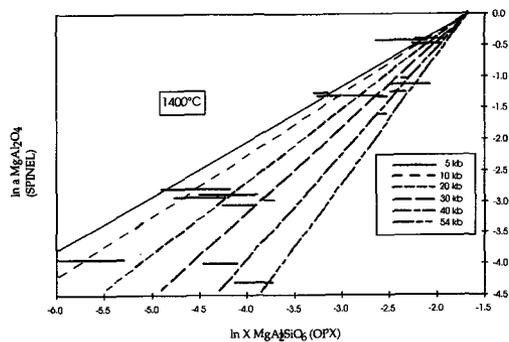


FIG. 2. The equilibrium between spinel and orthopyroxene in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Cr}_2\text{O}_3$ is also found to be pressure dependent. Depicted are experiments at 1400°C . Bars represent uncertainties while lines represent different pressures of equilibration.

mental study of Oka *et al.* (1984) is believed to be an important line of evidence for the attainment of equilibrium in our experiments.

References

- Gasparik, T. and Newton, R.C. (1984) *Contrib. Mineral. Petrol.*, **85**, 186–96.
 Oka, Y., Steinke, P. and Chatterjee, N.D. (1984) *Contrib. Mineral. Petrol.*, **87**, 196–204.