

THE GARNET-SPINEL TRANSITION IN REFRACTORY MANTLE COMPOSITIONS

Stephan Klemme¹

¹ University of Heidelberg, Germany

INTRODUCTION

From geophysics and experimental petrology it is well known that the Earth's mantle is stratified. The Earth's upper mantle consists of only four or five main minerals such as olivine, clinopyroxene, orthopyroxene and spinel. At higher pressure, however, the spinel bearing mineral assemblage converts into a garnet bearing assemblage.

The transition from spinel lherzolite to garnet lherzolite is one of the most important phase boundaries in the Earth's upper mantle. The garnet-spinel transition is well understood in simple (e.g. CaO-MgO-Al₂O₃-SiO₂ (Klemme and O'Neill 2000, Figure 1), and complex systems in fertile compositions (Green and Ringwood 1967, Robinson and Wood 1998), but there is scant information about the transition in refractory compositions. This is of relevance to the deeper continental mantle as evidence from diamond inclusions and xenoliths point to a rather refractory and Cr-rich mantle (e.g., Stachel and Harris 1997, Stachel et al. 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, Cr-bearing pyroxenes and Cr-bearing garnets, the latter of which are, unfortunately, rather unconstrained. The present study aims to fill this gap.

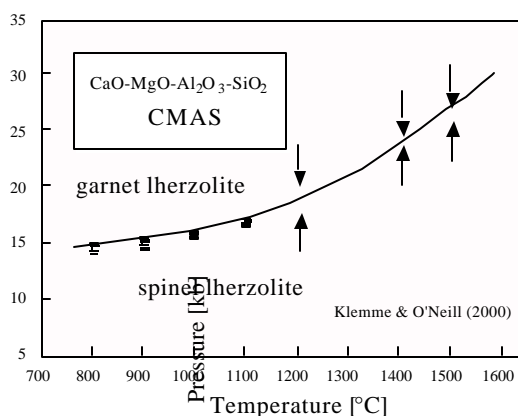
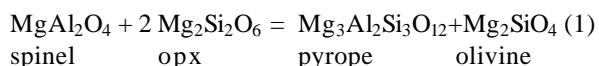
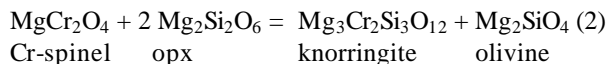


Figure 1: The transition from garnet lherzolite to spinel lherzolite in the system CaO-MgO-Al₂O₃-SiO₂. Data taken from Klemme and O'Neill (2000) and O'Neill (1981).

The simplest reaction describing the transition from spinel lherzolite to garnet lherzolite may be written as follows



This reaction has been studied previously in the system MgO-Al₂O₃-SiO₂ and CaO-MgO-Al₂O₃-SiO₂ which are excellent proxies for fertile, i.e. undepleted mantle compositions. Although there was some recent debate about the transition at higher temperatures (c.f., Klemme and O'Neill 2000), there is general agreement, however, that the garnet-spinel transition has a positive Clapeyron slope in both these simple systems. From previous experiments (Nickel 1986) and early thermodynamic calculations (Wood 1978, O'Neill 1981) it is well known that the addition of Cr to the system dramatically increases the stability of the spinel phase assemblage relative to the garnet-bearing mineral assemblage. Thermodynamic modelling in realistic mantle composition is unreliable, however, as thermodynamic data for Cr-spinels were shown to be in error (Klemme et al. 2000). To investigate both the influence of Cr on the garnet-spinel transition in a Cr-rich bulk composition and to derive thermodynamic data for Cr-garnets, the analogue reaction to (1) was investigated in an Al-free, but Cr-rich system, i.e.



EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Reversal experiments on reaction (2) were performed in a multi-anvil apparatus at pressures between 4.5 GPa and 11 GPa and at temperatures between 1200°C and 1600°C. The starting material contained all four phases that were synthesized prior to the commencement of the study. Enstatite, forsterite and magnesiochromite (MgCr₂O₄) were synthesized previously (Klemme and O'Neill 1997). Knorringite (Mg₃Cr₂Si₃O₁₂) was synthesized from stoichiometric mixtures of MgO,

Cr₂O₃ and SiO₂ in a multi-anvil apparatus at 16 GPa and 1600°C. Analysis of run products with X-ray diffraction and electron microprobe showed which phase assemblage grew and which was consumed.

RESULTS

Whilst the garnet-spinel transition in Cr-free (and in fertile) compositions is known to have a positive Clapeyron slope, experimental results on reaction (2) indicate a negative slope in pressure-temperature space at considerably higher pressures. Thermodynamic evaluation of the experimental results enable calculation of thermodynamic properties of khorringite garnets and, in conjunction with new data for Cr-spinels (Klemme and O'Neill 1997, Klemme et al. 2000) and Cr-bearing pyroxenes (Klemme and O'Neill 2000), calculations of phase equilibria in Cr-rich compositions. Whilst the garnet-spinel transition is univariant in the aforementioned compositions, i.e. MgO-Al₂O₃-SiO₂ and MgO-Cr₂O₃-SiO₂, there is a pressure-temperature range in Cr and Al-bearing systems where garnet and spinel coexist. It is well known from experiments that this garnet+spinel field is rather small in fertile compositions (Robinson and Wood 1998, Green and Ringwood 1967) but data in Cr-rich compositions are scarce.

Using the new thermodynamic data for Cr-spinels (Klemme et al. 2000), pyroxenes (Klemme and O'Neill 2000) and garnets (this study) some results of thermodynamic calculations will be presented.

REFERENCES

- Asimov, P. D., M. M. Hirschmann, M. S. Ghiorso, M. J. O'Hara, and E. M. Stolper, 1995, The effect of pressure induced solid-solid phase transitions on decompression melting of the mantle: *Geochimica et Cosmochimica Acta*, v. 59, p. 4489-4506.
- Green, D. H., and A. E. Ringwood, 1967, The stability field of aluminous pyroxene peridotite and garnet peridotite and their relevance in upper mantle structure: *Earth and Planetary Science Letters*, v. 3, p. 151-160.
- Klemme, S., and H. StC. O'Neill, 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 (MgCr₂O₄): *Contributions to Mineralogy and Petrology*, v. 130, p. 59-65.
- Klemme, S., and H. StC. O'Neill, 2000, The effect of Cr on the solubility of Al in orthopyroxene: experiments and thermodynamic modelling: *Contributions to Mineralogy and Petrology*, v. 140, p. 84-98.
- Klemme, S., and H. StC. O'Neill, 2000, The near-solidus transition from garnet lherzolite to spinel lherzolite: *Contributions to Mineralogy and Petrology*, v. 138, p. 237-248.
- Klemme, S., H. StC. O'Neill, W. Schnelle, and E. Gmelin, 2000, The heat capacity of MgCr₂O₄, FeCr₂O₄ and Cr₂O₃ at low temperatures and derived thermodynamic properties: *American Mineralogist*, v. 85, p. 1686-1693.
- Nickel, K. G., 1986, Phase equilibria in the system SiO₂-MgO-Al₂O₃-CaO-Cr₂O₃ (SMACCR) and their bearing on spinel/garnet lherzolite relationships: *Neues Jahrbuch für Mineralogie, Abhandlungen*, v. 155, p. 259-287.
- O'Neill, H. StC., 1981, The transition between spinel lherzolite and garnet lherzolite, and its use as a geobarometer: *Contributions to Mineralogy and Petrology*, v. 77, p. 185-194.
- Robinson, J. A. C., and B. J. Wood, 1998, The depth of the garnet/spinel transition in fractionally melting peridotite: *Earth and Planetary Science Letters*, v. 164, p. 277-284.
- Stachel, T., and J. W. Harris, 1997, Syngenetic inclusions in diamond from the Birim field (Ghana) - A deep peridotitic profile with a history of depletion and re-enrichment: *Contributions to Mineralogy and Petrology*, v. 127, p. 336-352.
- Stachel, T., J. W. Harris, G. P. Brey, and W. Joswig, 2000, Kankan diamonds (Guinea) II: lower mantle inclusion parageneses: *Contributions to Mineralogy and Petrology*, v. 140, p. 16-27.
- Wood, B. J., 1978, The influence of Cr₂O₃ on the relationships between spinel- and garnet-peridotites, *in* W. S. MacKenzie, ed., *Progress in Experimental Petrology*, Manchester, Natural Environment Research Council, p. 78-80.

Contact: S. Klemme, Mineralogisches Institut, University of Heidelberg, 69120 Heidelberg, Germany, E-mail: sklemme@min.uni-heidelberg.de