Thermodynamic modelling of Cr-bearing garnets and spinels in diamonds and peridotite xenoliths

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Diamonds are primarily found in mantle xenoliths that were brought to the surface by kimberlite magma. The chemical composition of many of the mantle xenoliths from kimberlites is often surprisingly Cr-rich when compared to mantle xenoliths from alkali basalts, which sample a shallower part of the mantle. The garnets found as inclusions inside diamonds are also often distinctively Cr-rich and Ca-poor. These features imply a correlation between garnet composition and the circumstances and conditions of diamond formation, and as a result Cr-pyrope garnet and Cr-rich spinel are usually the most important two diamond indicator minerals used in the diamond exploration industry (e.g., Fipke et al., 1995). However, this relation has only been empirically derived (e.g., Grütter et al. 2004). Here we present a novel approach trying to calculate phase relations based on a set of new thermodynamic data in Cr-rich systems relevant to the deeper Earth's mantle, which will allow quantitative assessment of the P-T conditions of diamond formation.

Experimental studies in the model system CaO-MgO-Al_2O_3-SiO_2 (CMAS) (O'Neill, 1981) show only a limited stability field for spinel up to less than 20kb on a normal continental steady-state geotherm (Fig. 1). However, in the system MgO-Cr_2O_3-SiO_2 the stability field is extended up to 70kb and more (Klemme, 2004).

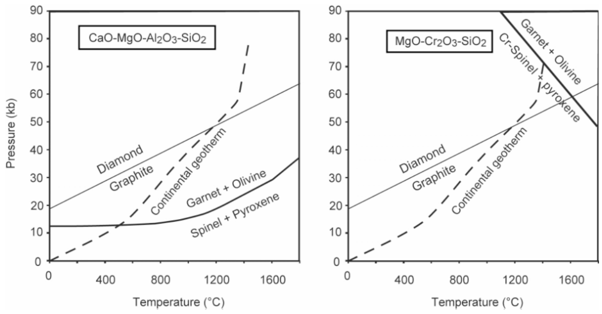

Fig. 1 Pressure-Temperature diagram illustrating the spinel (green) and garnet (red) stability fields in the Cr-free model mantle composition CaO-MgO-Al_2O_3-SiO_2 (O'Neill, 1981, Klemme and O'Neill 2000) and the simple MgO-Cr_2O_3-SiO_2 system (Klemme, 2004). Also given is the diamond-graphite reaction line (Kennedy and Kennedy, 1976), and a continental geotherm (McKenzie et al., 2005).

Recent experiments involving the Mg- and Cr-end members of garnet and spinel (i.e. knorringite and magnesiochromite, respectively) and pyroxenes (Brey et al., 1999; Brey et al., 1991; Girnis and Brey, 1999; Girnis et al., 2003; Klemme et al., 2000; Klemme and O'Neill, 1997, Klemme 2004) have allowed thermodynamic parameters in Cr-bearing systems to be established and thereby allow calculations of P-T conditions of formation of spinels and garnets over the whole range of Cr-Al compositions.

Here we would like to present a new thermodynamic model with which we can calculate phase relations, and garnet (and other mineral) compositions in complex and Cr-rich compositions at pressures and temperatures relevant to the deep continental lithosphere. This will allow us to quantify and explain the observed empirical trends in some diamond indicator garnets, and thereby refine exploration techniques. The model applies to a wide range of compositions and not just Ca-poor harzburgitic ones. To illustrate the thermodynamic model we will present calculated phase relations and mineral compositions for a small subset of well-characterized natural xenoliths, which cover a wide range of rock types ranging from low-Ca harzburgite, to higher Ca lherzolite and wehrlite.

We use a free-energy minimization algorithm (Connolly, 1990) to compute mineral compositions and mineral modes for specified bulk compositions, temperature and pressure. The database includes internally consistent thermodynamic data (Holland and Powell, 1998) with additional data for Cr-spinels, Cr-garnets, and Cr-pyroxenes based on a series of recent experimental and thermodynamic studies (Brey et al., 1999; Brey et al., 1991; Girnis and Brey, 1999; Girnis et al., 2003; Klemme et al., 2000; Klemme 2004; Klemme and O'Neill, 1997; Klemme et al., 2005). This allows Cr-rich peridotitic bulk rock compositions to be modelled thermodynamically in complex systems.

References

Brey, G.P., Doroshev, A.M., Girnis, A.V., Turkin, A.I., 1999. Garnet-spinel-olivine-orthopyroxene equilibria in the FeO-MgO-Al_2O_3-SiO_2-Cr_2O_3 system: I. Composition and molar volumes of minerals: European Journal of Mineralogy, 11, 599-617.

Brey, G.P., Doroshev, A.M., Kogarko, L., 1991. The join pyrope-knorringite: Experimental constraints for a new geothermometer for coexisting garnet and spinel., 5th International Kimberlite Conference, Volume 2/9: Brazilia, Companhai de Pesquisa de Recursos Mineralais, 26-28.

Connolly, J.A.D., 1990. Multivariable phase diagrams: Am algorithm base on generalized thermodynamics: American Journal of Science, 290, 666-718.

Fipke, C.E., Gurney, J.J., and Moore, R.O., 1995, Diamond exploration techniques emphasising indicator mineral geochemistry and Canadian examples: Geological Survey of Canada, v. 423, p. 1-86

Girnis, A.V., and Brey, G.P., 1999, Garnet-spinel-olivine-orthopyroxene equilibria in the FeO-MgO-Al_2O_3-SiO_2-Cr_2O_3 system: II. Thermodynamic analysis: European Journal of Mineralogy, v. 11, p. 619-636.

Girnis, A.V., Brey, G.P., Doroshev, A.M., Turkin, A.I., Simon, N., 2003. The system MgO-Al_2O_3-SiO_2-Cr_2O_3 revisited: reanalysis of Doroshev et al.'s (1997) experiments and new experiments: European Journal of Mineralogy, 15, 953-964.

Grütter, H.S., Gurney, J.J., Menzies, A.H., Winter, F., 2004. An updated classification scheme for mantle-derived garnet, for use by diamond explorers: Lithos, 77, 841-857.

Holland, T.J., Powell, R., 1998. An internally consistent thermodynamic data set for phases of petrological interest: Journal of Metamorphic Geology, 16, 309-343.

Kennedy, C.S., Kennedy, G.C., 1976. The equilibrium boundary between graphite and diamond: Journal of Geophysical Research, 81, 2467-2470.

Klemme, S., 2004. The influence of Cr on the garnet–spinel transition in the Earth's mantle: experiments in the system MgO–Cr_2O_3–SiO_2 and thermodynamic modeling: Lithos 77, 639–646.

Klemme, S., O'Neill, H.St.C., Schnelle, W., Gmelin, E., 2000. The heat capacity of $MgCr_2O_4$, $FeCr_2O_4$, and Cr_2O_3 at low temperatures and derived thermodynamic properties: American Mineralogist, 85, 1686-1693.

Klemme, S., O'Neill, H.St.C., 2000. The near-solidus transition from garnet lherzolite to spinel lherzolite: Contributions to Mineralogy and Petrology, 138, 237-248.

Klemme, S., O'Neill, H.St.C., 1997. The reaction $MgCr_2O_4$ + SiO_2 = Cr_2O_3 + $MgSiO_3$ and the free energy of formation of magnesiochromite ($MgCr_2O_4$): Contributions to Mineralogy and Petrology, 130, 59-65.

Klemme, S., van Miltenburg, J.C., Javorsky, P., Wastin, F., 2005. Thermodynamic properties of uvarovite garnet ($Ca_3Cr_2Si_3O_{12}$): American Mineralogist, 90, 663-666.

McKenzie, D., Jackson, J., Priestley, K., 2005. Thermal structure of oceanic and continental lithosphere: Earth and Planetary Science Letters, 233, 337-349.

O'Neill, H.St.C., 1981. The transition between spinel lherzolite and garnet lherzolite, and its use as a geobarometer: Contributions to Mineralogy and Petrology, 77, 185-194.