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Ferric iron contents of clinopyroxene from cratonic mantle and partitioning behaviour with garnet

A.B. Woodland

Institut für Geowissenschaften, Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany woodland@em.uni-frankfurt.de

Ferric iron is an important minor constituent in most mantle minerals, except for olivine. The interplay between Fe³⁺ and Fe²⁺ is controlled by several factors, including oxygen fugacity (fO_2) , crystal chemistry and bulk rock composition. The fO_2 is known to vary laterally as well as with depth in the cratonic mantle and this variable has a direct impact on diamond stability (e.g. Woodland & Peltonen 1999; Woodland & Koch 2003, McCammon & Kopylova 2004). Along with garnet or spinel, clinopyroxene (cpx) is known to be an important carrier of Fe^{3+} in peridotites (Canil & O'Neill 1996; Woodland et al. 2006). Therefore, it is important to understand the behaviour of Fe³⁺ in cpx under mantle conditions. In addition, the partitioning systematics of Fe³⁺ between cpx and either garnet or spinel could have an influence on the interpretation of observed variations in redox state. In this contribution, I focus on the behaviour of Fe^{3+} in cpx from garnet peridotites.

Ferric iron contents in cpx have been measured by Mössbauer spectroscopy from a suite of garnet peridotite xenoliths from several localities in northern Lesotho (Letseng-la-Tarae, Liqhobong, Matsoku) and South Africa (Kimberley, Jagersfontein, Frank Smith Mine, Finsch). Measurements were made on hand-picked optically clean separates from samples for which fO_2 values have been previously reported (Woodland & Koch 2003). Combining these results with data from Canil & O'Neill (1996) and Woodland & Peltonen (1999) yields a data set of over 50 garnet peridotite xenoliths from cratonic mantle beneath southern Africa and Finland. This enlarged data set allows a more robust analysis of the systematics of Fe³⁺ incorporation in cpx and Fe³⁺-partitioning behaviour between cpx and garnet than that previously attempted (Canil & O'Neill 1996).

Measured Fe^{3+}/Fe_{tot} in cpx ranges from 0.10-0.41 and overlaps with values found in cpx from spinel peridotites (e.g. Woodland et al. 2006). Values are elevated in samples that contain coarse phlogopite, consistent with metasomatism leading to addition of Fe^{3+} . A correlation between Na and Fe^{3+} is apparent, emphasising the importance of the aegerine, or NaFe³⁺Si₂O₆ component in these cpxs (Fig. 1a; use of Na-Cr accounts for the presence of a NaCrSi₂O₆



component that competes for Na). Such a relationship is not observed for cpx in spinel peridotites (Fig. 1b, Woodland et al. 2006; Canil & O'Neill 1995). In these rocks a number of competing substitution mechanisms appear to be operating in cpx, involving not only the NaFe³⁺Si₂O₆ component, but also a CaFe³⁺AlSiO₆ component and potentially others (Woodland et al. 2006). In garnet peridotites, the Al content of cpx is



Figure. 1 Fe^{3+} content of clinopyroxene plotted as a function of Na-Cr (both as cations per formula unit) for a) garnet peridotites, and b) spinel peridotites. The regression line in a) is for samples from this study from South Africa and Lesotho.

buffered to generally lower values by the coexistence of garnet with the result that the NaFe³⁺Si₂O₆ component becomes the dominant mechanism for incorporating Fe³⁺. Thus, passing from the spinel to the garnet peridotite facies causes a change in how Fe³⁺ substitutes in cpx.

Thermobarometry

The sample set covers a range in temperatures and pressures indicating that the individual samples originated from depth interval of ~120-220 km (e.g. see Woodland & Koch 2003; Canil & O'Neill 1995). For the majority of samples, temperatures computed using the two-pyroxene thermometer of Brey & Kohler (1990), [BKN], the garnet-cpx Mg-Fe exchange thermometer of Krogh (1988) and the garnet-olivine Mg-Fe exchange thermometer of O'Neill & Wood (1979) all agree within $\pm 80^{\circ}$, implying that the peridotite assemblage is well equilibrated. In a few cases, one of either the garnet-olivine thermometer or the garnet-cpx thermometer gave inconsistent results with BKN, but never both (e.g. Fig. 2). The reason for these deviations remains unclear. However, the role of Fe^{3+} can be excluded as there is no correlation between Fe^{3+} content in garnet or cpx and the degree of deviation from the BKN temperatures.



Figure 2. Comparison of temperatures calculated from the two-pyroxene thermometer of Brey & Köhler (1990) [BKN] and the garnet-cpx thermometer of Krogh (1988). Agreement within $\pm 80^{\circ}$ is apparent for most samples (grey region).

Temperature and Fe³⁺ content

Although there is a poor negative correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ in cpx and increasing temperature, no such overall relationship is observed for Fe^{3+} contents as cations per formula unit (Fig. 3). This lack of correlation can be understood in terms of two factors: 1) Fe^{3+} incorporation is controlled by a number of factors, including fO_2 , the degree of depletion of a given sample, as well as the composition of the cpx itself (i.e. Na content as shown in Fig. 1a); 2) $\text{Fe}^{3+}/\Sigma\text{Fe}$ in cpx will also be directly influenced by changes in



Fe²⁺ content, which is known to be temperature dependent in the presence of opx and garnet (e.g. Brey & Köhler 1990; Krogh 1988). This has the effect of partially decoupling Fe³⁺/ Σ Fe values from the actual Fe³⁺ contents. However, the lack of any obvious relationship between temperature and Fe³⁺ content does not necessarily imply that temperature has no effect on Fe³⁺ incorporation in cpx.



Figure 3. Fe³⁺ contents as cations per formula unit in cpx plotted against equilibration temperature, as given by the BKN geothermometer.

Partitioning Fe³⁺ between garnet and cpx

Canil & O'Neill (1995) considered the partitioning of Fe³⁺ between garnet and cpx in terms of a simple partition coefficient, $D^{gt/cpx}$ and found a significant temperature dependence favouring Fe³⁺ incorporation in garnet at higher temperatures. Exceptions to this were samples containing spinel or ilmenite, a point also corroborated by Woodland & Peltonen (1999). Thus, the partitioning systematics of Fe³⁺ between garnet and cpx can be potentially used as a test of whether spinel is indeed an equilibrium phase in garnet-spinel peridotites.

The derivation of this $D^{gt/cpx}$ was based upon a simplified treatment of the Fe³⁺-Al exchange between aegerine and jadeite components in cpx, and andradite and grossular components in garnet:

$$NaFe^{3+}Si_{2}O_{6} + 0.5 Ca_{3}Al_{2}Si_{3}O_{12} = cpx gt NaAlSi_{2}O_{6} + 0.5 Ca_{3}Fe^{3+}{}_{2}Si_{3}O_{12} (1) cpx gt$$

A more rigorous treatment of this exchange equilibrium can be made by considering the thermodynamic activities of these components in the natural garnet and cpx solid solutions. Activities of andradite and grossular were computed from the garnet compositions following the reciprocal solution model outlined by Gudmundsson & Wood (1995). For cpx, no satisfactory solution model really exists that covers the necessary compositional range containing Fe^{3+} . From Luth and Canil (1993)'s analysis it appears that mixing on sites is a reasonable simplification and this approach was used here. The log K for equilibrium 1 is plotted in

Figure 4 in terms of reciprocal temperature. Also plotted is the log K calculated from the Holland & Powell (1998) data set (version tc330).



Figure 4. log K for the Fe³⁺-Al exchange equilibrium (1) between garnet and cpx plotted as a function of reciprocal temperature. Also shown are the results of calculations for equilibrium 1 using the data of Holland & Powell (1998). The natural data reveal the tendency for Fe³⁺ to be incorporated in garnet with increasing temperature (see text).

agreement between the Although calculations presented here and Holland & Powell (1998)'s is generally pretty good, lying systematically lower by only 0.3-0.5 log units, there is a difference in slope (and temperature dependence) apparent. The scatter in the results from the natural data is no doubt related to the use of the mixing on sites model for the cpx. The effect of pressure on log K was ignored in the calculations since ΔV of equilibrium 1 is small, on the order of 0.1 log unit as illustrated by the difference in the two curves computed at 1 bar and 50 Kbar using the data of Holland & Powell (1998). The difference in slope between the natural data and Holland & Powell (1998)'s data set is likely due to a problem in the tabulated thermodynamic properties of one of the endmember compontents involved in equilibrium 1. Considering the number of experimental studies on these different compositions, aegerine (acmite) is the likely source of this error.

This treatment of the partitioning of Fe^{3+} between cpx and garnet reveals that this temperature dependence is much smaller than initially thought. Thus the increase in Fe^{3+} content of garnet with increasing temperature (also depth) observed by Canil & O'Neill (1995) and Woodland & Koch (2003) cannot be only attributed to a redistribution of Fe^{3+} from cpx. Some changes in bulk composition must also be entertained. Unfortunately, this analysis still suffers from lack of a good mixing model for complex mantle cpx, and especially from uncertainties in the thermodynamic properties of the aegerine endmember.

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