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

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ABSTRACT

Together with garnet and spinel, clinopyroxene is known to be an important carrier of Fe^{3+} in mantle-derived peridotites. The systematics of Fe^{3+} incorporation in clinopyroxene and the Fe^{3+}-partitioning behaviour between clinopyroxene and garnet have been investigated from a large suite of garnet peridotite xenoliths (>50) mostly originating from the upper mantle beneath the Kaapvaal craton (Southern Africa). A correlation between Na and Fe^{3+} is apparent that is not observed for clinopyroxene from spinel peridotites. This indicates a change in how Fe^{3+} substitutes into clinopyroxene when going from the spinel to the garnet peridotite facies in the upper mantle.

A general decrease in $Fe^{3+}/\sum Fe$ with increasing temperature is also observable, however, when considered in terms of Fe^{3+} cations per formula unit this negative correlation with temperature disappears. This partial decoupling $Fe^{3+}/\sum Fe$ values from the actual Fe^{3+} contents can be understood in terms of two factors: 1) Fe^{3+} incorporation is controlled by a number of parameters, including fO_2, the degree of depletion of a given sample, as well as the composition of the clinopyroxene itself, and 2) $Fe^{3+}/\sum Fe$ in clinopyroxene can also be directly influenced by changes in Fe^{2+} content, which is known to be temperature dependent in the presence of opx and garnet.

The partitioning of Fe^{3+} between clinopyroxene and garnet can be considered in terms of two different Fe^{3+}-Al exchange equilibria involving Na-bearing components in clinopyroxene and either Ca-bearing or Fe^{2+}-bearing components in the coexisting garnet.

Results from the natural samples suggest a temperature dependence, with Fe^{3+} being progressively partitioned into garnet with increasing temperature. However, the magnitude of this effect remains open due to uncertainties in available thermodynamic data. Analysis of the two exchange equilibria point to an error in the tabulated standard enthalpy of formation of $NaFe^{3+}Si_2O_6$ aegerine on the order of 25 kJ/mol.

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1. Introduction

Ferric iron is an important minor constituent in most mantle minerals, except for olivine. The interplay between Fe^{3+} and Fe^{2+} is controlled by several factors, including oxygen fugacity (fO_2), crystal chemistry of the individual minerals and bulk rock composition. The fO_2 of the cratonic mantle is known to vary laterally as well as with depth and this can have a direct impact on diamond stability (e.g. Luth and Canil, 1993; Woodland and Peltonen, 1999; Woodland and Koch, 2003; McCammon and Kopylova, 2004). Together with garnet or spinel, clinopyroxene is known to be an important carrier of Fe^{3+} in peridotites (Canil and O'Neill, 1996; Woodland et al., 2006). Currently very little data are available on the Fe^{3+}-content of mantle clinopyroxene coexisting with garnet (Canil and O'Neill, 1996; Woodland and Peltonen, 1999). Therefore, the goal of this study is to increase our understanding of the geochemical behaviour of Fe^{3+} in clinopyroxene under mantle conditions. This includes assessing the mechanisms of

Fe^{3+} substitution. Of further interest are the partitioning systematics of Fe^{3+} between clinopyroxene and either garnet or spinel, which 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 clinopyroxene from garnet-bearing peridotites. Combining the new measurements presented here (see also Lazarov et al., this issue) with literature data, yields a 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 Fe^{3+} incorporation in mantle clinopyroxene than previously possible.

2. Analytical methods

The ferric iron content in clinopyroxene was measured in the Mössbauer spectroscopy laboratory at the University of Frankfurt 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). The fO_2 values of many of these samples have been previously reported by

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Table 1
Representative chemical compositions of clinopyroxene, including ferric iron contents, in the xenolith suite.

Sample	Let 1	Let 6	Let 7	Let 9	Let 21	Let 22	Let 39	Liq 1	Liq 5	Liq 10	Liq 11	Mat 2
locality	Letseng	Letseng	Letseng	Letseng	Letseng	Letseng	Letseng	Liqhobong	Liqhobong	Liqhobong	Liqhobong	Matsoku
rock type[a]	gt-lherz	gt-sp-lherz	gt-sp-lherz	sheared	gt-lherz	gt-lherz	gt-lherz	gt-lherz	gt-harz	gt-harz	gt-lherz	gt-lherz
phase	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx
SiO_2	55.28	54.83	54.92	56.12	55.02	55.13	54.98	55.40	55.54	56.56	55.04	55.14
TiO_2	0.12	0.09	0.03	0.19	0.07	0.08	0.11	0.10	nd	0.20	nd	0.03
Al_2O_3	3.41	4.35	1.24	2.31	1.71	2.33	2.21	3.15	1.84	3.06	2.42	2.46
Cr_2O_3	3.14	3.34	1.38	0.76	1.98	2.30	1.38	2.16	1.37	2.33	1.76	1.60
FeO^b	2.21	2.11	1.84	3.87	1.95	1.89	2.16	2.41	1.88	2.35	2.16	2.48
MnO	0.04	0.05	nd	0.10	0.02	0.05	0.08	0.07	0.07	0.08	0.09	0.09
NiO	0.05	nd	nd	0.06	0.06	0.09	0.06	0.06	0.09	0.05	nd	0.08
MgO	14.94	14.06	17.37	20.50	16.94	16.52	17.01	15.80	17.34	16.02	16.78	16.98
CaO	17.44	17.24	22.08	14.98	20.56	19.52	19.84	17.94	20.50	18.97	19.52	19.68
Na_2O	3.24	4.01	1.10	1.48	1.65	2.13	1.81	2.66	1.50	2.87	2.05	1.99
Total	99.87	100.08	99.96	100.37	99.99	100.01	99.64	99.78	100.09	102.44	99.90	100.53
$Fe^{3+}/\sum Fe$	0.228	0.350	0.262	0.098	0.164	0.191	0.165	0.307	0.204	0.291	0.234	0.189
T °C [BKN][c]	1113	928	912	1429	1029	1066	1083	1157	1079	1083	1083	1042
P GPa[d]	4.50	3.43	3.72	6.36	4.42	4.35	4.64	4.63	4.52	4.22	4.47	4.21

Several previously unpublished garnet compositions are also provided. nd = not detected.
 [a] Lherz = lherzolite, harz = harzburgite.
 [b] All Fe as FeO.
 [c] 2-Pyroxene thermometer of Brey and Köhler (1990).
 [d] Orthopyroxene-garnet barometer of Brey and Köhler (1990).

Woodland and Koch (2003). Measurements were made on hand-picked, optically clean separates. The samples (~15–30 mg) were prepared in a manner similar to that described in Woodland and Koch (2003). Sample thicknesses were ≤5 mg Fe/cm² to avoid potential saturation effects. Spectra were obtained at room temperature with the spectrometer operating in constant acceleration mode with a velocity ramp of ±5 mm/s. Details of fitting the spectra are given in Woodland et al. (2006) and are similar to that employed by others (e.g. Luth and Canil, 1993; Canil and O'Neill, 1996; McCammon et al., 1998). The hyperfine parameters resulting from the spectra fits are reported in Table 1S. Uncertainties in the area ratios of the Fe^{3+} component relative to that of Fe^{2+} generally lie in the range of ±0.01–0.02 (Table 1S).

The determined $Fe^{3+}/\sum Fe$ values were combined with microprobe data to derive the Fe^{3+} and Fe^{2+} cations per formula unit (cpfu), which for clinopyroxene are calculated on a 6 oxygen basis. Chemical compositions were determined using the Cameca SX-51 and the Jeol JXA 8900R microprobes at the Mineralogisches Institut, Universität Heidelberg, Germany and the Institut für Geowissenschaften, Universität Frankfurt, Germany, respectively. A few analyses were also obtained with the Jeol JXA 8900R microprobe located at the University of Alberta, Canada. Operating conditions were 15 kV and 15 or 20 nA and a focused beam. All analyses were made in wavelength-dispersive mode using a variety of synthetic and natural standards. The PAP (Cameca) and ZAF (Jeol) correction procedures were applied to the raw counts. Major element compositions for the clinopyroxenes are reported in Table 1.

The composition of coexisting garnet is required to determine the partitioning behaviour of Fe^{3+} with clinopyroxene. Chemical analyses of garnet from the majority of the samples are reported in Woodland and Koch (2003), along with some new data for Finsch presented in Lazarov et al. (this issue). The garnet compositions from additional samples are provided in Table 1.

3. Results and discussion

The clinopyroxenes studied are Cr-diopsides with compositions typical for mantle peridotites (Table 1). Although secondary clinopyroxene is apparent in many of the samples, they are easily distinguished from "primary" grains by their textures and major element compositions (Woodland, 2002; Simon et al., 2003). Much of the secondary clinopyroxene is fine grained and occurs either along grain boundaries (often in contact with orthopyroxene, but also with olivine), or within late stage kelyphite rims around garnet. The grain boundary clinopyroxene has much lower Na, Al and Cr contents and is richer in Mg, Fe and Ti, compared with the coarser "primary" grains and is most likely the product of metasomatism (Woodland, 2002). The kelyphite clinopyroxene is notable for its high Al content. These two types of secondary clinopyroxene are so fine grained that they were easily avoided when picking the mineral separates for Mössbauer spectroscopy. In some cases, larger clinopyroxene grains have spongy or cloudy rims/overgrowths and these domains have intermediate compositions that reflect interaction with the metasomatic agent responsible for the fine grained clinopyroxenes. Although the inclusion of some of this material in the mineral separates cannot be completely excluded, the cloudiness of such domains means that they were generally avoided in the picking procedure.

A number of recent trace element studies have concluded that much clinopyroxene has been introduced through metasomatic interaction with percolating melts (e.g. van Achterbergh et al., 2001; Grégoire et al., 2003; Simon et al., 2003). However, considering the long history and metamorphic nature of mantle peridotite, a question always remains as to which phases, if any can be considered "primary" (what does primary actually mean in this context?). In fact, given enough time after a metasomatic event, the phases will re-equilibrate with one another. The time required for re-equilibration is a complex function of many parameters, meaning that in a given peridotite xenolith certain elements may partially (or totally) preserve different signatures in different grains, while the inter-mineral distribution of other elements has been mostly or completely reset. In the latter case, the question of whether a mineral is "primary" or secondary is irrelevant; a new equilibrium condition has been locally reached.

Measured $Fe^{3+}/\sum Fe$ ranges from 0.10–0.41, indicating that a significant proportion of the Fe in clinopyroxene is present in the ferric state (Table 1). This range overlaps with values found in clinopyroxenes from spinel peridotites (e.g. Luth and Canil, 1993; Woodland et al., 2006). Ratios tend to be elevated in samples that contain coarse phlogopite, consistent with metasomatism leading to addition of Fe^{3+}. The incorporation of Fe^{3+} into calcic clinopyroxene requires some sort of coupled substitution for charge balance. A correlation between Na and Fe^{3+} is apparent in the current data set, emphasising the importance of the aegerine, or $NaFe^{3+}Si_2O_6$, component in these clinopyroxenes. This is apparent in Fig. 1a, where the