Ferric-ferrous iron ratios of experimental majoritic garnet and clinopyroxene as a function of oxygen fugacity

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Abstract

The oxidation state of iron in upper mantle minerals is widely used to constrain the Earth mantle’s oxidation state. Previous studies showed high levels of ferric iron in high-pressure majoritic garnets and pyroxenes despite reducing conditions. To disentangle the effects of pressure and increasing oxygen fugacity on the Fe$^{3+}$/ΣFe ratios of garnet and clinopyroxene, we performed high-pressure experiments at pressures of 10 GPa in a 1000-ton Walker-type multi-anvil apparatus at the University of Münster. We synthesized majoritic garnets and clinopyroxenes with a total iron content close to natural mantle values at different oxygen fugacities, ranging from IW+4.7 to metal saturation at IW+0.9. We analyzed the iron oxidation state in garnets with the electron microprobe “flank method”. Furthermore, we investigated the oxidation state of iron in garnets and clinopyroxenes with transmission electron microscopy (TEM) electron energy loss spectroscopy (EELS). Although the flank method measurements are systematically lower than the EELS measurements, Fe$^{3+}$/ΣFe obtained with both methods agree well within 2σ errors. The "flank method" has the advantage of being much faster and more easily to set-up, whereas TEM-EELS has a much higher spatial resolution can be applied to a variety of non-cubic minerals such as orthopyroxenes and clinopyroxenes. We used our experimental results to compare two geobarometers that contain a term for ferric iron in garnet (Beyer and Frost 2017, Tao et al. 2018) with two geobarometers that do not account for ferric iron (Collerson et al. 2010, Wijbrans et al. 2016). We found that garnets with low total Fe and Fe$^{3+}$ (like many natural garnets) pressures can be calculated without including the ferric iron content.

Keywords
majorite, multi anvil apparatus, electron energy loss spectroscopy, transmission electron microscopy, flank method, ferric iron, oxygen fugacity, Earth mantle

Introduction

The oxidation state of the Earth’s upper mantle is still a matter of debate, mainly because rock samples from depths > 250 km are virtually absent except for rare ultradepth xenoliths (Haggerty and Sautter 1990; Sautter et al. 1991) and mineral inclusions in diamond (e.g. Pearson et al. 2014). However, the oxidation state of the Earth’s mantle exerts a significant influence on the stability of C-O-H-volatiles and therefore has important implications for the phase relations and melting behavior (Kushiro et al. 1968; Taylor and Green 1988; Ballhaus and Frost 1994; Gaetani and Grove 1998; Dasgupta and Hirschmann 2006; Foley 2011; Tumiati et al. 2012; Stagno et al. 2013), hydrogen incorporation (e.g. Kohlstedt et al. 1996) and the rheology of the mantle (Mackwell et al. 1985) as well as for diamond/graphite vs. carbonate stability (Dasgupta and Hirschmann 2010; Stagno and Frost 2010; Rohrbach and Schmidt 2011; Stagno et al. 2013; Luth and Stachel 2014; Yaxley et al. 2017). The oxidation state of the upper mantle can be determined by the Fe\textsuperscript{3+}/\Sigma Fe content of mantle minerals since iron is a major element in Earth’s mantle and is incorporated into every mantle mineral (e.g. O’Neill et al. 1993b; Luth and Canil 1993; Canil and O’Neill 1996). The oxygen fugacity (fO\textsubscript{2}) of the uppermost mantle predominantly lies between FMQ+2 and FMQ-2 as indicated by xenoliths and samples of basaltic melts and peridotite massifs (Luth et al. 1990; Ballhaus 1993; Frost and McCammon 2008). With increasing depth, the upper mantle becomes more reduced, approaching \Delta \log fO\textsubscript{2} values of FMQ-4 at 220 km depth (Woodland and Koch 2003; McCammon and Kopylova 2004; Frost and McCammon 2008; Stagno and Frost 2010; Yaxley et al. 2012). In the upper mantle the fO\textsubscript{2} correlates with the ferric iron content of minerals, so that spinels in harzburgite and lherzolite at pressures up to 2.7 GPa show a decrease of ferric iron with
decreasing $fO_2$ tending towards zero when metallic iron is a stable phase (Ballhaus et al. 1991).

This linear relationship between $fO_2$ and $Fe^{3+}/ΣFe$ is not observed in experimental phase assemblages at pressures corresponding to the lowermost upper mantle, the transition zone or the lower mantle, where majoritic garnet and bridgmanite with high ferric iron contents coexist with metallic iron (O’Neill et al. 1993a; McCammon 1997; McCammon and Ross 2003; Frost et al. 2004; Rohrbach et al. 2007; 2011). In a typical upper mantle assemblage, ferric iron is concentrated in modally minor phases like clinopyroxene and spinel since olivine incorporates negligible ferric iron and orthopyroxene incorporates only between 0.2 and 0.6 wt% $Fe_2O_3$ at low $Fe^{3+}/ΣFe$ between 0.03 and 0.10 (O’Neill et al. 1993b; Canil and O’Neill 1996; Woodland and Koch 2003; Yaxley et al. 2012). Above 6 GPa, pyroxene components become more soluble in garnet and substitute continuously into the garnet structure (Akaogi and Akimoto 1979; Irifune 1989; Rohrbach et al. 2011; Wijbrans et al. 2016; Beyer and Frost 2017; Kiseeva et al. 2018). Assuming that the transition zone has the same bulk chemical composition as the upper mantle, including the $Fe^{3+}/ΣFe$ content, the $fO_2$ of the transition zone consequently must depend on how well its minerals can incorporate ferric iron. Since most transition zone minerals can incorporate some ferric iron (see compilation in Frost and McCammon 2008), the average amount of around 2000 µg/g $Fe_2O_3$ (O’Neill et al. 1993a), will be partitioned into a wider range of minerals within the transition zone than in the upper mantle. This leads to a dilution effect and a decreased ferric iron activity, which results in decreased $fO_2$ (O’Neill et al. 1993a Ballhaus 1995). The presence of high amounts of ferric iron in transition zone majoritic garnet or in lower mantle bridgmanite in spite of low $fO_2$ can either be explained by a reduction of oxidized volatiles as $CO_2$ and $H_2O$ to $CH_4$ or more likely, by disproportionation of $3Fe^{2+}O = Fe_2^{3+}O_3 + Fe^0$ (O’Neill et al. 1993a; Frost et al. 2004; Rohrbach et al. 2007).
In order to track redox conditions of the upper mantle and the transition zone, ferric iron contents of garnets have been used extensively. Garnet has several advantages, because it is stable over a wide range of pressures and temperatures from the upper mantle into the transition zone (e.g., Klemme and O’Neill 2000; Klemme and Fumagalli, 2015), and is consequently one of the most common rock-forming minerals of the Earth’s interior (Ringwood 1967; Ringwood and Major 1971). Therefore, the incorporation of ferric iron in pyroxene-garnet solid solutions at high pressures has been repeatedly studied (McCammon and Ross 2003; Rohrbach et al. 2007; 2011; Beyer and Frost, 2017). All former studies agree about the onset of majorite stability in garnet solid solutions at around 6 GPa. Pyroxenes dissolve increasingly into the garnet structure to form majoritic garnet with increasing depth and consequently the majorite component can be used for geobarometry (Collerson et al. 2010; Wijbrans et al. 2016; Beyer and Frost 2017; Tao et al. 2018). Compared to regular garnets, where the dodecahedral site is occupied by divalent cations and the octahedral site by trivalent cations, majorites incorporate Si$^{4+}$ and Mg$^{2+}$ on the octahedral site.

In this study, we performed high-pressure multi-anvil experiments at different oxygen fugacities with a total iron content of 8 wt% reflecting the iron content of the mantle (Palme and O’Neill 2003). We quantified the ferric iron contents of our garnets and clinopyroxenes and used them to review several majorite geobarometers (Collerson et al. 2010; Wijbrans et al. 2016; Beyer and Frost 2017; Tao et al. 2018). The quantification of ferric iron was performed with two different methods using the same samples: transmission electron microscopy - electron energy loss spectroscopy (TEM-EELS; van Aken et al. 1998; van Aken and Liebscher 2002) and the electron microprobe (EPMA) flank method (Höfer 2002; Höfer and Brey 2007).

**Experimental and analytical methods**
The high-pressure experiments were performed with a synthetic starting material representing a primitive mantle composition (Palme and O’Neill 2003; Table 1). To increase the modal amounts of ferric iron-bearing minerals such as clinopyroxene and garnet, we subtracted 30 wt% olivine from that composition. We prepared a mixture of all elements except iron from high purity oxides and carbonates (Alfa Aesar) in an agate mortar under acetone. This mixture was decarbonated over night at 1000 °C. We then added reagent grade FeO (Alfa Aesar) to the mixture and homogenized the starting material again for 30 minutes in an agate mortar. The Mg# (Mg/(Mg+Fe); atoms per formula unit) of the starting material is 0.8 at a total FeO content of 8 wt%, to obtain phase compositions directly comparable to natural minerals. The downside of low FeO contents in minerals is a generally low count rate during TEM-EELS and EPMA measurements.

In order to constrain the relationship between the fO2 and the Fe3+/ΣFe for clinopyroxene and garnet, we synthesized these phases at different redox conditions between IW+0.9 and IW+4.7. The most reducing experiment at IW+0.9 (MaLm11) was performed by using a double capsule technique. The starting material was contained in a welded shut noble metal (Au80Pd20) inner capsule, which was surrounded by an outer iron metal capsule. The hydrogen source between the two capsules was brucite. In experiment MaLm6 we added 1 wt% Si metal to the starting material. This triggers a reaction of silicon metal and iron(II)oxide to metallic iron and silicon dioxide and reduces the intrinsic fO2 of the sample (Tsuno et al. 2013). We fixed the fO2 of the samples MaLm1 and MaLm2 to values close to the enstatite-magnesite-olivine-diamond (EMOD) buffer by adding 1 wt% graphite to our starting material (Eggler et al. 1979). Furthermore, 5 wt% stearic acid was added to all samples to produce a C-O-H fluid component (Sokol et al. 2010) at experimental P and T which lowers the intrinsic fO2 of the composition and facilitates reaching equilibrium in subsolidus runs. The most oxidized experiments, where fO2 was not buffered (MaLm9 and MaLm12), were performed in welded Au80Pd20 capsules. The experiments were performed
between 1450 to 1550 °C at 10 GPa in a 1000-ton Walker-type multi-anvil apparatus at the
University of Münster. All run conditions are presented in Table 2 and in the Supplementary
material (Table S1). The experiments were performed using a 14/8 assembly (14 mm octahedron
edge length, 8 mm truncated edge length) employing Cr-doped MgO octahedron and a zirconia
insulating sleeve around a stepped LaCrO$_3$ furnace. For details regarding the pressure calibration
of the press see Wijbrans et al. (2016). Run temperatures were measured with type C-
thermocouples and controlled within ± 5°C by an Eurotherm controller. Experiments were
quenched by turning off the power supply.

All samples were mounted in an acrylic resin and polished down to the center of the capsule.
Backscattered electron images were performed with a JEOL JSM-6510LA scanning electron
microscope at the University of Münster. Major and minor element analyses were performed with
a JEOL JXA-8530F electron microprobe at the University of Münster using natural minerals as
standards. The following standards were used for quantification: hypersthene (Si), disthene (Al),
fayalite (Fe), olivine (Mg, Ni), diopside (Ca), jadeite (Na). For garnet analysis we used natural
pyrope as standard for Si, Al and Mg. The EPMA acceleration voltage was 15 kV and the beam
current was 15 nA. The spot sizes were 1-5 μm depending on the grain size. Counting times were
20 s on the peak and 10 s on the background for metals and garnets, for other silicates 15 s on the
peak and 5 s on the background.

The EPMA flank method measurements of the garnets were performed with the JEOL JXA
8900RL Superprobe at Goethe University in Frankfurt. The measurements were carried out at an
acceleration voltage of 15 kV, and a beam current of 120 nA and a beam diameter of 1 μm. Each
Fe$^{3+}$/ΣFe determination with simultaneous major element analysis resulted from the average of 25
independent measurements on different grains to achieve an uncertainty of below 0.02 in Fe$^{3+}$/ΣFe
(1σ). Counting times were 20 to 30 s on the peak and background for all main elements besides iron (60 s), and 140 s for each FeLα and FeLβ measurement. In general, the flank method combines measuring the shift of the peak position and the change in intensity ratios of FeLα and FeLβ, which systematically varies with the Fe3+/ΣFe content, resulting in the high sensitivity and high precision of this method (Höfer and Brey 2007). The garnet standards used to calibrate and to quantify Fe3+/ΣFe in our samples contain between 6 and 21 wt% total iron: oxyAlm: 20.21 wt% ΣFe, 0.03 wt% Fe3+/ΣFe (Höfer and Brey 2007; Vasilyev 2016); UA5: 6.49 wt% ΣFe, 0.11 Fe3+/ΣFe (Vasilyev 2016; Li et al. 2018); UA17: 6.25 wt% ΣFe, 0.06 Fe3+/ΣFe (Vasilyev 2016); Damknolle: 15.18 wt% ΣFe, 0.04 Fe3+/ΣFe (Höfer and Brey 2007; Vasilyev 2016). Fe3+/ΣFe of all garnet standards were measured by Mössbauer spectroscopy prior to the flank measurements (McGuire et al. 1992; Rankenburg et al. 2002; Höfer and Brey 2007). The empirically determined 1σ error is ± 0.02 for these samples (Höfer and Brey 2007). The flank method was already successfully used to quantify Fe3+/ΣFe in garnets (Malaspina et al. 2009; 2010; Höfer and Brey 2007; Tao et al. 2018), sodic amphiboles (Enders et al. 2002) and wustites (e.g. Höfer et al. 2000). Furthermore, several groups are currently working on flank-method calibrations for other minerals and glasses (Malaspina et al. 2010; Zhang et al. 2018). For TEM analysis, the former EMPA samples were prepared by ultramicrotomy, in order to avoid a change in their chemical composition, and put onto carbon-film copper TEM-grids. Preparation resulted in slices of 70 nm thickness, which is specifically important for EELS analysis to avoid multiple scattering effects. Although the mechanical stress induced by the diamond knife resulted in severe shattering of the samples, no chemical disturbance of analyzed minerals can be expected, perhaps in contrast to ion beam techniques. EELS measurements were performed on a Zeiss Libra 200FE TEM at the University of Münster equipped with a Schottky-type field emission gun (200
kV) and a Köhler illumination system providing strongly parallel illumination conditions at all brightness indices. Samples were initially documented by conventional Brightfield (BF) and Scanning TEM- High Angle Annular Darkfield (HAADF, contrast proportional to average Z) imaging. Energy filtering was performed through an in-column Omega filter in TEM mode using a 200 µm filter entrance aperture giving an effective aperture of about 100 nm on the sample surface. The energy spread of the field emitter is 0.7 eV as determined from the full width at half maximum of the zero loss peak (ZLP). Convergence angle was about 0.1 milliradian (quasi-parallel Köhler illumination). The following routine was used to record EELS spectra: First, the ZLP was recorded with a low brightness index to avoid damage of the slow-scan CCD camera Gatan UltraScan 4000 (5 frames at 0.1 or 0.2 s integration time). Afterwards, the Fe L\textsubscript{2,3} edge was recorded with a much higher brightness index and longer exposure times (10 frames at 5 s integration time). We analyzed up to 9 grains of garnet and clinopyroxene per sample, measurements with more than 2σ variation of the mean were considered as outliers and thus excluded from the calculation of the mean. Due to the required total iron content of at least several wt% it was only possible to measure three samples: the rather oxidized samples MaLm1 and MaLm9 and the metal saturated sample MaLm11. All EELS measurements were examined with the MATLAB® script EELSA (Prescher et al. 2014). EELSA uses the two basic procedures described by van Aken and Liebscher (2002). The first approach applies two 2 eV wide integration windows to the Fe L\textsubscript{3} maximum (Fe\textsuperscript{3+}) and the Fe L\textsubscript{2} maximum (Fe\textsuperscript{2+}) of the sample. By dividing the ferrous iron content at L\textsubscript{2} by the ferric iron content at L\textsubscript{3} the Fe\textsuperscript{3+}/ΣFe content of the sample can be determined from the spectrum. The second approach employs several Gaussian functions describing the spectral features and one Arctan function to fit the remainder of the EELS spectrum (van Aken and Liebscher 2002). Both approaches make use of the significant shapes of the FeL\textsubscript{2,3} edges that depend on the valence state of iron. Minerals with simply divalent iron content show a sharp peak of their L\textsubscript{3} edge at 707.8 eV.
and a weaker peak at 710.5 eV. Samples with trivalent iron only show a sharp peak of their $L_3$ edge
at 709.5 eV with a weaker pre-peak at 708.0 eV (van Aken and Liebscher 2002). The difference
between $L_3$ and $L_2$ edge is a result of spin-orbit splitting (Colliex et al. 1991; Garvie et al. 1994;
van Aken et al. 1998). The absolute 1σ error of the quantification technique is ± 0.02 (van Aken
and Liebscher 2002).

**Results**

**Experimental results and phase compositions**

Backscattered electron (BSE) images of typical run products from this study are shown in Figure
1. Olivine is the most abundant phase in our run products with modal amounts between 37 and 45
vol%. The second most abundant phase is majoritic garnet (22-39 vol%). Clinopyroxenes are
present between 19 and 33 vol%, whereas orthopyroxene is only a minor phase (2 to 15 vol%). The
modal proportions were calculated via mass balancing and agree well with the phase proportions
observed in the scanning electron microscope (SEM) images. Most run products contain olivine,
clinopyroxene, majoritic garnet and orthopyroxene, i.e. a regular mantle mineral assemblage. The
mineral assemblages in MaLm2 and MaLm12 differ from the other samples such that MaLm12
contains little orthopyroxene and MaLm2 contains orthopyroxene, garnet, magnesite, diamond and
carbonate/carbonatite melt but no olivine (Fig. 1a,b). The sample MaLm1 also contains small
magnesite grains, but no related melt component. The appearance of carbonatite melt is most likely
the result of adding stearic acid to the charges which produces minor amounts of CO$_2$ when it
decomposes at high T in a starting material with high intrinsic fO$_2$. CO$_2$ could also result from
incomplete decarbonation of the starting material, which would be rather beneficial to buffer fO$_2$
close to EMOD. The Mg# of all minerals are around 0.90 (Table 3). The Si-metal modified sample
MaLm6 contains olivine, orthopyroxene, clinopyroxene and garnet (Fig. 1c). The metal-saturated sample MaLm11 still contains the Ir-Fe alloy with high Fe content (Fig. 1d,e). Sample MaLm12 contains little orthopyroxene, but olivine, clinopyroxene and majoritic garnet (Fig. 1f). The phases throughout the charge are homogeneous in terms of chemical compositions and also when comparing different run products (Table 3 and Supplementary material Tables S2 and S3).

All garnets from this study are considered majoritic, since they contain more than three silicon cations per 12 oxygens. The composition of our majorites is a solid solution among majorite (Mg$_4$Si$_4$O$_{12}$), grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$), almandine (Fe$_3$Al$_2$Si$_3$O$_{12}$), pyrope (Mg$_4$Si$_4$O$_{12}$) and andradite (Ca$_3$Fe$_{3+2}$Si$_3$O$_{12}$) components (Supplementary material Table S2, after Locock 2008).

Garnets are more pyrope-rich and majorite-poor compared to garnets synthesized at 10 GPa by Rohrbach et al. (2011) due to the overall higher Mg# of our starting material. However, our garnets generally show a lower Mg# than the pyroxenes, which is consistent with results from previous studies (Rohrbach et al. 2007; 2011).

Orthopyroxenes generally have a higher Mg# (0.90-0.96) than the corresponding clinopyroxenes (0.88-0.97). All clinopyroxenes and orthopyroxene compositions are close to Di$_{86}$Ja$_{11}$Ae$_3$ and En$_{92}$Fs$_6$Wo$_2$.

**Oxygen fugacity**

Oxygen fugacities of all samples were monitored by adding 3 wt% iridium to all starting compositions as a redox sensor (Woodland and O’Neill 1997; Stagno and Frost 2010; Rohrbach and Schmidt 2011). During an experiment iron dissolves into the iridium metal which can be analyzed by EPMA (Supplementary material, Table S1). Oxygen fugacities were calculated using the method described in Rohrbach and Schmidt (2011). Uncertainties on the fO$_2$ calculation are
difficult to quantify but are perhaps within 0.3 to 0.5 log units (see discussion in Stagno and Frost 2010).

Comparison of the flank method and EELS

We measured a maximum of 25 garnets per experimental sample with the flank method. The uncertainty of ± 0.02 is an empirically proven 1σ error according to the calibration of the method (Höfer and Brey 2007). Calculated 2σ errors were ± 0.04 except for MaLm11 (± 0.06). We performed a maximum of nine EELS measurements per phase per sample. We found that our EELS measurements required a total iron content of at least 5 wt% to gain a sufficient signal-to-noise ratio in the spectra for reliable quantification. We obtained accurate EELS results for three samples: MaLm1, MaLm9 and MaLm11.

The results of the two analytical methods overlap within 2σ and show a similar correlation between fO₂ and Fe³⁺/ΣFe in our experimental charges. However, EELS results of our garnets seem to indicate slightly higher ferric iron contents compared to flank method results, a trend that is also evident in the dataset of Malaspina et al. (2009). One possible explanation for this slight discrepancy could be that the higher number of EPMA measurements per phase more easily compensates for statistical spikes than the comparably lower number of EELS measurements. A possible zonation of our garnets in a µm-range would have been detected during flank method measurements and this would have led to much higher errors than ± 0.04. If any zonation existed at smaller (i.e., nm) scales, it may not have been detected and may have led to average values, whereas EELS analyses would have been able to distinguish these different garnet regions. Another explanation for the higher EELS results might be due to a slight oxidation of our TEM samples during preparation at least on the surface of the lamellae. Nevertheless, ultramicrotomy is considered to prevent a chemical alteration of samples, which was the reason to choose this
preparation technique. Furthermore, the low 1σ error of 0.02 for the flank method is based on a
calibration with garnets containing 6 to 21 wt% total iron. Some of the garnets in the present study
have even lower iron contents so that the error may be larger in some samples. Moreover, our EELS
results agree well with the corresponding values by Rohrbach et al. (2007).

Overall, both measurement techniques lead to comparable results within 2σ and can therefore be
used for the successful determination of Fe$^{3+}/\Sigma$Fe. The choice of a technique should therefore rather
depend on the available time span, sample amount and desired spatial resolution. One of the main
advantages of the EELS method however is, that non-cubic crystals like pyroxenes can be analyzed.

All Fe$^{3+}/\Sigma$Fe determinations were additionally compared with Fe$^{3+}/\Sigma$Fe calculated by charge
balance calculations. The results fit surprisingly well and agree within 2σ errors both with EELS
and flank measurements (Table 3 and Supplementary material, Table S4).

**Fe$^{3+}/\Sigma$Fe in majoritic garnets and clinopyroxenes**

The electron microprobe flank method yields slightly lower Fe$^{3+}/\Sigma$Fe contents than corresponding
EELS measurements (Fig. 2, Table 3) but agree within 2σ uncertainty (Fe$^{3+}/\Sigma$Fe flank: 0.07(6);
Fe$^{3+}/\Sigma$Fe EELS: 0.11(4), and within 2σ of 0.13(2) determined by Rohrbach et al. (2011). These
values represent the minimum Fe$^{3+}/\Sigma$Fe at metal saturated conditions at 10 GPa. Our results are
within the general trend regarding the extent of majorite substitution with increasing pressures as
illustrated in Figure 3.

The two effects that are responsible for increasing Fe$^{3+}/\Sigma$Fe in garnet are increasing pressure and
increasing fO$_2$ (Fig. 4). Experimental metal saturated samples (this study and Rohrbach et al., 2007;
IW-0.5 to IW-1.3) define the increase in Fe$^{3+}/\Sigma$Fe at minimum fO$_2$ due to disproportionation of
FeO, majoritic garnets from slightly more oxidized environments (this study; Woodland and Koch
2003, IW+1.4 to IW+2.9 and Kiseeva et al. 2018, IW-0.3 to IW+3) are systematically shifted to the left of the trend (Fig. 4). Natural non-majoritic garnets span a similar range in Fe$^{3+}$/ΣFe than the experimental samples.

The clinopyroxenes in our samples tend to have a higher Fe$^{3+}$/ΣFe content than the majorites, which is in line with results from natural samples by Lazarov et al. (2009) but different to earlier studies where clinopyroxenes had higher Fe$^{3+}$/ΣFe than the coexisting garnet/majorite (Canil and O’Neill 1996; Rohrbach et al., 2007). One possible explanation might be that the Fe$^{3+}$/ΣFe in clinopyroxenes is more dependent on bulk composition and Mg# than in garnets. Since the correlation of fO$_2$ and clinopyroxene has not been systematically studied so far, we cannot draw definite conclusions.

Discussion

Correlation of oxygen fugacity with analyzed Fe$^{3+}$/ΣFe contents of garnets and clinopyroxenes

All Fe$^{3+}$/ΣFe measurements using both analytical techniques show a positive correlation with the calculated fO$_2$ of our samples equilibrated at the same P and T (Fig. 5).

High oxygen fugacities therefore correlate with high ferric iron contents and decrease at more reducing conditions until metal saturation is reached. This is evidence for the fact that our experimental approach as well as ferric iron measurements were successful. Our most reduced and metal saturated sample MaLm11 shows Fe$^{3+}$/ΣFe between 0.07(6) and 0.11(4) measured by the flank method and EELS (2σ). Our clinopyroxenes measured with EELS show the same positive correlation between Fe$^{3+}$/ΣFe and fO$_2$ at slightly higher ferric iron contents. In order to explain the ferric iron content despite metal saturation of MaLm11, disproportionation must be the dominant
process, because no Fe$_2$O$_3$ was added and no carbonated fluid or melt was involved, perhaps contrary to the natural samples examined by Kiseeva et al. (2018). We expect to see a correlation between Fe$^{3+}$/ΣFe and fO$_2$ natural samples as well, but only if a group of garnet or pyroxene equilibrated at roughly the same P, T and chemical environment. To test this hypothesis, we divided the Ekati garnet dataset of Yaxley et al. (2017) into three subgroups of similar equilibration P and T and found a distinct positive correlation between Fe$^{3+}$/ΣFe and fO$_2$ for each subgroup, which is not obvious when plotting the entire dataset (Supplementary Fig. S1). This relationship, however, remains to be tested at other locations.

**Application of determined Fe$^{3+}$/ΣFe contents to majoritic geobarometers**

We performed geobarometric calculations with four different geobarometers from Collerson et al. (2010), Wijbrans et al. (2016), Beyer and Frost (2017) and Tao et al. (2018). Since all four geobarometric calculations take the majorite substitution into account, every single one can be used to calculate pressures in natural high-pressure garnets or run pressures of high P-T-experiments. Two of the geobarometers employ a distinct term for ferric iron (Beyer and Frost 2017; Tao et al. 2018).

The geobarometer by Collerson et al. (2010) describes the extent of majoritic substitution as excess of Si and Ti on the octahedral site of garnet and the respective depletion in Al$^{3+}$ and Cr$^{3+}$. This geobarometers is also dependent on the Na content but does not include the ferric iron content. The geobarometer by Tao et al. (2018) is based on the geobarometer by Collerson et al. (2010), but only accounts for excess Si on the octahedral site of majorite and for the respective depletion of Al$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$. The geobarometer by Beyer and Frost (2017) is the most complex model considering the normal majorite substitution (Al$^{3+}$ =Si$^{4+}$ + Mg$^{2+}$) the Na-majorite substitution (Mg$^{2+}$ + Al$^{3+}$ = Si$^{4+}$ + Na$^+$) and accounts for Fe$^{3+}$, Cr$^{3+}$, Ti$^{4+}$ and Ca$^{2+}$ contents in majorite. The pressure calculated
by the geobarometer of Wijbrans et al. (2016) for peridotitic compositions solely depends on excess
Si$^{4+}$ on the octahedral site and on the Cr$^{3+}$ content of the majorite.

The geobarometer that results in the best fit for our majorites with low ferric iron and low Na
contents is the one by Wijbrans et al. (2016) that leads to pressures within a mean $\Delta P$ of 0.9 GPa
from our experimental pressure of 10 GPa (Fig. 6). We note, however, that the experiments of
Wijbrans et al. (2016) were performed using the same experimental equipment as the present study
and thus on the same pressure calibration. The dataset used by Wijbrans et al. (2016) to calibrate
the barometer is much larger than so we do not expect a large bias of the results.

When we use geobarometry on the experimental majorites of Rohrbach et al. (2011) which have a
high total FeO content as well as rather high Na$^+$ and ferric iron contents, it seems important to
apply a geobarometer which reflect this chemical complexity. The Tao et al. (2018) calibration
reproduces experimental run pressures best for this dataset but the Collerson et al. (2010) and Beyer
and Frost (2017) geobarometers are also well suited for these rather special majorites. The
calibration of Wijbrans et al. (2016) for peridotitic compositions shows rather large pressure
discrepancies if applied to this dataset (Supplementary material, Fig. S2).

All four majorite geobarometers agree well with pressures calculated via Al-in-orthopyroxene
barometry for garnet peridotites by Woodland and Koch (2003). We have chosen only the highest
pressure garnets from the dataset for this comparison. These high pressure garnets have a low
concentration of Fe$^{3+}$ and Na$^+$ and are only slightly majoritic. (Supplementary material, Fig. S3).

Based on the analysis above we would recommend to apply all geobarometers to the sample of
interest. For garnets with low total Fe and presumably low Fe$^{3+}$ (like many natural garnets) it seems
acceptable to calculate pressures without knowing the precise ferric iron content.
Implications

Our results confirm that two factors determine the Fe\textsuperscript{3+}/ΣFe in majoritic garnets and high pressure pyroxenes. Metal saturated low fO\textsubscript{2} experimental garnets and pyroxenes set the minimum Fe\textsuperscript{3+}/ΣFe at a given pressure and higher fO\textsubscript{2} raises the Fe\textsuperscript{3+}/ΣFe additionally. We furthermore conclude that both TEM-EELS and the EPMA flank method for the quantitative measurement of ferric iron in silicate minerals yield comparable results within 2σ. Measurements with the "flank method" are much faster and set-up of the method is relatively straight forward when a set of standards with independently measured Fe\textsuperscript{3+}/ΣFe ratios is available. However, EMPA measurements cannot resolve possible nanoscale heterogeneities of measured samples, and the flank method can only be used for garnets, amphiboles and glasses. TEM-EELS on the other hand has a much higher spatial resolution on a nm-scale and can be applied to a variety of non-cubic minerals such as orthopyroxene and clinopyroxene. Nevertheless, TEM measurements and sample preparations are far more time-consuming and allow to measure only a limited numbers of grains. We would like to emphasize that a correct quantitative measurement of ferric iron in garnets is important not only for its accuracy but also for some geobarometric applications and to model the deeper upper mantle and below.

Acknowledgments

We thank Maik Trogisch and Ursula Heitmann for the preparation of samples and Beate Schmitte for helping with the EPMA analysis. Furthermore, we thank Clemens Prescher for providing his MATLAB\textregistered script EELSA for the quantification of our EELS spectra. We thank Christian Liebske and an anonymous reviewer for thorough reviews and Sylvie Demouchy for helpful comments and editorial handling. This work was financially supported by the DFG (SFB TRR 170).
References


Akaogi, M., and Akimoto, S. (1977) Pyroxene-garnet solid-solution equilibria in the systems Mg$_4$Si$_4$O$_{12}$-Mg$_3$Al$_2$Si$_3$O$_{12}$ and Fe$_4$Si$_4$O$_{12}$-Fe$_3$Al$_2$Si$_3$O$_{12}$ at high pressures and temperatures. Physics of the Earth and Planetary Interiors, 15, 90–106.


**Figure captions**
Figure 1 Backscattered electron (BSE) images of run products. a) Carbonate melt containing sample MaLm2 with garnet-clusters (Grt) and orthopyroxene (Opx). b) Close-up of sample MaLm2 with magnesite (Mgs) and carbonatite melt (C. melt). c) Sample MaLm6 with clinopyroxene-clusters (Cpx). d) Overview of sample MaLm11 with Fe-Ir metal phase with high Fe content. e) Close-up of MaLm11 with garnet and Fe-Ir metal phase. f) Sample MaLm12 with garnet and clinopyroxene-clusters. Small bright particles in all charges are Ir-Fe metal alloys.

Figure 2 Comparison of electron energy loss spectroscopy (EELS) and flank method measurements. Flank measurements are systematically lower in Fe$^{3+}/\Sigma$Fe than EELS measurements, although results are within 2σ. The black line represents a 1:1 correlation line.

Figure 3 Extent of majorite substitution as function of pressure in natural and synthetic garnets. The number of Si$^{4+}$ cations per formula unit in garnet increases at pressures higher than ~6 GPa. This increase with pressure is more pronounced in iron rich compositions (Rohrbach et al. 2007).

Figure 4 Influence of pressure and fO$_2$ on the Fe$^{3+}/\Sigma$Fe content of garnet. The metal saturated sample MaLm11 plots within the range of earlier studies by Woodland and Koch (2003), Rohrbach et al. (2007) and Kiseeva et al. (2018). Black crosses are literature data of natural high-pressure but non-majoritic garnets by Creighton et al. (2008), Lazarov et al. (2009), Creighton et al. (2010), Yaxley et al. (2012; 2017).

Figure 5 Positive correlation between the fO$_2$ and the Fe$^{3+}/\Sigma$Fe contents of our garnets and clinopyroxenes analyzed with EELS and flank method. Fe$^{3+}/\Sigma$Fe contents from both analytical procedures are comparable within 2σ. The maximum uncertainty on the fO$_2$ is ± 0.5 log units.
Figure 6 Four different geobarometers by Collerson et al. (2010), Wijbrans et al. (2016), Beyer and Frost (2017) and Tao et al. (2018) applied to our experimental dataset. All calculated pressures are comparable within errors when using the EELS results instead of the flank results.
Table 1 Primitive mantle composition and experimental starting composition analogues.

<table>
<thead>
<tr>
<th>Oxide (wt%)</th>
<th>Palme and O’Neill, 2003</th>
<th>Rohrbach et al., 2011</th>
<th>Irifune, 1987</th>
<th>This study</th>
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<tr>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>TiO₂</td>
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<td>0.29</td>
<td>0.58</td>
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</table>
The composition by Palme and O’Neill (2003) correlates with the major element composition of the PM (Mg# of 0.89). Rohrbach et al. (2011) depleted the composition by Palme and O’Neill (1993) by 30% in its normative olivine content and raised the molar Mg# to around 0.5. Irifune (1987) used a rather basaltic starting composition, that was created by subtraction of an olivine from a pyrolitic composition. The Mg# used was similar to the one proposed for the PM (Palme and O’Neill, 2003). The starting composition from this study was based on the PM composition by Palme and O’Neill (1993), however, 10% of normative olivine were subtracted. All three starting compositions are calculated starting compositions which is why no errors are stated here.

<table>
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Table 2 Experimental conditions

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<th>Temperature (°C)/run duration</th>
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<td>MaLm9</td>
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<td>1550/24 h</td>
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<td>MaLm11</td>
<td>SC</td>
<td>Au$<em>{80}$Pd$</em>{20}$(inner capsule) Fe (outer capsule)</td>
<td>1450/24 h</td>
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<td>MaLm12</td>
<td>SC</td>
<td>Au$<em>{80}$Pd$</em>{20}$</td>
<td>1450/24 h</td>
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SC corresponds to the starting composition of this study and includes the starting composition (Table 1) plus 5 wt% C$_{18}$H$_{36}$O$_{2}$ and 3 wt% Ir. All experiments were performed at 10 GPa.
Table 3 Average phase compositions, Fe\textsuperscript{3+}/ΣFe and oxygen fugacities

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</tr>
<tr>
<td>Fe$^{3+}$/ΣFe (c.b.)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#Mg</td>
<td>0.91</td>
<td>0.88</td>
<td>0.92</td>
<td>0.84</td>
<td>0.91</td>
<td>0.90</td>
<td>0.92</td>
<td>0.84</td>
<td>0.96</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>Δlog fO$_2$ [FMQ]</td>
<td>-0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Δlog fO$_2$ [EMOD]</td>
<td>+1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Δlog fO$_2$ [IW]</td>
<td>+4.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Average major element analyses in wt%, Mg# and fO$_2$ of all experiments including olivine (Ol), clinopyroxene (Cpx), orthopyroxene (Opx) and majoritic garnets (Grt). Cation Fe$^{3+}$/ΣFe (c.b.) values refer to ferric iron contents derived from charge balance calculations (see also Supplementary material, Table S4). Uncertainties of the EPMA measurements are 1σ, errors of the Fe$^{3+}$/ΣFe values are 2σ. Total FeO$^*$ of garnet was divided into FeO and Fe$_2$O$_3$ according to Fe$^{3+}$/ΣFe measured by the flank method, other values are reported in Supplementary material, Table 4. n.d. = not determined.
Figure 2

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Figure 3

Number of Si cations per 12 O atoms

- This work
- Kiseeva et al., 2018
- Wijbrans et al., 2016
- Rohrbach et al., 2007
- Woodland and Koch, 2003
- Irifune, 1987

Typical mean 1 s.d.

Pressure (GPa)
Figure 4

The figure shows a plot of $\text{Fe}^{3+}/\Sigma\text{Fe}$ versus the number of Si cations per 12 O atoms. The data points are labeled with different symbols representing various works:

- Diamond: This work (EELS)
- Square: This work (Flank)
- Circle: Kiseeva et al., 2018
- Triangle: Rohrbach et al., 2007
- Rectangle: Woodland and Koch, 2003

The axes are labeled as follows:

- Y-axis: $\text{Fe}^{3+}/\Sigma\text{Fe}$
- X-axis: Number of Si cations per 12 O atoms

The figure also includes annotations for increasing $f_0$ and increasing $P$, with typical mean and 1 s.d.

Additional text:

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Figure 5

\[ \Delta \log f_O^2 \] vs \( \text{Fe}^{3+}/\Sigma \text{Fe} \)

- **MaLm12**
- **MaLm9**
- **MaLm1**
- **MaLm6**
- **MaLm11**

**Markers:**
- **Grt (EELS)**
- **Grt (Flank)**
- **Cpx (EELS)**

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Figure 6

\[ \Delta P \]

- **Tao et al., 2018 (Flank)**
- **Beyer and Frost, 2017 (Flank)**
- **Wijbrans et al., 2016 (Flank)**
- **Collerson et al., 2010 (Flank)**
- **Tao et al., 2018 (EELS)**
- **Beyer and Frost, 2017 (EELS)**
- **Wijbrans et al., 2016 (EELS)**

MaLm1, MaLm2, MaLm6, MaLm9, MaLm11, MaLm12