

1 **Revision 2**

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

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Abstract

22 The oxidation state of iron in upper mantle minerals is widely used to constrain the Earth mantle's
23 oxidation state. Previous studies showed high levels of ferric iron in high-pressure majoritic garnets
24 and pyroxenes despite reducing conditions. To disentangle the effects of pressure and increasing
25 oxygen fugacity on the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of garnet and clinopyroxene, we performed high-pressure
26 experiments at pressures of 10 GPa in a 1000-ton Walker-type multi-anvil apparatus at the
27 University of Münster. We synthesized majoritic garnets and clinopyroxenes with a total iron
28 content close to natural mantle values at different oxygen fugacities, ranging from IW+4.7 to metal
29 saturation at IW+0.9. We analyzed the iron oxidation state in garnets with the electron microprobe
30 "flank method". Furthermore, we investigated the oxidation state of iron in garnets and
31 clinopyroxenes with transmission electron microscopy (TEM) electron energy loss spectroscopy
32 (EELS). Although the flank method measurements are systematically lower than the EELS
33 measurements, $\text{Fe}^{3+}/\Sigma\text{Fe}$ obtained with both methods agree well within 2σ errors. The "flank
34 method" has the advantage of being much faster and more easily to set-up, whereas TEM-EELS
35 has a much higher spatial resolution can be applied to a variety of non-cubic minerals such as
36 orthopyroxenes and clinopyroxenes. We used our experimental results to compare two
37 geobarometers that contain a term for ferric iron in garnet (Beyer and Frost 2017, Tao et al. 2018)
38 with two geobarometers that do not account for ferric iron (Collerson et al. 2010, Wijbrans et al.
39 2016). We found that garnets with low total Fe and Fe^{3+} (like many natural garnets) pressures can
40 be calculated without including the ferric iron content.

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Keywords

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

44 **Introduction**

45 The oxidation state of the Earth's upper mantle is still a matter of debate, mainly because rock
46 samples from depths > 250 km are virtually absent except for rare ultradeep xenoliths (Haggerty
47 and Sautter 1990; Sautter et al. 1991) and mineral inclusions in diamond (e.g. Pearson et al. 2014).
48 However, the oxidation state of the Earth's mantle exerts a significant influence on the stability of
49 C-O-H-volatiles and therefore has important implications for the phase relations and melting
50 behavior (Kushiro et al. 1968; Taylor and Green 1988; Ballhaus and Frost 1994; Gaetani and Grove
51 1998; Dasgupta and Hirschmann 2006; Foley 2011; Tumiati et al. 2012; Stagno et al. 2013),
52 hydrogen incorporation (e.g. Kohlstedt et al. 1996) and the rheology of the mantle (Mackwell et
53 al. 1985,) as well as for diamond/graphite vs. carbonate stability (Dasgupta and Hirschmann 2010;
54 Stagno and Frost 2010; Rohrbach and Schmidt 2011; Stagno et al. 2013; Luth and Stachel 2014;
55 Yaxley et al. 2017). The oxidation state of the upper mantle can be determined by the $\text{Fe}^{3+}/\Sigma\text{Fe}$
56 content of mantle minerals since iron is a major element in Earth's mantle and is incorporated into
57 every mantle mineral (e.g. O'Neill et al. 1993b; Luth and Canil 1993; Canil and O'Neill 1996).
58 The oxygen fugacity ($f\text{O}_2$) of the uppermost mantle predominantly lies between FMQ+2 and FMQ-
59 2 as indicated by xenoliths and samples of basaltic melts and peridotite massifs (Luth et al. 1990;
60 Ballhaus 1993; Frost and McCammon 2008). With increasing depth, the upper mantle becomes
61 more reduced, approaching $\Delta\log f\text{O}_2$ values of FMQ-4 at 220 km depth (Woodland and Koch 2003;
62 McCammon and Kopylova 2004; Frost and McCammon 2008; Stagno and Frost 2010; Yaxley et
63 al. 2012). In the upper mantle the $f\text{O}_2$ correlates with the ferric iron content of minerals, so that
64 spinels in harzburgite and lherzolite at pressures up to 2.7 GPa show a decrease of ferric iron with

65 decreasing fO_2 tending towards zero when metallic iron is a stable phase (Ballhaus et al. 1991).
66 This linear relationship between fO_2 and $Fe^{3+}/\Sigma Fe$ is not observed in experimental phase
67 assemblages at pressures corresponding to the lowermost upper mantle, the transition zone or the
68 lower mantle, where majoritic garnet and bridgmanite with high ferric iron contents coexist with
69 metallic iron (O'Neill et al. 1993a; McCammon 1997; McCammon and Ross 2003; Frost et al.
70 2004; Rohrbach et al. 2007; 2011). In a typical upper mantle assemblage, ferric iron is concentrated
71 in modally minor phases like clinopyroxene and spinel since olivine incorporates negligible ferric
72 iron and orthopyroxene incorporates only between 0.2 and 0.6 wt% Fe_2O_3 at low $Fe^{3+}/\Sigma Fe$ between
73 0.03 and 0.10 (O'Neill et al. 1993b; Canil and O'Neill 1996; Woodland and Koch 2003; Yaxley et
74 al. 2012). Above 6 GPa, pyroxene components become more soluble in garnet and substitute
75 continuously into the garnet structure (Akaogi and Akimoto 1979; Irifune 1989; Rohrbach et al.
76 2011; Wijbrans et al. 2016; Beyer and Frost 2017; Kiseeva et al. 2018). Assuming that the transition
77 zone has the same bulk chemical composition as the upper mantle, including the $Fe^{3+}/\Sigma Fe$ content,
78 the fO_2 of the transition zone consequently must depend on how well its minerals can incorporate
79 ferric iron. Since most transition zone minerals can incorporate some ferric iron (see compilation
80 in Frost and McCammon 2008), the average amount of around 2000 $\mu g/g$ Fe_2O_3 (O'Neill et al.
81 1993a), will be partitioned into a wider range of minerals within the transition zone than in the
82 upper mantle. This leads to a dilution effect and a decreased ferric iron activity, which results in
83 decreased fO_2 (O'Neill et al. 1993a; Ballhaus 1995). The presence of high amounts of ferric iron in
84 transition zone majoritic garnet or in lower mantle bridgmanite in spite of low fO_2 can either be
85 explained by a reduction of oxidized volatiles as CO_2 and H_2O to CH_4 or more likely, by
86 disproportionation of $3Fe^{2+}O = Fe_2^{3+}O_3 + Fe^0$ (O'Neill et al. 1993a; Frost et al. 2004; Rohrbach et
87 al. 2007).

88 In order to track redox conditions of the upper mantle and the transition zone, ferric iron contents
89 of garnets have been used extensively. Garnet has several advantages, because it is stable over a
90 wide range of pressures and temperatures from the upper mantle into the transition zone (e.g.,
91 Klemme and O'Neill 2000; Klemme and Fumagalli, 2015), and is consequently one of the most
92 common rock-forming minerals of the Earth's interior (Ringwood 1967; Ringwood and Major
93 1971). Therefore, the incorporation of ferric iron in pyroxene-garnet solid solutions at high
94 pressures has been repeatedly studied (McCammon and Ross 2003; Rohrbach et al. 2007; 2011;
95 Beyer and Frost, 2017). All former studies agree about the onset of majorite stability in garnet solid
96 solutions at around 6 GPa. Pyroxenes dissolve increasingly into the garnet structure to form
97 majoritic garnet with increasing depth and consequently the majorite component can be used for
98 geobarometry (Collerson et al. 2010; Wijbrans et al. 2016; Beyer and Frost 2017; Tao et al. 2018).
99 Compared to regular garnets, where the dodecahedral site is occupied by divalent cations and the
100 octahedral site by trivalent cations, majorites incorporate Si^{4+} and Mg^{2+} on the octahedral site.
101 In this study, we performed high-pressure multi-anvil experiments at different oxygen fugacities
102 with a total iron content of 8 wt% reflecting the iron content of the mantle (Palme and O'Neill
103 2003). We quantified the ferric iron contents of our garnets and clinopyroxenes and used them to
104 review several majorite geobarometers (Collerson et al. 2010; Wijbrans et al. 2016; Beyer and Frost
105 2017; Tao et al. 2018). The quantification of ferric iron was performed with two different methods
106 using the same samples: transmission electron microscopy - electron energy loss spectroscopy
107 (TEM-EELS; van Aken et al. 1998; van Aken and Liebscher 2002) and the electron microprobe
108 (EPMA) flank method (Höfer 2002; Höfer and Brey 2007).

109 **Experimental and analytical methods**

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

120 In order to constrain the relationship between the $f\text{O}_2$ and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ for clinopyroxene and
121 garnet, we synthesized these phases at different redox conditions between IW+0.9 and IW+4.7.
122 The most reducing experiment at IW+0.9 (MaLm11) was performed by using a double capsule
123 technique. The starting material was contained in a welded shut noble metal ($\text{Au}_{80}\text{Pd}_{20}$) inner
124 capsule, which was surrounded by an outer iron metal capsule. The hydrogen source between the
125 two capsules was brucite. In experiment MaLm6 we added 1 wt% Si metal to the starting material.
126 This triggers a reaction of silicon metal and iron(II)oxide to metallic iron and silicon dioxide and
127 reduces the intrinsic $f\text{O}_2$ of the sample (Tsuno et al. 2013). We fixed the $f\text{O}_2$ of the samples MaLm1
128 and MaLm2 to values close to the enstatite-magnesite-olivine-diamond (EMOD) buffer by adding
129 1 wt% graphite to our starting material (Eggler et al. 1979). Furthermore, 5 wt% stearic acid was
130 added to all samples to produce a C-O-H fluid component (Sokol et al. 2010) at experimental P
131 and T which lowers the intrinsic $f\text{O}_2$ of the composition and facilitates reaching equilibrium in
132 subsolidus runs. The most oxidized experiments, where $f\text{O}_2$ was not buffered (MaLm9 and
133 MaLm12), were performed in welded $\text{Au}_{80}\text{Pd}_{20}$ capsules. The experiments were performed

134 between 1450 to 1550 °C at 10 GPa in a 1000-ton Walker-type multi-anvil apparatus at the
135 University of Münster. All run conditions are presented in Table 2 and in the Supplementary
136 material (Table S1). The experiments were performed using a 14/8 assembly (14 mm octahedron
137 edge length, 8 mm truncated edge length) employing Cr-doped MgO octahedron and a zirconia
138 insulating sleeve around a stepped LaCrO₃ furnace. For details regarding the pressure calibration
139 of the press see Wijbrans et al. (2016). Run temperatures were measured with type C-
140 thermocouples and controlled within $\pm 5^\circ\text{C}$ by an Eurotherm controller. Experiments were
141 quenched by turning off the power supply.

142 All samples were mounted in an acrylic resin and polished down to the center of the capsule.
143 Backscattered electron images were performed with a JEOL JSM-6510LA scanning electron
144 microscope at the University of Münster. Major and minor element analyses were performed with
145 a JEOL JXA-8530F electron microprobe at the University of Münster using natural minerals as
146 standards. The following standards were used for quantification: hypersthene (Si), disthene (Al),
147 fayalite (Fe), olivine (Mg, Ni), diopside (Ca), jadeite (Na). For garnet analysis we used natural
148 pyrope as standard for Si, Al and Mg. The EPMA acceleration voltage was 15 kV and the beam
149 current was 15 nA. The spot sizes were 1-5 μm depending on the grain size. Counting times were
150 20 s on the peak and 10 s on the background for metals and garnets, for other silicates 15 s on the
151 peak and 5 s on the background.

152 The EPMA flank method measurements of the garnets were performed with the JEOL JXA
153 8900RL Superprobe at Goethe University in Frankfurt. The measurements were carried out at an
154 acceleration voltage of 15 kV, and a beam current of 120 nA and a beam diameter of 1 μm . Each
155 $\text{Fe}^{3+}/\Sigma\text{Fe}$ determination with simultaneous major element analysis resulted from the average of 25
156 independent measurements on different grains to achieve an uncertainty of below 0.02 in $\text{Fe}^{3+}/\Sigma\text{Fe}$

157 (1 σ). Counting times were 20 to 30 s on the peak and background for all main elements besides
158 iron (60 s), and 140 s for each FeL α and FeL β measurement. In general, the flank method combines
159 measuring the shift of the peak position and the change in intensity ratios of FeL α and FeL β , which
160 systematically varies with the Fe³⁺/ Σ Fe content, resulting in the high sensitivity and high precision
161 of this method (Höfer and Brey 2007). The garnet standards used to calibrate and to quantify
162 Fe³⁺/ Σ Fe in our samples contain between 6 and 21 wt% total iron: oxyAlm: 20.21 wt% Σ Fe, 0.03
163 wt% Fe³⁺/ Σ Fe (Höfer and Brey 2007; Vasilyev 2016); UA5: 6.49 wt% Σ Fe, 0.11 Fe³⁺/ Σ Fe
164 (Vasilyev 2016; Li et al. 2018); UA17: 6.25 wt% Σ Fe, 0.06 Fe³⁺/ Σ Fe (Vasilyev 2016); Damknonle:
165 15.18 wt% Σ Fe, 0.04 Fe³⁺/ Σ Fe (Höfer and Brey 2007; Vasilyev 2016). Fe³⁺/ Σ Fe of all garnet
166 standards were measured by Mössbauer spectroscopy prior to the flank measurements (McGuire
167 et al. 1992; Rankenburg et al. 2002; Höfer and Brey 2007). The empirically determined 1 σ error is
168 \pm 0.02 for these samples (Höfer and Brey 2007). The flank method was already successfully used
169 to quantify Fe³⁺/ Σ Fe in garnets (Malaspina et al. 2009; 2010; Höfer and Brey 2007; Tao et al.
170 2018), sodic amphiboles (Enders et al. 2002) and wustites (e.g. Höfer et al. 2000). Furthermore,
171 several groups are currently working on flank-method calibrations for other minerals and glasses
172 (Malaspina et al. 2010; Zhang et al. 2018).

173 For TEM analysis, the former EMPA samples were prepared by ultramicrotomy, in order to avoid
174 a change in their chemical composition, and put onto carbon-film copper TEM-grids. Preparation
175 resulted in slices of 70 nm thickness, which is specifically important for EELS analysis to avoid
176 multiple scattering effects. Although the mechanical stress induced by the diamond knife resulted
177 in severe shattering of the samples, no chemical disturbance of analyzed minerals can be expected,
178 perhaps in contrast to ion beam techniques. EELS measurements were performed on a Zeiss Libra
179 200FE TEM at the University of Münster equipped with a Schottky-type field emission gun (200

180 kV) and a Köhler illumination system providing strongly parallel illumination conditions at all
181 brightness indices. Samples were initially documented by conventional Brightfield (BF) and
182 Scanning TEM- High Angle Annular Darkfield (HAADF, contrast proportional to average Z)
183 imaging. Energy filtering was performed through an in-column Omega filter in TEM mode using
184 a 200 μm filter entrance aperture giving an effective aperture of about 100 nm on the sample
185 surface. The energy spread of the field emitter is 0.7 eV as determined from the full width at half
186 maximum of the zero loss peak (ZLP). Convergence angle was about 0.1 milliradian (quasi-parallel
187 Köhler illumination). The following routine was used to record EELS spectra: First, the ZLP was
188 recorded with a low brightness index to avoid damage of the slow-scan CCD camera Gatan
189 UltraScan 4000 (5 frames at 0.1 or 0.2 s integration time). Afterwards, the $\text{Fe}L_{2,3}$ edge was recorded
190 with a much higher brightness index and longer exposure times (10 frames at 5 s integration time).
191 We analyzed up to 9 grains of garnet and clinopyroxene per sample, measurements with more than
192 2σ variation of the mean were considered as outliers and thus excluded from the calculation of the
193 mean. Due to the required total iron content of at least several wt% it was only possible to measure
194 three samples: the rather oxidized samples MaLm1 and MaLm9 and the metal saturated sample
195 MaLm11. All EELS measurements were examined with the MATLAB® script EELSA (Prescher
196 et al. 2014). EELSA uses the two basic procedures described by van Aken and Liebscher (2002).
197 The first approach applies two 2 eV wide integration windows to the $\text{Fe}L_3$ maximum (Fe^{3+}) and the
198 $\text{Fe}L_2$ maximum (Fe^{2+}) of the sample. By dividing the ferrous iron content at L_2 by the ferric iron
199 content at L_3 the $\text{Fe}^{3+}/\Sigma\text{Fe}$ content of the sample can be determined from the spectrum. The second
200 approach employs several Gaussian functions describing the spectral features and one Arctan
201 function to fit the remainder of the EELS spectrum (van Aken and Liebscher 2002). Both
202 approaches make use of the significant shapes of the $\text{Fe}L_{2,3}$ edges that depend on the valence state
203 of iron. Minerals with simply divalent iron content show a sharp peak of their L_3 edge at 707.8 eV

204 and a weaker peak at 710.5 eV. Samples with trivalent iron only show a sharp peak of their L_3 edge
205 at 709.5 eV with a weaker pre-peak at 708.0 eV (van Aken and Liebscher 2002). The difference
206 between L_3 and L_2 edge is a result of spin-orbit splitting (Colliex et al. 1991; Garvie et al. 1994;
207 van Aken et al. 1998). The absolute 1σ error of the quantification technique is ± 0.02 (van Aken
208 and Liebscher 2002).

209 **Results**

210 **Experimental results and phase compositions**

211 Backscattered electron (BSE) images of typical run products from this study are shown in Figure
212 1. Olivine is the most abundant phase in our run products with modal amounts between 37 and 45
213 vol%. The second most abundant phase is majoritic garnet (22-39 vol%). Clinopyroxenes are
214 present between 19 and 33 vol%, whereas orthopyroxene is only a minor phase (2 to 15 vol%). The
215 modal proportions were calculated via mass balancing and agree well with the phase proportions
216 observed in the scanning electron microscope (SEM) images. Most run products contain olivine,
217 clinopyroxene, majoritic garnet and orthopyroxene, i.e. a regular mantle mineral assemblage. The
218 mineral assemblages in MaLm2 and MaLm12 differ from the other samples such that MaLm12
219 contains little orthopyroxene and MaLm2 contains orthopyroxene, garnet, magnesite, diamond and
220 carbonate/carbonatite melt but no olivine (Fig. 1a,b). The sample MaLm1 also contains small
221 magnesite grains, but no related melt component. The appearance of carbonatite melt is most likely
222 the result of adding stearic acid to the charges which produces minor amounts of CO_2 when it
223 decomposes at high T in a starting material with high intrinsic $f\text{O}_2$. CO_2 could also result from
224 incomplete decarbonation of the starting material, which would be rather beneficial to buffer $f\text{O}_2$
225 close to EMOD. The Mg# of all minerals are around 0.90 (Table 3). The Si-metal modified sample

226 MaLm6 contains olivine, orthopyroxene, clinopyroxene and garnet (Fig. 1c). The metal-saturated
227 sample MaLm11 still contains the Ir-Fe alloy with high Fe content (Fig. 1d,e). Sample MaLm12
228 contains little orthopyroxene, but olivine, clinopyroxene and majoritic garnet (Fig. 1f). The phases
229 throughout the charge are homogeneous in terms of chemical compositions and also when
230 comparing different run products (Table 3 and Supplementary material Tables S2 and S3).

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

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

239 Orthopyroxenes generally have a higher Mg# (0.90-0.96) than the corresponding clinopyroxenes
240 (0.88-0.97). All clinopyroxenes and orthopyroxene compositions are close to $\text{Di}_{86}\text{Ja}_{11}\text{Ae}_3$ and
241 $\text{En}_{92}\text{Fs}_6\text{Wo}_2$.

242 **Oxygen fugacity**

243 Oxygen fugacities of all samples were monitored by adding 3 wt% iridium to all starting
244 compositions as a redox sensor (Woodland and O'Neill 1997; Stagno and Frost 2010; Rohrbach
245 and Schmidt 2011). During an experiment iron dissolves into the iridium metal which can be
246 analyzed by EPMA (Supplementary material, Table S1). Oxygen fugacities were calculated using
247 the method described in Rohrbach and Schmidt (2011). Uncertainties on the $f\text{O}_2$ calculation are

248 difficult to quantify but are perhaps within 0.3 to 0.5 log units (see discussion in Stagno and Frost
249 2010).

250 **Comparison of the flank method and EELS**

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

258 The results of the two analytical methods overlap within 2σ and show a similar correlation between
259 fO_2 and $Fe^{3+}/\Sigma Fe$ in our experimental charges. However, EELS results of our garnets seem to
260 indicate slightly higher ferric iron contents compared to flank method results, a trend that is also
261 evident in the dataset of Malaspina et al. (2009). One possible explanation for this slight
262 discrepancy could be that the higher number of EPMA measurements per phase more easily
263 compensates for statistical spikes than the comparably lower number of EELS measurements. A
264 possible zonation of our garnets in a μm -range would have been detected during flank method
265 measurements and this would have led to much higher errors than ± 0.04 . If any zonation existed
266 at smaller (i.e., nm) scales, it may not have been detected and may have led to average values,
267 whereas EELS analyses would have been able to distinguish these different garnet regions. Another
268 explanation for the higher EELS results might be due to a slight oxidation of our TEM samples
269 during preparation at least on the surface of the lamellae. Nevertheless, ultramicrotomy is
270 considered to prevent a chemical alteration of samples, which was the reason to choose this

271 preparation technique. Furthermore, the low 1σ error of 0.02 for the flank method is based on a
272 calibration with garnets containing 6 to 21 wt% total iron. Some of the garnets in the present study
273 have even lower iron contents so that the error may be larger in some samples. Moreover, our EELS
274 results agree well with the corresponding values by Rohrbach et al. (2007).

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

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

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

283 The electron microprobe flank method yields slightly lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents than corresponding
284 EELS measurements (Fig. 2, Table 3) but agree within 2σ uncertainty ($\text{Fe}^{3+}/\Sigma\text{Fe}$ flank: 0.07(6);
285 $\text{Fe}^{3+}/\Sigma\text{Fe}$ EELS: 0.11(4), and within 2σ of 0.13(2) determined by Rohrbach et al. (2011). These
286 values represent the minimum $\text{Fe}^{3+}/\Sigma\text{Fe}$ at metal saturated conditions at 10 GPa. Our results are
287 within the general trend regarding the extent of majorite substitution with increasing pressures as
288 illustrated in Figure 3.

289 The two effects that are responsible for increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet are increasing pressure and
290 increasing $f\text{O}_2$ (Fig. 4). Experimental metal saturated samples (this study and Rohrbach et al., 2007;
291 IW-0.5 to IW-1.3) define the increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ at minimum $f\text{O}_2$ due to disproportionation of
292 FeO, majoritic garnets from slightly more oxidized environments (this study; Woodland and Koch

293 2003, IW+1.4 to IW+2.9 and Kiseeva et al. 2018, IW-0.3 to IW+3) are systematically shifted to
294 the left of the trend (Fig. 4). Natural non-majoritic garnets span a similar range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ than
295 the experimental samples.

296 The clinopyroxenes in our samples tend to have a higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ content than the majorites, which
297 is in line with results from natural samples by Lazarov et al. (2009) but different to earlier studies
298 where clinopyroxenes had higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ than the coexisting garnet/majorite (Canil and O'Neill
299 1996; Rohrbach et al., 2007). One possible explanation might be that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in
300 clinopyroxenes is more dependent on bulk composition and Mg# than in garnets. Since the
301 correlation of $f\text{O}_2$ and clinopyroxene has not been systematically studied so far, we cannot draw
302 definite conclusions.

303 Discussion

304 Correlation of oxygen fugacity with analyzed $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents of garnets and 305 clinopyroxenes

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

308 High oxygen fugacities therefore correlate with high ferric iron contents and decrease at more
309 reducing conditions until metal saturation is reached. This is evidence for the fact that our
310 experimental approach as well as ferric iron measurements were successful. Our most reduced and
311 metal saturated sample MaLm11 shows $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 0.07(6) and 0.11(4) measured by the
312 flank method and EELS (2σ). Our clinopyroxenes measured with EELS show the same positive
313 correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ at slightly higher ferric iron contents. In order to explain the
314 ferric iron content despite metal saturation of MaLm11, disproportionation must be the dominant

315 process, because no Fe_2O_3 was added and no carbonated fluid or melt was involved, perhaps
316 contrary to the natural samples examined by Kiseeva et al. (2018). We expect to see a correlation
317 between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ natural samples as well, but only if a group of garnet or pyroxene
318 equilibrated at roughly the same P, T and chemical environment. To test this hypothesis, we divided
319 the Ekati garnet dataset of Yaxley et al. (2017) into three subgroups of similar equilibration P and
320 T and found a distinct positive correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ for each subgroup, which is
321 not obvious when plotting the entire dataset (Supplementary Fig. S1). This relationship, however,
322 remains to be tested at other locations.

323 **Application of determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents to majoritic geobarometers**

324 We performed geobarometric calculations with four different geobarometers from Collerson et al.
325 (2010), Wijbrans et al. (2016), Beyer and Frost (2017) and Tao et al. (2018). Since all four
326 geobarometric calculations take the majorite substitution into account, every single one can be used
327 to calculate pressures in natural high-pressure garnets or run pressures of high P-T-experiments.
328 Two of the geobarometers employ a distinct term for ferric iron (Beyer and Frost 2017; Tao et al.
329 2018).

330 The geobarometer by Collerson et al. (2010) describes the extent of majoritic substitution as excess
331 of Si and Ti on the octahedral site of garnet and the respective depletion in Al^{3+} and Cr^{3+} . This
332 geobarometer is also dependent on the Na content but does not include the ferric iron content. The
333 geobarometer by Tao et al. (2018) is based on the geobarometer by Collerson et al. (2010), but only
334 accounts for excess Si on the octahedral site of majorite and for the respective depletion of Al^{3+} ,
335 Cr^{3+} and Fe^{3+} . The geobarometer by Beyer and Frost (2017) is the most complex model considering
336 the normal majorite substitution ($\text{Al}^{3+} = \text{Si}^{4+} + \text{Mg}^{2+}$) the Na-majorite substitution ($\text{Mg}^{2+} + \text{Al}^{3+} =$
337 $\text{Si}^{4+} + \text{Na}^+$) and accounts for Fe^{3+} , Cr^{3+} , Ti^{4+} and Ca^{2+} contents in majorite. The pressure calculated

338 by the geobarometer of Wijbrans et al. (2016) for peridotitic compositions solely depends on excess
339 Si^{4+} on the octahedral site and on the Cr^{3+} content of the majorite.

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

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

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

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

360

Implications

361 Our results confirm that two factors determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in majoritic garnets and high pressure
362 pyroxenes. Metal saturated low $f\text{O}_2$ experimental garnets and pyroxenes set the minimum $\text{Fe}^{3+}/\Sigma\text{Fe}$
363 at a given pressure and higher $f\text{O}_2$ raises the $\text{Fe}^{3+}/\Sigma\text{Fe}$ additionally. We furthermore conclude that
364 both TEM-EELS and the EPMA flank method for the quantitative measurement of ferric iron in
365 silicate minerals yield comparable results within 2σ . Measurements with the "flank method" are
366 much faster and set-up of the method is relatively straight forward when a set of standards with
367 independently measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios is available. However, EMPA measurements cannot
368 resolve possible nanoscale heterogeneities of measured samples, and the flank method can only be
369 used for garnets, amphiboles and glasses. TEM-EELS on the other hand has a much higher spatial
370 resolution on a nm-scale and can be applied to a variety of non-cubic minerals such as
371 orthopyroxene and clinopyroxene. Nevertheless, TEM measurements and sample preparations are
372 far more time-consuming and allow to measure only a limited numbers of grains. We would like
373 to emphasize that a correct quantitative measurement of ferric iron in garnets is important not only
374 for its accuracy but also for some geobarometric applications and to model the deeper upper mantle
375 and below.

376

Acknowledgments

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

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585 **Figure captions**

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

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

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

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

603 Figure 5 Positive correlation between the $f\text{O}_2$ and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents of our garnets and
604 clinopyroxenes analyzed with EELS and flank method. $\text{Fe}^{3+}/\Sigma\text{Fe}$ contents from both analytical
605 procedures are comparable within 2σ . The maximum uncertainty on the $f\text{O}_2$ is ± 0.5 log units.

606 Figure 6 Four different geobarometers by Collerson et al. (2010), Wijbrans et al. (2016), Beyer and
607 Frost (2017) and Tao et al. (2018) applied to our experimental dataset. All calculated pressures are
608 comparable within errors when using the EELS results instead of the flank results.

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Tables

624 Table 1 Primitive mantle composition and experimental starting composition analogues.

Oxide (wt%)	Palme and O'Neill, 2003	Rohrbach et al., 2011	Irifune, 1987	This study
SiO ₂	45.40	47.50	50.36	46.54
MgO	36.77	14.70	22.80	35.24
FeO	8.10	26.20	3.46	8.20
Al ₂ O ₃	4.49	6.45	11.38	5.10
CaO	3.65	3.80	9.24	4.14
Na ₂ O	0.50	0.50	1.03	0.57
NiO	0.19	-	-	0.21
TiO ₂	-	0.29	0.58	-

Cr ₂ O ₃	-	0.56	1.16	-
Mg#	0.89	0.36	0.88	0.81

625 *The composition by Palme and O'Neill (2003) correlates with the major element composition of*
626 *the PM (Mg# of 0.89). Rohrbach et al. (2011) depleted the composition by Palme and O'Neill*
627 *(1993) by 30% in its normative olivine content and raised the molar Mg# to around 0.5. Irifune*
628 *(1987) used a rather basaltic starting composition, that was created by subtraction of an olivine*
629 *from a pyrolitic composition. The Mg# used was similar to the one proposed for the PM (Palme*
630 *and O'Neill, 2003). The starting composition from this study was based on the PM composition*
631 *by Palme and O'Neill (1993), however, 10% of normative olivine were subtracted. All three*
632 *starting compositions are calculated starting compositions which is why no errors are stated*
633 *here.*

Table 2 Experimental conditions

Experiment	Composition	Capsule material	Temperature (°C)/run duration
MaLm1	SC, 1wt% C	Au ₈₀ Pd ₂₀	1500/24 h
MaLm2	SC, 1wt% C	Au ₈₀ Pd ₂₀	1550/24 h
MaLm6	SC, 1wt% Si-metal	Au ₈₀ Pd ₂₀	1450/24 h
MaLm9	SC	Au ₈₀ Pd ₂₀	1550/24 h
MaLm11	SC	Au ₈₀ Pd ₂₀ (inner capsule) Fe (outer capsule)	1450/24 h
MaLm12	SC	Au ₈₀ Pd ₂₀	1450/24 h

SC corresponds to the starting composition of this study and includes the starting composition (Table 1) plus 5 wt% C₁₈H₃₆O₂ and 3 wt% Ir. All experiments were performed at 10 GPa.

Table 3 Average phase compositions, Fe³⁺/ΣFe and oxygen fugacities

Exp	MaLm1				MaLm2				MaLm6			
	Ol	Cpx	Opx	Grt	Ol	Cpx	Opx	Grt	Ol	Cpx	Opx	Grt
n	17	22	2	14			23	22	9	25	16	25
SiO ₂	40.50(47)	56.34(37)	57.75(24)	42.91(46)	-	-	58.64(38)	45.01(30)	41.87(17)	56.77(36)	59.36(27)	44.76(24)
Al ₂ O ₃	0.14(17)	1.73(36)	0.34(11)	21.01(82)	-	-	0.75(14)	20.36(38)	0.03(1)	1.63(28)	0.30(2)	20.31(19)
Fe ₂ O ₃	n.d.	n.d.	n.d.	1.41	-	-	n.d.	0.71	n.d.	n.d.	n.d.	0.77
FeO	n.d.	n.d.	n.d.	6.88	-	-	n.d.	3.70	n.d.	n.d.	n.d.	4.36
FeO*	9.14(33)	5.69(35)	7.08(21)	8.29(36)	-	-	3.08(24)	4.41(35)	4.66(52)	2.51(41)	2.90(55)	5.13(55)
MgO	48.65(68)	23.89(64)	33.96(71)	22.56(53)	-	-	36.84(41)	25.71(35)	53.82(56)	21.06(41)	37.68(44)	24.23(37)
CaO	0.13(7)	10.98(96)	0.43(4)	3.82(19)	-	-	1.42(15)	2.98(18)	0.07(2)	17.53(62)	0.55(8)	4.16(15)
Na ₂ O	0.06(2)	1.30(11)	0.08(2)	0.14(2)	-	-	0.21(5)	0.11(1)	0.02(2)	1.12(7)	0.09(2)	0.13(1)
NiO	1.82(36)	0.44(10)	0.83(17)	0.17(5)	-	-	0.13(3)	0.03(1)	0.07(2)	0.02(2)	0.03(3)	0.01(1)
Total	100.44	100.37	100.47	98.83	-	-	101.07	98.61	100.54	100.64	100.91	98.73
Fe ³⁺ /ΣFe (flank)	-	-	-	0.17(4)	-	-	-	0.16(4)	-	-	-	0.15(4)
n	-	-	-	14	-	-	-	22	-	-	-	25
Fe ³⁺ /ΣFe (EELS)	-	0.29(12)	-	0.27(6)	-	-	-	n.d.	-	-	-	n.d.
n	-	9	-	7	-	-	-	-	-	-	-	-
Fe ³⁺ /ΣFe (c.b.)	-	-	-	0.28	-	-	-	0.18	-	-	-	0.14
#Mg	0.90	0.88	0.90	0.83	-	-	0.96	0.91	0.95	0.94	0.96	0.89
Δlog fO ₂ [FMQ]	-1.7				-				-1.8			
Δlog fO ₂ [EMOD]	+0.2				-				+0.1			
Δlog fO ₂ [IW]	+3.4				-				+3.3			

Exp	MaLm9				MaLm11				MaLm12			
	Ol	Cpx	Opx	Grt	Ol	Cpx	Opx	Grt	Ol	Cpx	Opx	Grt
n	24	23	3	19	12	2	5	7	20	22	1	21
SiO ₂	41.06(22)	57.02(32)	58.65(36)	44.38(66)	41.25(49)	57.34(1)	58.74(42)	43.58(55)	42.19(18)	56.91(23)	59.68	44.41(43)
Al ₂ O ₃	0.05(2)	1.37(7)	0.42(12)	18.73 (1.28)	0.08(5)	1.65(11)	0.34(5)	22.52(94)	0.05(2)	1.70(57)	0.26	20.82(88)
Fe ₂ O ₃	n.d.	n.d.	n.d.	2.25	n.d.	n.d.	n.d.	0.51	n.d.	n.d.	n.d.	0.80
FeO	n.d.	n.d.	n.d.	6.08	n.d.	n.d.	n.d.	6.72	n.d.	n.d.	n.d.	2.84
FeO*	8.82(19)	6.26(47)	5.24(12)	8.33(86)	9.14(1.38)	4.32(10)	5.19(48)	7.23(34)	3.69(27)	1.31(16)	2.51	3.64(32)
MgO	49.72(23)	25.62(78)	34.62(88)	23.87(36)	49.45(1.35)	22.35(44)	34.91(53)	22.31(31)	55.00(33)	20.50(63)	38.47	24.61(78)
CaO	0.11(3)	8.92(66)	1.57(81)	3.22(12)	0.16(20)	14.23(18)	0.97(27)	3.54(14)	0.05(2)	19.21(70)	0.34	4.63(33)
Na ₂ O	0.07(3)	1.16(6)	0.19(6)	0.13(1)	0.05(3)	1.09(7)	0.16(5)	0.21(4)	0.07(3)	1.29(41)	0.08	0.16(3)
NiO	0.45(4)	0.15(3)	0.15(8)	0.04(1)	0.09(2)	0.04(1)	0.13(5)	0.01(1)	0.06(3)	0.02(2)	0.04	0.01(1)
Total	100.28	100.50	100.84	98.70	100.2	101.02	100.44	99.40	101.11	100.94	101.38	98.28
Fe ³⁺ /ΣFe (flank)	-	-	-	0.27(4)	-	-	-	0.07(6)	-	-	-	0.22(4)
n	-	-	-	17	-	-	-	13	-	-	-	19
Fe ³⁺ /ΣFe (EELS)	-	0.54(14)	-	0.31(14)	-	0.17(10)	-	0.11(4)	-	-	-	-
n	-	5	-	8	-	9	-	6	-	-	-	-
Fe ³⁺ /ΣFe (c.b.)	-	-	-	0.31	-	-	-	0.06	-	-	-	0.26
#Mg	0.91	0.88	0.92	0.84	0.91	0.90	0.92	0.84	0.96	0.97	0.96	0.92
Δlog fO ₂ [FMQ]	-0.4				-4.3				-0.5			
Δlog fO ₂ [EMOD]	+1.5				-2.4				+1.4			
Δlog fO ₂ [IW]	+4.7				+0.9				+4.6			

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 $Fe^{3+}/\Sigma Fe$ (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 $Fe^{3+}/\Sigma Fe$ values are 2σ . Total FeO^ of garnet was divided into FeO and Fe_2O_3 according to $Fe^{3+}/\Sigma Fe$ measured by the flank method, other values are reported in Supplementary material, Table 4. n.d. = not determined.*

Figure 1

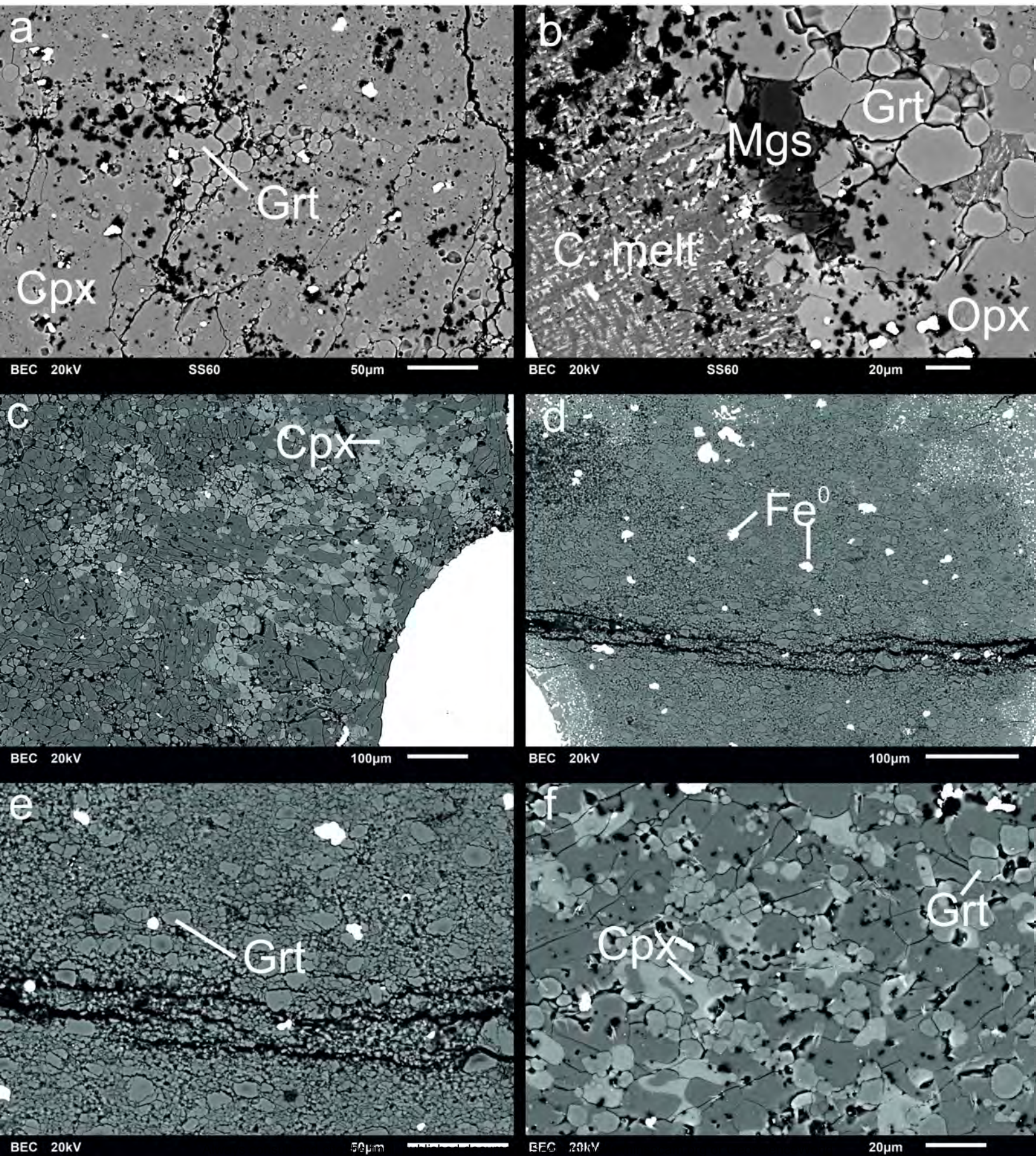


Figure 2

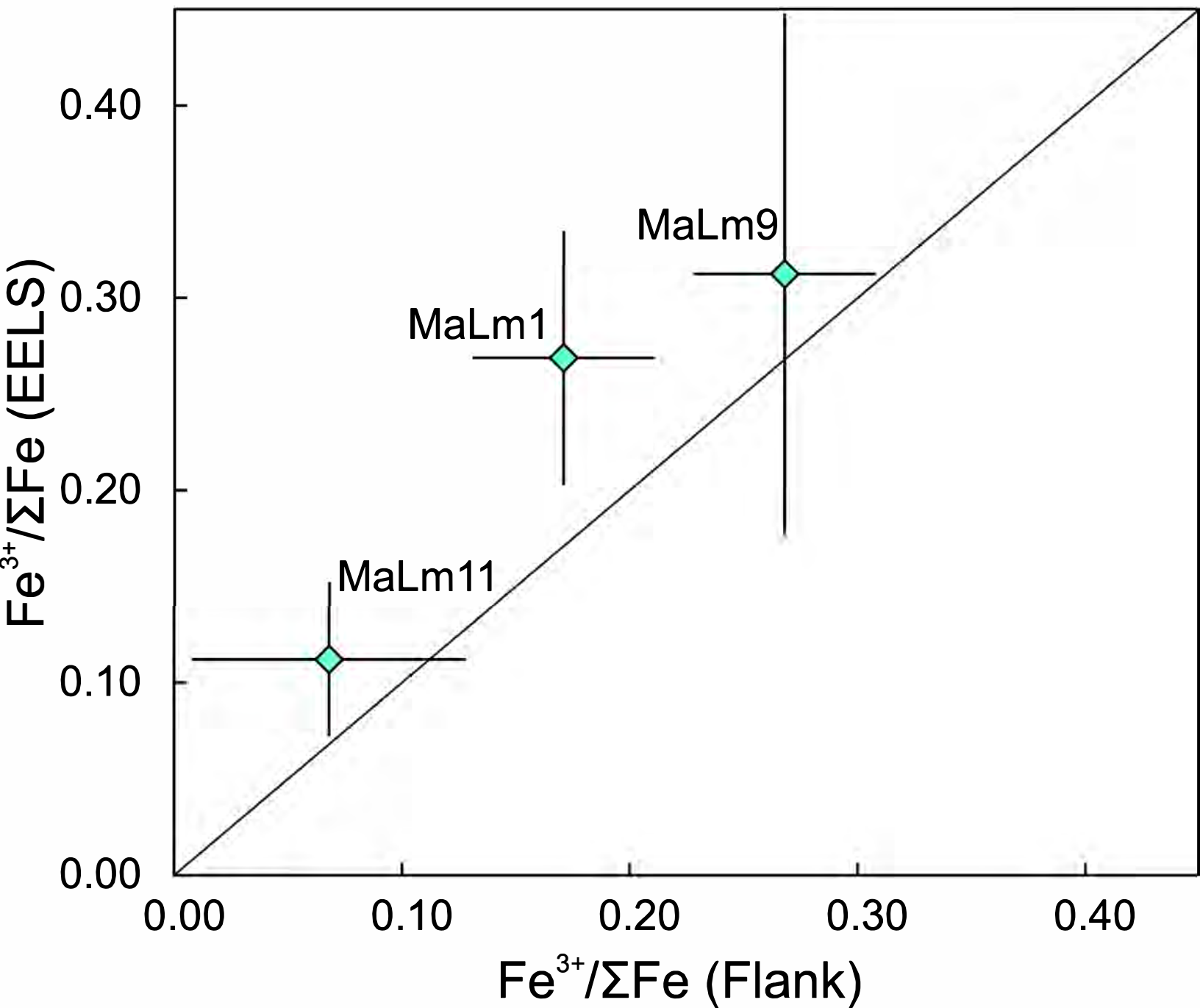


Figure 4

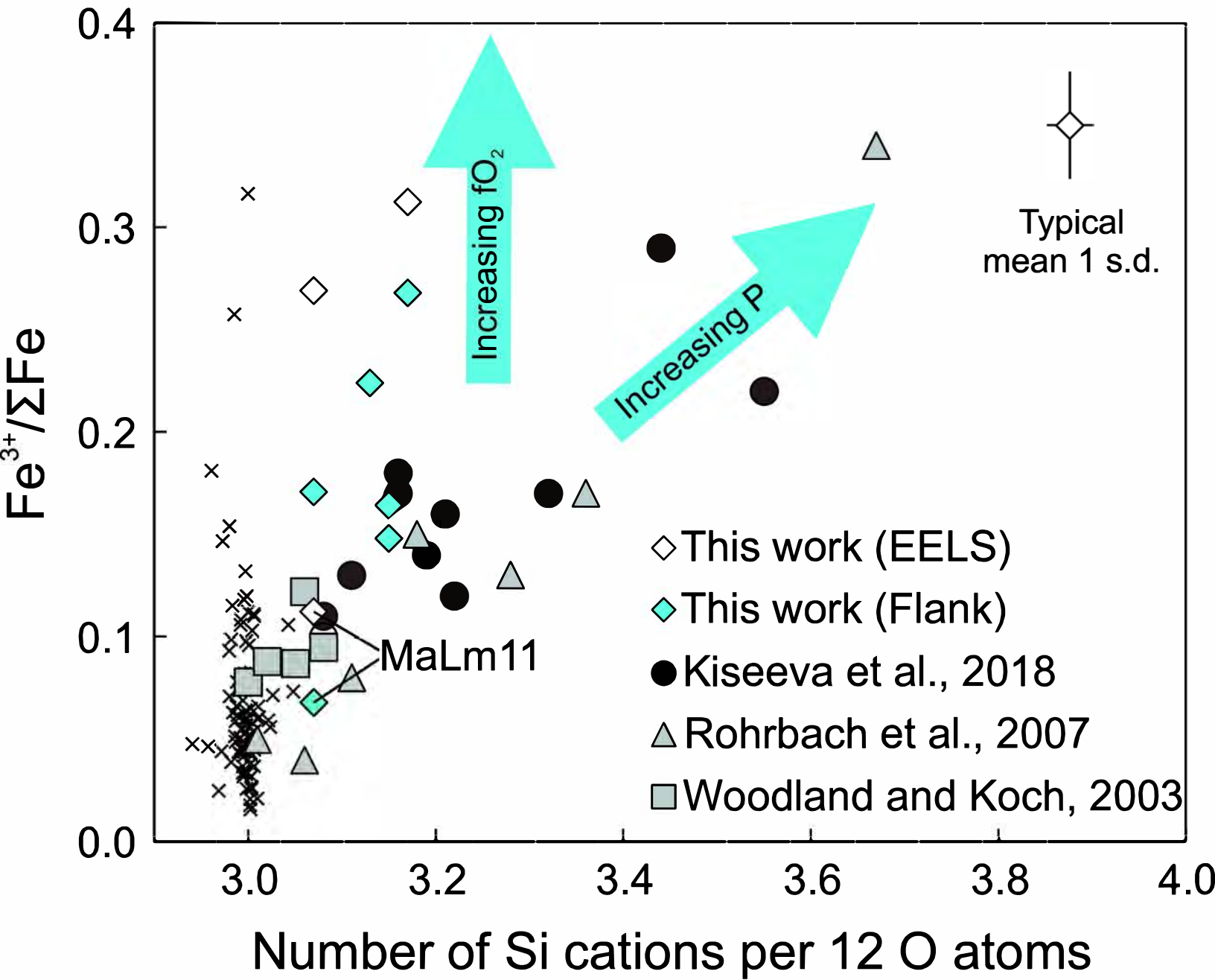


Figure 5

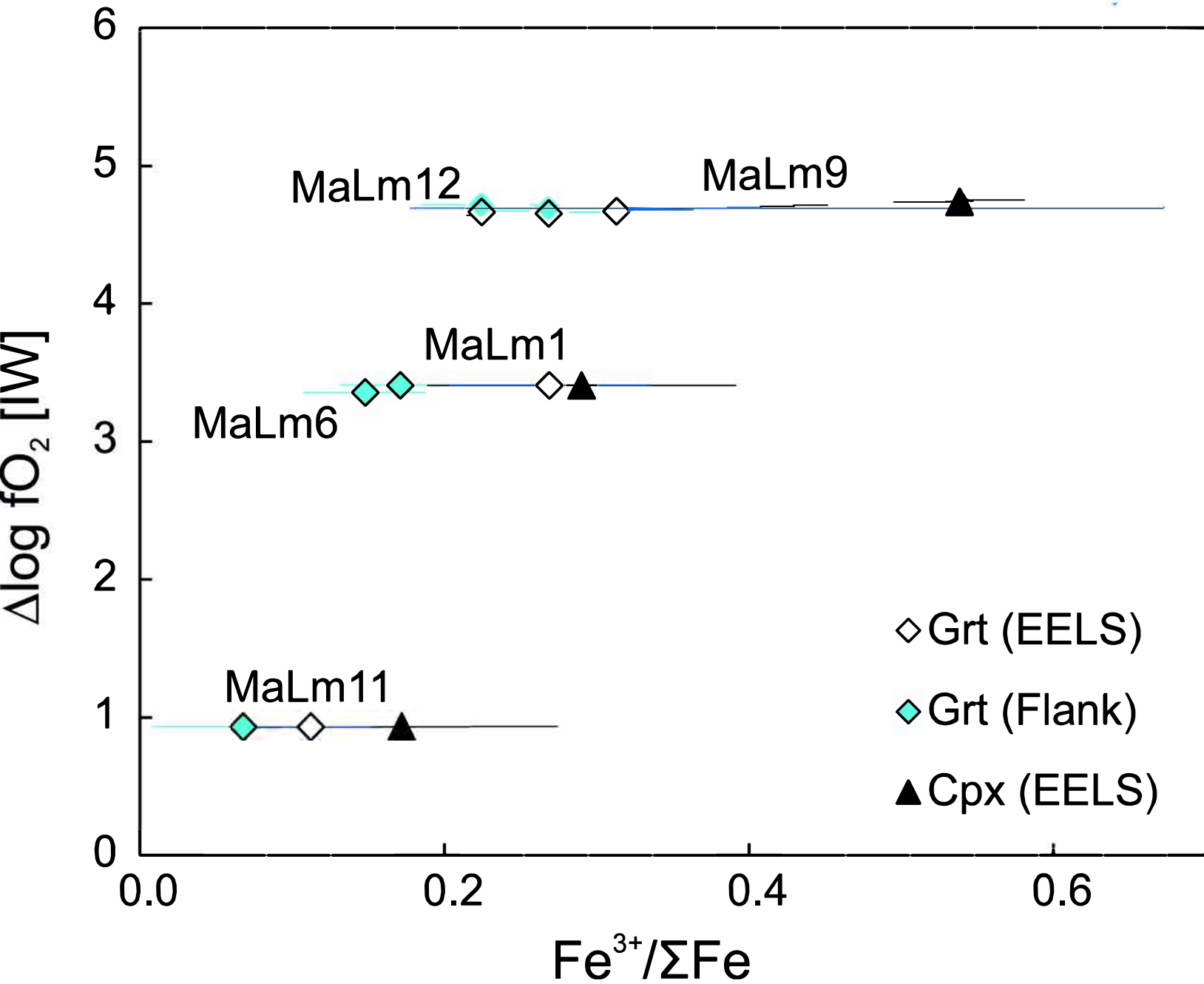


Figure 6

