Revisiting the electron microprobe method of spinel-olivine-orthopyroxene oxybarometry applied to spinel peridotites

Fred A. Davis, Elizabeth Cottrell, Suzanne K. Birner, Jessica M. Warren, and Oscar G. Lopez

Abstract

Natural peridotite samples containing olivine, orthopyroxene, and spinel can be used to assess the oxygen fugacity ($f_{O_2}$) of the upper mantle. The calculation requires accurate and precise quantification of spinel Fe$^{3+}$/$\Sigma$Fe ratios. Wood and Virgo (1989) presented a correction procedure for electron microprobe (EPMA) measurements of spinel Fe$^{3+}$/$\Sigma$Fe ratios that relies on a reported correlation between the difference in Fe$^{3+}$/$\Sigma$Fe ratio by Mössbauer spectroscopy and by electron microprobe ($\Delta$Fe$^{3+}$/$\Sigma$Fe$_{Möss-EPMA}$) and the Cr# [Cr/(Al+Cr)] of spinel. This procedure has not been universally adopted, in part, because of debate as to the necessity and effectiveness of the correction. We have performed a series of replicate EPMA analyses of several spinels, previously characterized by Mössbauer spectroscopy, to test the accuracy and precision of the Wood and Virgo correction. While we do not consistently observe a correlation between Cr# and $\Delta$Fe$^{3+}$/ΣFe$_{Möss-EPMA}$ in measurements of the correction standards, we nonetheless find that accuracy of Fe$^{3+}$/ΣFe ratios determined for spinel samples treated as unknowns improves when the correction is applied. Uncorrected measurements have a mean $\Delta$Fe$^{3+}$/ΣFe$_{Möss-EPMA}$ = 0.031 and corrected measurements have a mean $\Delta$Fe$^{3+}$/ΣFe$_{Möss-EPMA}$ = –0.004. We explain how the reliance of the correction on a global correlation between Cr# and MgO concentration in peridotitic spinels improves the accuracy of Fe$^{3+}$/ΣFe ratios despite the absence of a correlation between $\Delta$Fe$^{3+}$/ΣFe$_{Möss-EPMA}$ and Cr# in some analytical sessions.

Precision of corrected Fe$^{3+}$/ΣFe ratios depends on the total concentration of Fe, and varies from ±0.012 to ±0.032 (1σ) in the samples analyzed; precision of uncorrected analyses is poorer by approximately a factor of two. We also present an examination of the uncertainties in the calculation contributed by the other variables used to derive $f_{O_2}$. Because there is a logarithmic relationship between the activity of magnetite and log$f_{O_2}$, the uncertainty in $f_{O_2}$ relative to the QFM buffer contributed by the electron microprobe analysis of spinel is asymmetrical and larger at low ferric Fe concentrations (+0.3/–0.4 log units, 1σ, at Fe$^{3+}$/ΣFe = 0.10) than at higher ferric Fe concentrations (±0.1 log units, 1σ, at Fe$^{3+}$/ΣFe = 0.40). Electron microprobe analysis of olivine and orthopyroxene together contribute another ±0.1 to ±0.2 log units of uncertainty (1σ). Uncertainty in the temperature and pressure of equilibration introduce additional errors on the order of tenths of log units to the calculation of relative $f_{O_2}$. We also document and correct errors that appear in the literature when formulating $f_{O_2}$ that, combined, could yield errors in absolute $f_{O_2}$ greater than 0.75 log units—even with perfectly accurate Fe$^{3+}$/ΣFe ratios. Finally, we propose a strategy for calculating the activity of magnetite in spinel that preserves information gained during analysis about the ferric iron content of the spinel. This study demonstrates the superior accuracy and precision of corrected EPMA measurements of spinel Fe$^{3+}$/ΣFe ratios compared to uncorrected measurements. It also provides an objective method for quantifying uncertainties in the calculation of $f_{O_2}$ from spinel peridotite mineral compositions.

Keywords: Mössbauer spectroscopy, oxygen fugacity, electron microprobe, oxybarometry, xenolith
$f_{\text{O}_2}$ in the upper mantle and play a key role in deciphering past and present mantle $f_{\text{O}_2}$ conditions.

We can determine upper mantle $f_{\text{O}_2}$ directly from peridotites containing the assemblage olivine+orthopyroxene+spinel if we know or assume the pressure-temperature conditions following the reaction:

$$6\text{Fe}_2\text{Si}_3\text{O}_8 + 3\text{Fe}_2\text{SiO}_4 + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + 3\text{Fe}_2\text{O}_4 + 2\text{Fe}_2\text{O}_3.$$  \hspace{1cm} (1)

Several studies have parameterized $f_{\text{O}_2}$ based on this equilibrium (O’Neill and Wall 1987; Mattioli and Wood 1988; Wood 1991), and Wood (1990) tested this equilibrium experimentally. An accurate measurement of the oxidation state of Fe in the spinel phase is required to apply these parameterizations. The ratio of ferric iron to total iron (Fe$^{3+}$/ΣFe = Fe$^{3+}$/(Fe$^{3+}$ + Fe$^{2+}$)) in spinel can be measured by Mössbauer spectroscopy (e.g., Wood and Virgo 1989); however, traditional Mössbauer analysis is restricted to large volumes of sample. Removing spinel from its host rock for bulk Mössbauer analysis is labor intensive, can lead to averaging of spinels that are chemically heterogeneous on the hand-sample scale, and may lead to contamination of the Mössbauer spectra by other phases (Wood and Virgo 1989; Ballhaus et al. 1991; Woodland et al. 1992). In addition, Mössbauer analysis requires equipment that is expensive to run and expertise that may not be readily available. Thus, Wood and Virgo (1989) developed the electron probe microanalysis (EPMA) technique for determining Fe$^{3+}$/ΣFe ratios in spinel by in situ analysis.

Spinel Fe$^{3+}$/ΣFe ratios can be determined from an EPMA measurement by assuming ideal stoichiometry of the spinel phase and assigning cations of Fe as ferric in a proportion that balances the negative charge that arises from the initial assumption that all the iron is ferrous (Stormer 1983). This method can lead to large uncertainties on calculated Fe$^{3+}$/ΣFe ratios because the analytical errors for each oxide propagate through the calculation (e.g., Dyar et al. 1989; Wood and Virgo 1989). Wood and Virgo (1989) lessened this uncertainty by correcting their analyses using a set of spinel standards with Fe$^{3+}$/ΣFe ratios that they determined by Mössbauer spectroscopy. Their correction, hereafter referred to as “W&V89” used a reported correlation between the difference in Fe$^{3+}$/ΣFe ratio by Mössbauer and by EPMA ($\Delta$Fe$^{3+}$/ΣFe$^{\text{Möss-EPMA}}$) and the Cr# ($\text{Cr}/[\text{Al}+\text{Cr}]$) of the spinels.

Subsequent studies of spinel peridotite oxybarometry have disagreed over the value and effectiveness of the W&V89 correction. The W&V89 correction has been applied as originally described in many studies (e.g., Woodland et al. 1992; Parkinson and Pearce 1998; Dare et al. 2009). Others have challenged the premise of the correction or modified its application. Ballhaus et al. (1991) questioned the need to apply any correction to Fe$^{3+}$/ΣFe ratios measured by EPMA, noting in particular a close agreement between log $f_{\text{O}_2}$ calculated from both EPMA and Mössbauer analyses of the same spinel samples. Luhr and Aranda-Gómez (1997) required a correction to their spinel analyses to reproduce the Mössbauer Fe$^{3+}$/ΣFe ratios of their spinel standards, but did not observe the correlation between $\Delta$Fe$^{3+}$/ΣFe$^{\text{Möss-EPMA}}$ and the Cr# described by Wood and Virgo (1989). They chose to apply a single, constant-offset correction to their spinel Fe$^{3+}$/ΣFe ratios rather than apply the W&V89 correction in the absence of an underlying correlation.

Below we demonstrate that the W&V89 correction substantially improves both accuracy and precision of spinel Fe$^{3+}$/ΣFe ratios determined by EPMA. Biases in uncorrected EPMA determinations of Fe$^{3+}$/ΣFe ratios do not result from any inherent bias in the EPMA analysis or the applied matrix corrections, but instead result from session-to-session variations in analyses of primary standards. We present replicate analyses by EPMA of several spinels previously characterized by Mössbauer spectroscopy, which demonstrate the effectiveness of the W&V89 correction and elucidate the underlying mechanisms that drive the W&V89 correction. In particular, we focus on the relationship between $\Delta$Fe$^{3+}$/ΣFe$^{\text{Möss-EPMA}}$ and Cr# described by Wood and Virgo (1989) and how the W&V89 correction functions when this correlation is weak or absent. We also demonstrate that a global correlation between Cr# and MgO concentration in natural peridotite-hosted spinels allows the W&V89 correction to improve accuracy and precision of Fe$^{3+}$/ΣFe ratios, even when elements other than Al and Cr are responsible for the analytical bias.

Our replicate analyses of Mössbauer-characterized spinels allow us to estimate the precision of Fe$^{3+}$/ΣFe ratios determined by EPMA and corrected following the W&V89 method. We also discuss the propagation of uncertainties in the measurements of spinel, olivine, and orthopyroxene and in the estimates of pressure and temperature of equilibration through the $f_{\text{O}_2}$ calculation. We present new analyses of several spinel peridotites from Hawaii to demonstrate the effect of precision in the analysis of spinel Fe$^{3+}$/ΣFe concentration on calculated $f_{\text{O}_2}$. We present analyses of spinels from a peridotite from Tonga to demonstrate the diminished precision of the Fe$^{3+}$/ΣFe measurement of unknown spinels with compositions that depart from the Cr#-MgO trend of the correction standards.

**SAMPLES AND METHODS**

**Samples analyzed**

We analyzed 32 spinel samples, kindly provided by B. Wood, for major and minor elements by electron microprobe with the goal of determining Fe$^{3+}$/ΣFe ratios. These spinels, which we refer to collectively as the “Wood spinels,” were previously examined by Wood and Virgo (1989), Bryndzia and Wood (1990), and Ionov and Wood (1992). Each has been previously analyzed by Mössbauer spectroscopy, which provides an independent estimate of the Fe$^{3+}$/ΣFe ratio. The Wood spinels are separates from peridotites representing a diversity of major element compositions (Cr# = 0.04–0.57), Fe oxidation states (Mössbauer Fe$^{3+}$/ΣFe = 0.058–0.32), and geological environments (continental and arc peridotite xenoliths, abyssal peridotites).

Four spinel peridotite samples from Hawaii were analyzed to test the individual contributions of each mineral phase (e.g., olivine and orthopyroxene in addition to spinel) to the total uncertainty in the $f_{\text{O}_2}$ calculation. The Hawaiian samples are spinel lherzolite xenoliths from Salt Lake Crater, Oahu, originally collected by E. Dale Jackson and now part of the National Rock and Ore Collection at the Smithsonian Institution National Museum of Natural History. We also analyzed spinels from a harzburgite (BMRG08-98-2-2) dredged from the Tonga trench during the 1996 Boomerang cruise (Bloomer et al. 1996; Wright et al. 2000); the spinel in this sample has Cr# and MgO concentrations that depart significantly from the trend of the spinels used to correct Fe$^{3+}$/ΣFe ratios.

**Analytical methods**

We analyzed spinel, olivine, and orthopyroxene at the Smithsonian Institution using a JEOL 8900 Superprobe with five wavelength-dispersive spectrometers (WDS). Table 1 provides information on our primary standards, count times, and detector crystals, and additional information about the electron microprobe analyses is given in the Supplemental Material.

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1Deposit item AM-17-25823, Table 2, Supplemental material, and Supplementary Tables. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocan.org/MSA/AmMin/TOC/2017/Feb2017_data/Feb2017_data.html).
We analyzed spinels in two different types of analytical sessions. First, we analyzed the 32 Wood spinels without correcting Fe$^{3+}$/ΣFe ratios (sessions S1–S3, Table 1 and Supplementary Table S1) to determine the range of compositions present, to reveal compositional systematics, and to check for intra- and intergranular heterogeneity of the samples. Out of the 32 Wood spinels, we chose 7 as correction standards (hereafter, the correction set; selection criteria given in Results). The correction set spinels are the standards that we use to determine the Fe$^{3+}$/ΣFe correction to be applied to a given analytical session. In this second type of analytical session the correction set was analyzed along with another subset of the Wood spinels treated as unknowns (hereafter, the validation set) and the Tongan and Hawaiian spinels (sessions A1–A4 and B1–B4, Supplementary Table S2).

In sessions S1–S3, we analyzed one to six individual grains of each of the Wood spinels. From each grain, we analyzed 3–10 points, depending upon the total number of grains analyzed (Supplementary Table S1), except for the samples made from crushed Mössbauer powders. We collected only one analytical point on each grain of these powdered samples. We analyzed secondary standards of chromite, Cr-augite, and hypersthene (Jarosewich et al. 1980, 1987) every 2–4 h during the session to monitor instrumental drift.

In sessions A1–A4 and B1–B4, we collected three analytical points on each sample in the correction set both before and after analyzing unknowns, corresponding to re-analysis of the correction standards after 12–14 h. We analyzed secondary standards at regular intervals as described above. In these sessions, individual analyses were discarded when totals fell outside the range 97–101%; this range is asymmetrical around 100% because we expect samples with high Fe$^{2+}$ to give relatively low totals when total Fe is calculated as FeO. We also excluded individual analyses that contained SiO$_2$ > 0.3 wt% to avoid analyses that may have sampled surrounding silicate material. To ensure that each session could be considered separately in terms of interobservation reproducibility, the filament was turned down and allowed to cool for at least 12 h and then saturated again at the start of each new session, even when these sessions occurred on consecutive days.

We analyzed the major-element compositions of olivine and orthopyroxene from the four Hawaiian xenoliths in a single analytical session by analyzing the core compositions of 10 different grains of each mineral in each sample (Table 3).

### The spinel Fe$^{3+}$/ΣFe ratio correction method

We applied the W&V89 correction to spinels analyzed in sessions A1–A4 and B1–B4. We calculated Fe$^{3+}$/ΣFe ratio and Cr# of each of the correction set spinels measured at both the beginning and the end of the analytical session. We calculated the Fe$^{3+}$/ΣFe ratios of the spinels by normalizing the spinel cation proportions to 3 total cations, treating all Fe as Fe$^{2+}$, and then adjusting the Fe$^{3+}$/ΣFe ratio to balance the charge deficiency or excess (Stormer 1983). Occasionally, spinels with low Fe$^{3+}$/ΣFe ratios gave a small positive charge excess, which was balanced by allowing negative contributions to Fe$^{2+}$.

We calculated Fe$^{3+}$/ΣFe$_{Möss-EPMA}$ for each measurement and determined the best fit line through all measurements of the correction set to determine slope and intercept (Wood and Virgo 1989):

$$\Delta Fe^{3+}/ΣFe_{Möss-EPMA} = A \cdot Cr# + B.$$  

We used the resulting slope and intercept to correct the calculated Fe$^{3+}$/ΣFe ratios of all other spinels measured during that session. To maintain consistency in data processing, we applied this correction irrespective of whether ΔFe$^{3+}/ΣFe_{Möss-EPMA}$ and Cr# were strongly correlated. We explain the rationale for this procedure in the discussion.

### Results

**Compositions of the Wood spinels and selection of correction and validation standards**

We present the uncorrected EPMA analyses of the 32 Wood spinels in Table 2. We used these measurements to look for compositional systematics in the entire set of Wood spinels and to select the samples for the correction and validation sets. Figure 1 shows uncorrected Fe$^{3+}$/ΣFe ratios determined by EPMA compared to Fe$^{3+}$/ΣFe ratios determined by Mössbauer (Wood and Virgo 1989; Bryndzia and Wood 1990; Ionov and Wood 1992). The uncorrected Fe$^{3+}$/ΣFe ratios determined by EPMA analysis

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**Table 1.** Elements, detector crystals, count times, and primary standards used in EPMA analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Detector crystal</th>
<th>Peak count time (s)</th>
<th>Background time (s)</th>
<th>Primary standard (Smithsonian catalog number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>TAP</td>
<td>30</td>
<td>15</td>
<td>San Carlos olivine (NMNH 111312-44)</td>
</tr>
<tr>
<td>Ti</td>
<td>PETJ</td>
<td>40</td>
<td>20</td>
<td>Kankanai hornblende (NMNH 143965)</td>
</tr>
<tr>
<td>Al</td>
<td>TAP</td>
<td>40</td>
<td>20</td>
<td>Spinel (NMNH 136804)</td>
</tr>
<tr>
<td>Cr</td>
<td>LiFH</td>
<td>30</td>
<td>15</td>
<td>Tiebaghi Mine chromeite (NMNH 117075)</td>
</tr>
<tr>
<td>Fe</td>
<td>LiFH</td>
<td>30</td>
<td>15</td>
<td>San Carlos olivine</td>
</tr>
<tr>
<td>Mn</td>
<td>LiF</td>
<td>30</td>
<td>15</td>
<td>Manganite (NMNH 157972)</td>
</tr>
<tr>
<td>Mg</td>
<td>TAP</td>
<td>30</td>
<td>15</td>
<td>San Carlos olivine</td>
</tr>
<tr>
<td>Ca</td>
<td>PETJ</td>
<td>30</td>
<td>15</td>
<td>Wollastonite (synthetic, F.R. Boyd, no catalog no.)</td>
</tr>
<tr>
<td>Na</td>
<td>TAP</td>
<td>30</td>
<td>15</td>
<td>Kankanai hornblende</td>
</tr>
<tr>
<td>Ni</td>
<td>LiF</td>
<td>40</td>
<td>20</td>
<td>San Carlos olivine</td>
</tr>
</tbody>
</table>

**Olivine and orthopyroxene analysis**

| Si      | TAP              | 20                  | 10                  | Olivine (S.C. olivine, orthopyroxene); Johnstown Meteorite hypersthen (USNM 746) |
| Ti      | PETJ             | 20                  | 10                  | Kankanai hornblende                            |
| Al      | TAP              | 20                  | 10                  | Spinel (NMNH 136804)                          |
| Cr      | LiFH             | 20                  | 10                  | Tiebaghi Mine chromeite (NMNH 117075)         |
| Fe      | LiFH             | 20                  | 10                  | San Carlos olivine                            |
| Mn      | LiF              | 20                  | 10                  | Manganite (NMNH 157972)                       |
| Mg      | TAP              | 20                  | 10                  | San Carlos olivine                            |
| Ca      | PETJ             | 20                  | 10                  | Wollastonite (synthetic, F.R. Boyd, no catalog no.) |
| Na      | TAP              | 20                  | 10                  | Roberts Victor Mine omphacite (NMNH 110607)    |
| K      | PETJ             | 20                  | 10                  | Asbestos microcline (NMNH 143963)              |
| Ni      | LiF              | 20                  | 10                  | San Carlos olivine                            |

**Notes:** All standards from Jarosewich et al. (1980), except as noted below.

* Smithsonian internal reference standard (compositions given in Supplementary Table S5).

* Smith and Ribbe (1966).

**Table 3.** Compositions of Hawaiian xenolith olivine and orthopyroxene by EPMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>68-SAL-69</th>
<th>69-SAL-57</th>
<th>69-SAL-56</th>
<th>69-SAL-57</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMNH catalog no.</td>
<td>114923-41</td>
<td>114923-56</td>
<td>114923-57</td>
<td>114923-57</td>
</tr>
<tr>
<td>Phases</td>
<td>68-SAL-51-20</td>
<td>114885-3</td>
<td>69-SAL-41</td>
<td>114923-41</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>40.0(4)</td>
<td>55.4(18)</td>
<td>40.3(5)</td>
<td>54.5(28)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>n.d.</td>
<td>0.025(1)</td>
<td>n.d.</td>
<td>0.112(4)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>n.d.</td>
<td>2.66(1)</td>
<td>n.d.</td>
<td>4.77(18)</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>n.d.</td>
<td>0.74(5)</td>
<td>n.d.</td>
<td>0.42(4)</td>
</tr>
<tr>
<td>FeO$^*$</td>
<td>8.89(7)</td>
<td>5.70(7)</td>
<td>9.75(5)</td>
<td>6.20(5)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.136(19)</td>
<td>0.141(15)</td>
<td>0.149(15)</td>
<td>0.148(23)</td>
</tr>
<tr>
<td>MgO</td>
<td>50.0(3)</td>
<td>33.0(25)</td>
<td>49.38(20)</td>
<td>32.66(25)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.033(8)</td>
<td>2.0(4)</td>
<td>0.040(5)</td>
<td>0.70(9)</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.135(22)</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.133(18)</td>
</tr>
<tr>
<td>NiO</td>
<td>0.39(4)</td>
<td>0.103(25)</td>
<td>0.360(27)</td>
<td>0.096(14)</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>99.9</td>
<td>99.7</td>
</tr>
</tbody>
</table>

**Note:** FeO$^*$ is total Fe calculated as FeO.
DAVIS ET AL.: REVISITING EPMA METHOD OF SPL-OL-OPX OXYBAROMETRY

The correction set used in this study spans a similar range of Cr# and standards used by Wood and Virgo (1989) are as reported in that study. Measurements from this study (Table 2), while values for the correction set and validation set. All other Wood spinels are represented with diamonds. Circles represent samples chosen for the correction set, and triangles represent samples chosen for the validation set. All other Wood spinels are represented with diamonds.

From the Wood spinels, we selected seven samples for the correction set and six samples for the validation set. These samples are indicated in Table 2. The selection criteria for the correction and validation sets are given in the Supplementary Material.

**Uncorrected and corrected Fe**\(^{3+}\)/ΣFe ratios of the validation set spinels

Compositions of the validation set spinels were determined by averaging the replicate analyses from analytical sessions A1–A4 and B1–B4 (Table 4). Full results of all analytical sessions are presented in the Supplementary Material (Supplementary Table S2). Figure 3 shows several illustrative examples of uncorrected and corrected Fe\(^{3+}\)/ΣFe ratios of the correction and validation set spinels compared with Fe\(^{3+}\)/ΣFe ratios determined by Mössbauer, and Figure 4 shows the relationship between ΔFe\(^{3+}\)/ΣFe\(^{\text{Möss}}\)-EPMA and Cr#. Below, we discuss the implications of these results for the accuracy and precision of spinel Fe\(^{3+}\)/ΣFe ratios determined by EPMA.

**Discussion**

**Accuracy and precision of the correction method**

Since the Wood group presented their correction method and measurements of spinel peridotite f\(_{O2}\) (Wood and Virgo 1989; Bryndzia and Wood 1990; Ionov and Wood 1992), the application of this correction method to spinel peridotite f\(_{O2}\) studies has been sporadic. Some groups adopted the Wood and Virgo (1989) approach (e.g., Ionov and Wood 1992; Woodland et al. 1992; Luhr and Aranda-Gómez 1997; Parkinson and Pearce 1998; Parkinson and Arculus 1999; Bryant et al. 2007; Wang et al. 2007, 2008; Dare et al. 2009), while others presented data with no correction (e.g., Ballhaus 1993; Qi et al. 1995; Fedortchouk et al. 2005; Canil et al. 2006; Nasir et al. 2010; Wang et al. 2012).

Ballhaus et al. (1991) questioned whether Fe\(^{3+}\)/ΣFe ratios determined from EPMA require correction, and additionally suggested that such a correction may introduce additional error. Their argument was based in part on a compilation of log f\(_{O2}\) calculated from analyses of spinels in peridotites and basalts, including spinel Fe\(^{3+}\)/ΣFe ratios that had been measured both by Mössbauer spectroscopy and EPMA. They found that differences in calculated f\(_{O2}\) seldom varied by greater than 0.4 log units and concluded that correcting EPMA data was unnecessary; however, plotting calculated log f\(_{O2}\) rather than spinel Fe\(^{3+}\)/ΣFe ratios disguises the true effects of the uncertainty in the EPMA measurements. Uncertainty in spinel Fe\(^{3+}\)/ΣFe ratio has a decreasing
influence on calculated $f_{O_2}$ as $Fe^{3+}/ΣFe$ ratio increases (Ballhaus et al. 1991; Parkinson and Arculus 1999). Plotting $Fe^{3+}/ΣFe$ ratios determined by EPMA and Mössbauer across several studies of natural spinels (Fig. 5) shows that disagreement between the two methods can be substantial. In aggregate, the uncorrected $Fe^{3+}/ΣFe$ ratios from previous studies (Fig. 5a) are offset to low $Fe^{3+}/ΣFe$ ratios compared to Mössbauer ($ΔFe^{3+}/ΣFe_{Möss-EPMA} = 0.022 ± 0.049$, 1σ). This may indicate a common analytical bias between laboratories. Bias to low values of uncorrected $Fe^{3+}/ΣFe$ ratios could be caused by an overestimate of cations with valence ≥3 or an underestimate of cations with valence ≤2. Possible sources of this bias include treating all Cr as trivalent when a significant fraction may be divalent (Lucas et al. 1988) and omission of divalent minor cations, such as Zn, from the analysis. Corrected $Fe^{3+}/ΣFe$ ratios from these same studies are in closer agreement with Mössbauer $Fe^{3+}/ΣFe$ ratios and are more evenly distributed around the linear trend between the two measurements ($ΔFe^{3+}/ΣFe_{Möss-EPMA} = -0.007 ± 0.021$, 1σ; Fig. 5b).

Ballhaus et al. (1991) also argued that EPMA analyses of spinel should be corrected only if non-stoichiometry is suspected. But the Wood and Virgo (1989) correction does not imply non-stoichiometry of the spinel sample; it corrects for error in the determination of $Fe^{3+}/ΣFe$ ratios that results from forcing an imperfectly analyzed composition into a perfect stoichiometric calculation. The corrected compositions in this study are still stoichiometric (Supplementary1 Table S2) with total cations between 2.99 and 3.01 when calculated on a four oxygen basis. We tested the accuracy and precision of the W&V89 correction using our replicate analyses of spinels from the validation set, BMRG08-98-2-2, and Hawaiian xenoliths analyzed in sessions A1–A4 and B1–B4 (Supplementary1 Table S2, Figs. 3 and 4). If we assume that the Mössbauer analyses of the Wood spinels accurately represent their $Fe^{3+}/ΣFe$ ratios, then we can use the validation set to demonstrate that the W&V89 correction improves the accuracy of $Fe^{3+}/ΣFe$ ratios determined by EPMA. Figure 6 shows the averages and 1σ ranges of both corrected and

### Table 4. Multi-session average compositions of validation set spinels

<table>
<thead>
<tr>
<th>Sample name</th>
<th>PS211</th>
<th>PS212</th>
<th>OC231350</th>
<th>KLL8304</th>
<th>MRB8313</th>
<th>V314-58</th>
<th>IOS650</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>75</td>
<td>76</td>
<td>36</td>
<td>66</td>
<td>70</td>
<td>67</td>
<td>31</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.070(4)</td>
<td>0.022(3)</td>
<td>0.067(10)</td>
<td>0.103(5)</td>
<td>0.213(11)</td>
<td>0.076(3)</td>
<td>0.051(8)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.8(8)</td>
<td>37.4(10)</td>
<td>50.9(16)</td>
<td>60.7(12)</td>
<td>49.1(10)</td>
<td>59.2(12)</td>
<td>56.3(12)</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>35.8(4)</td>
<td>32.0(4)</td>
<td>17.1(6)</td>
<td>6.1(7)</td>
<td>17.1(16)</td>
<td>8.3(46)</td>
<td>13.35(11)</td>
</tr>
<tr>
<td>FeO*</td>
<td>15.0(4)</td>
<td>13.16(25)</td>
<td>11.57(21)</td>
<td>11.09(14)</td>
<td>12.8(15)</td>
<td>10.6(11)</td>
<td>10.7(3)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.190(7)</td>
<td>0.170(8)</td>
<td>0.122(5)</td>
<td>0.101(8)</td>
<td>0.126(7)</td>
<td>0.108(6)</td>
<td>0.111(10)</td>
</tr>
<tr>
<td>MgO</td>
<td>15.28(19)</td>
<td>16.28(11)</td>
<td>18.78(17)</td>
<td>21.05(27)</td>
<td>19.33(21)</td>
<td>20.41(19)</td>
<td>19.51(20)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.002(2)</td>
<td>0.002(2)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.019(7)</td>
<td>0.010(5)</td>
<td>n.d.</td>
</tr>
<tr>
<td>NiO</td>
<td>0.145(5)</td>
<td>0.157(7)</td>
<td>0.283(12)</td>
<td>0.357(13)</td>
<td>0.345(7)</td>
<td>0.381(11)</td>
<td>0.305(14)</td>
</tr>
<tr>
<td>Total</td>
<td>99.1</td>
<td>99.1</td>
<td>99.0</td>
<td>99.5</td>
<td>98.3</td>
<td>99.2</td>
<td>100.2</td>
</tr>
</tbody>
</table>

Note: FeO* is total Fe calculated as FeO. Complete analyses can be found in Supplementary1 Table S1.

### Table 5. Multi-session average compositions of Hawaiian and Tongan spinels

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Hawaiian xenoliths</th>
<th>Tonga Peridotite</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.040(3)</td>
<td>0.100(6)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.0(10)</td>
<td>35.2(10)</td>
</tr>
<tr>
<td>FeO*</td>
<td>16.83(15)</td>
<td>16.83(15)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.100(4)</td>
<td>0.100(4)</td>
</tr>
<tr>
<td>MgO</td>
<td>14.4(4)</td>
<td>14.4(4)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.011(1)</td>
<td>0.011(1)</td>
</tr>
<tr>
<td>NiO</td>
<td>0.144(5)</td>
<td>0.144(5)</td>
</tr>
<tr>
<td>Total</td>
<td>98.7</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Note: FeO* is total Fe calculated as FeO. Complete analyses can be found in Supplementary1 Table S1.

1 For Hawaiian samples, the sample number assigned by E.D. Jackson is given first then the NMNH collection number.
2 Li et al. (1995).
3 MELTS Supplemental Calculator.
uncorrected Fe$^{3+}$/ΣFe ratios of the validation set spinels measured across all analytical sessions (Table 4). Corrected Fe$^{3+}$/ΣFe ratios are distributed closely around the 1:1 line with an average offset of +0.004 from the Mössbauer Fe$^{3+}$/ΣFe ratios. The uncorrected Fe$^{3+}$/ΣFe ratios of these spinels are offset below the 1:1 line by an average of −0.031 from the Mössbauer Fe$^{3+}$/ΣFe ratios. Similar to the offset in the literature data described above (Fig. 5a).

We can assess the improvement in precision of Fe$^{3+}$/ΣFe ratios achieved by using the W&V89 correction by quantifying the intersession variability of Fe$^{3+}$/ΣFe ratios that we calculated for the validation set spinels. Values of 1σ around mean uncorrected Fe$^{3+}$/ΣFe ratios of the validation set spinels vary from ±0.029 to ±0.065 (Table 4) with a mean of ±0.049. Values of 1σ around mean corrected Fe$^{3+}$/ΣFe ratios of the validation set spinels vary from ±0.012 to ±0.032 (Table 4) with a mean of ±0.023, which suggests greater than a factor of two increase in precision when using the W&V89 correction. The variations in 1σ around these averages are not random. Intersession variability in corrected and

**Figure 3.** Examples of the W&V89 correction applied to spinels from several independent analytical sessions. The first column (a, c, and e) shows uncorrected Fe$^{3+}$/ΣFe ratios by EPMA of the correction set spinels measured at the start of each session and at the end of each session, along with validation set spinels analyzed in between. These are plotted against their published Fe$^{3+}$/ΣFe ratios measured by Mössbauer. The second column (b, d, and f) shows the same measurements after correction of the EPMA data using the Wood and Virgo (1989) method. Uncorrected EPMA analyses from session A1 plot around the 1:1 line (a), and the W&V89 correction causes only imperceptible changes to the corrected Fe$^{3+}$/ΣFe ratios (b). Uncorrected EPMA analyses from session B3 (c and d) are offset from the 1:1 line and display a relatively high degree of scatter around the trend with Mössbauer data (e). The W&V89 correction decreases scatter in the data and shifts it upward so that the corrected data lie on the 1:1 line (d). Uncorrected EPMA analyses from session B4 (e and f) are offset from the 1:1 line but are relatively tightly clustered along a linear trend with the Mössbauer data (e). The W&V89 correction shifts Fe$^{3+}$/ΣFe ratios onto the 1:1 line (f).
Uncorrected Fe$^{3+}$/ΣFe ratios are greater in samples with lower total Fe. The stoichiometric calculation produces a concentration of Fe$^{3+}$ with uncertainty resulting from the accumulated analytical errors from each element propagated through the stoichiometric calculation. When this error is propagated through the calculation of the Fe$^{3+}$/ΣFe ratio, it scales with the total concentration of Fe. We approximate errors on corrected Fe$^{3+}$/ΣFe ratios by dividing the error on Fe$^{3+}$ by the amount of total Fe. We demonstrate this relationship by plotting the magnitude of 1σ variations in corrected Fe$^{3+}$/ΣFe ratios from validation set and Hawaiian spinels as a function of the inverse of total Fe per 3 formula cations (Fig. 7a). A line fit through the origin gives the following relationship:

$$1\sigma \times X_{\Sigma Fe} = 0.006 / X_{\Sigma Fe}$$

where $1\sigma$ describes the magnitude of 1 st.dev. around a corrected spinel Fe$^{3+}$/ΣFe ratio, 0.006 is the magnitude of 1σ variation around the mean molar Fe$^{3+}$ concentration per 3 formula cations, and $X_{\Sigma Fe}$ is the molar concentration of total Fe per 3 formula cations. This relationship describes an error envelope for corrected Fe$^{3+}$/ΣFe ratios that depends on the total concentration of Fe in the spinel. Figure 7b shows the error envelope with measurements of Fe$^{3+}$/ΣFe ratios from the validation set, Hawaiian, and Tongan spinels presented as deviations from the mean. Equation 3 describes the precision of the EPMA method of determining Fe$^{3+}$/ΣFe ratios when using the W&V89 correction.

It is likely that the accuracy of uncorrected Fe$^{3+}$/ΣFe ratios and the precision of Fe$^{3+}$/ΣFe ratios corrected using the W&V89 method can be improved further by analyzing additional minor elements. As we described above, our uncorrected spinel Fe$^{3+}$/ΣFe ratios measured by EPMA and those in previous studies skew low compared to Mössbauer Fe$^{3+}$/ΣFe ratios, consistent with under-sampling of divalent cations. We examined the spinel data set hosted in the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/, accessed 30 June 2016). In 139 peridotite-hosted spinels (those with host rock listed as peridotite, lherzolite, harzburgite, or dunite) with both major and trace first-row transition elements given, only three transition elements have average concentrations in excess of 100 ppm: V (620 ± 390), Co (270 ± 220), and Zn (960 ± 690). Forty-two of these samples have measured V, Co, and Zn, and in that subset V is positively correlated with both Co ($r^2 = 0.54$) and Zn ($r^2 = 0.33$; Supplementary Fig. S1). In all but 4 of these spinel samples (Co+Zn) is greater than V; therefore, it is likely that by excluding these elements from the analysis, we have introduced a bias that could lead to underestimated Fe$^{3+}$/ΣFe ratios that are underestimated by 0.003 to 0.013 (see Supplementary Materials for calculations). The W&V89 correction accounts for the systematic underestimation of Fe$^{3+}$/ΣFe, but variations in V, Co, and Zn in standard and unknown spinels may lead to diminished precision of the corrected Fe$^{3+}$/ΣFe ratios on the order of 0.01 if these elements are not analyzed.

**Underlying mechanics of the Wood and Virgo Correction**

Although the W&V89 correction demonstrably improves agreement between measurements of spinel Fe$^{3+}$/ΣFe ratios by Mössbauer and EPMA, no studies by the Wood group nor any subsequent studies have explained how the method works in detail. Wood and Virgo (1989) report that ΔFe$^{3+}$/ΣFeMöss-EPMA is generally linearly related to Cr#: they suggest a simple linear relationship can be determined in each EPMA analytical session by comparing EPMA analyses of a set of spinel standards that have been characterized by Mössbauer. We explore two
complications in this section: (1) How should correction proceed when this linear relationship is not observed, even when agreement between EPMA and Mössbauer measurements of the standards is poor? (2) How does this correction, based only on two measured elements, work to correct a multi-element analysis? The first question was raised by Luhr and Aranda-Gómez (1997), who reported that their EPMA measurements of spinel \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \) and Cr\# were not correlated. We also do not observe a correlation between \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \) and Cr\# in some of our analytical sessions (e.g., session B4, Fig. 4). The second question was addressed briefly by Wood and Virgo (1989), who suggested that Al was subject to greater systematic errors than other elements, at least in their own data set; therefore a correction relying on Cr\# addressed the greatest source of uncertainty. As we demonstrate below, systematic error of any element in the EPMA analysis can lead to increases in the magnitude of \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \), but the W&V89 correction can still correct for these biases. That is, the correction works, even when bias is introduced by elements other than Cr or Al, largely because of a correlation between Cr\# and MgO in the global spinel peridotite data set (Fig. 8); however, this means that the correction may be less effective for samples that fall off the MgO-Cr\# trend. This aspect of the W&V89 correction needs to be accounted for by workers analyzing off-trend spinels, either by adjusting estimates of uncertainty or by choosing correction standards that are compositionally relevant to their particular sample set.

Biases in EPMA can lead to two different effects on calculated \( Fe^{3+}/\Sigma Fe \) ratios of a group of spinels for which independent Mössbauer \( Fe^{3+}/\Sigma Fe \) ratios are available. The whole set of EPMA-derived \( Fe^{3+}/\Sigma Fe \) ratios may be offset from the EPMA-Mössbauer 1:1 line. Alternatively, scatter around the linear trend between Mössbauer and EPMA \( Fe^{3+}/\Sigma Fe \) ratios may increase as spinels with different compositions are variably affected by measurement bias. These two effects are not mutually exclusive.

When the correction set yields a constant offset (e.g., sessions B1 and B4, Fig. 3e), uncorrected \( Fe^{3+}/\Sigma Fe \) ratios of the correction and validation set spinels plot mostly below the 1:1 line and \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \) and Cr\# are also uncorrelated (r\(^2\) ≈ 0.10; Fig. 4c). In such instances, EPMA-derived \( Fe^{3+}/\Sigma Fe \) ratios display systematic bias, but it is not clear that a correction scheme that relies on a correlation between \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \) and Cr\# should be applied when those parameters are uncorrelated. Luhr and Arranda-Gómez (1997) observed just such a scenario when they attempted to apply the W&V89 correction to their own spinel peridotite xenolith suite. They chose not to apply the W&V89 correction and instead determined the average value of \( \Delta Fe^{3+}/\Sigma Fe^{\text{Möss-EPMA}} \) for all their correction standards, which did not vary with Cr\#. They then made a single, constant-value adjustment to the calculated \( Fe^{3+}/\Sigma Fe \) ratio of all samples run during that session. This method of correction...
can improve $Fe^{3+}/\Sigma Fe$ ratio accuracy in the case where the offset between EPMA and Mössbauer is roughly constant for all samples; however, devising a separate correction for such a case is unnecessary. The W&V89 correction contains this same functionality: when $\Delta Fe^{3+}/\Sigma Fe^{\text{Moss-EPMA}}$ and Cr# are uncorrelated, the slope of the best-fit line will be approximately zero, and the W&V89 correction functions as a constant $Fe^{3+}/\Sigma Fe$ ratio offset correction. The two correction methods are, in effect, equivalent.

The W&V89 correction is valuable because it addresses the differential effects of measurement bias on spinels of variable composition. Hence, the correction can also decrease scatter in EPMA measurements of $Fe^{3+}/\Sigma Fe$ ratios when these data show large deviations from the linear trend with $Fe^{3+}/\Sigma Fe$ ratios by Mössbauer. Sessions A3 (Figs. 3a and 3b) and B3 are examples of this effect. The initial stoichiometric calculation of spinel $Fe^{3+}/\Sigma Fe$ ratio is sensitive to systematic errors in all elements analyzed. Wood and Virgo (1989) explain their choice of Cr# as the compositional parameter for correcting $Fe^{3+}/\Sigma Fe$ ratios because, among the major elements, $Al_2O_3$ concentrations determined by EPMA were the most affected by the choice of matrix correction schemes. This explanation does not account for systematic biases of elements other than Al and Cr that may result from imperfect analysis of primary standards.

$MgO$ is a major element in peridotitic spinels and is just as likely as Al or Cr to be the root of systematic offsets of calculated $Fe^{3+}/\Sigma Fe$ ratios from ideality. Interestingly, the W&V89 correction is able to correct for bias in the MgO analysis because MgO and Cr# are correlated in the spinels studied by the Wood group (Wood and Virgo 1989; Bryndzia and Wood 1990; Ionov and Wood 1992) and in peridotitic spinels globally (Figs. 2

**Figure 7.** Relationship between analytical precision of spinel $Fe^{3+}/\Sigma Fe$ ratios and total concentration of Fe for spinels from the validation set, Hawaiian xenoliths and Tonga. Magnitude of 1 st.dev. in corrected $Fe^{3+}/\Sigma Fe$ ratios measured across all sessions (A1–A4 and B1–B4, Supplementary Table S2) for validation set and Hawaiian spinels as a function of the inverse of the multi-session average total Fe concentration on a 3 cation basis (a). In black is the best fit line through the origin ($r^2 = 0.57$), Tonga sample BMRO8-98-2-2 was not included in this fit because it does not plot near the global trend in Cr#-MgO (Fig. 8). The equation for this line is given in the text (Eq. 3), and we use it to calculate precision in our corrected measurements of $Fe^{3+}/\Sigma Fe$ ratios of unknown spinel samples. Deviations of each session average (Supplementary Table S2) from their respective multisession means (Table 4) plotted as a function of total Fe concentration on a 3 cation basis (b). The 1σ error envelope is calculated using Equation 3.

**Figure 8.** Relationship between MgO concentration and Cr# of natural peridotite spinels. Samples are separated by tectonic setting: abyssal peridotites ($n = 743$) from the compilation of Warren (2016); (Prinz et al. 1976; Hamlyn and Bonatti 1980; Dick and Bullen 1984; Michael and Bonatti 1985; Shibata and Thompson 1986; Dick 1989; Bryndzia and Wood 1990; Johnson et al. 1990; Juteau et al. 1990; Komor et al. 1990; Bonatti et al. 1992, 1993; Cannat et al. 1992; Johnson and Dick 1992; Snow 1993; Constantin et al. 1995; Arai and Matsukage 1996; Dick and Natland 1996; Ghose et al. 1996; Jaroslow et al. 1996; Niida 1997; Ross and Elthon 1997; Stephens 1997; Hellebrand et al. 2002a, 2002b; Brunelli et al. 2003; Hellebrand and Snow 2003; Seyler et al. 2003, 2007; Coogan et al. 2004; Workman and Hart 2005; Morishita et al. 2007; Cipriani et al. 2009; Warren et al. 2009; Brunelli and Seyler 2010; Dick et al. 2010; Warren and Shimizu 2010; Zhou and Dick 2013; Lassiter et al. 2014; Mallick et al. 2014; D’Errico et al. 2016), continental xenoliths not associated with subduction ($n = 154$): (Wood and Virgo 1989; Ionov and Wood 1992; Woodland et al. 1992), and supra-subduction zone for xenoliths and seafloor drilled samples from subduction-related settings ($n = 85$): (Wood and Virgo 1989; Canil et al. 1990; Luhr and Aranda-Gómez 1997; Parkinson and Pearce 1998). MgO and Cr# are correlated in the global data set (solid line, $r^2 = 0.82$, slope = $-15.0 \pm 0.2$, intercept = $21.46 \pm 0.07$, 1σ). The slope defined by the correction set used in this study (dashed line, $r^2 = 0.94$, n = 7, slope = $-11.6 \pm 1.4$, intercept = $21.5 \pm 0.2$, 1σ) is shallower, as is the line defined by the Wood spinels (not shown, $r^2 = 0.92$, n = 32, slope = $-12.7 \pm 0.7$, intercept = $21.80 \pm 0.17$, 1σ). Also shown are Hawaiian xenoliths and Tonga peridotite BMRO8-98-2-2 from this study.
and 8). The correlation between MgO and Cr# in peridotitic spinels is an expected consequence of the dependence of the Fe\textsuperscript{3+}/Mg exchange coefficient between olivine and spinel on the Cr concentration in the spinel (Irvine 1965; Wood and Nicholls 1978). This relationship in the spinel data increases the effectiveness of the W&V89 correction when unknown spinel samples overlap with the compositional range of the correction standards, but the correction may not be as effective for samples that fall significantly off that compositional trend. In the Supplementary\textsuperscript{1} Materials, we present calculations that demonstrate how the W&V89 correction improves the accuracy of spinel Fe\textsuperscript{3+}/ΣFe ratios when elements other than Cr and Al are biased during the analysis. These calculations also demonstrate that corrected Fe\textsuperscript{3+}/ΣFe ratios from spinels that depart from the MgO-Cr# trend of the correction set, such as Tonga sample BMG08-98-2-2, are subject to degraded precision.

In summary, the W&V89 correction can effectively correct for systematic biases in EPMA derived Fe\textsuperscript{3+}/ΣFe ratios, even when the correlation between ΔFe\textsuperscript{3+}/ΣFe\textsuperscript{Mg-EPMA} and Cr# is weak or absent. The W&V89 method also corrects for bias in measured elements other than Al\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3}, due predominantly to the correlation of spinel Cr# with MgO. Precision of corrected Fe\textsuperscript{3+}/ΣFe ratios decreases for samples that fall outside the compositional range of the correction standards used, but accuracy is no worse than if the correction had not been applied. This effect could be mitigated by choosing a different set of correction standards that are compositionally similar to the unknowns being analyzed.

Effect of the matrix correction scheme

Wood and Virgo (1989) investigated the effect of the choice of matrix correction schemes on EPMA measurements of spinels. They found that different matrix correction schemes led to systematic differences in the calculated magnetite activity in spinel compositions before applying the W&V89 Fe\textsuperscript{3+}/ΣFe correction. We have reprocessed the analyses from analytical sessions A1–A4 using the PAP matrix correction (Pouchou and Pichoir 1986; Supplementary\textsuperscript{1} Table S3), also considered by Wood and Virgo (1989). We find that, compared to the ZAF correction we have used throughout our study, the PAP correction results in systematically lower Al\textsubscript{2}O\textsubscript{3} (averaging 1.4 rel%), FeO (0.4%), and MgO (0.6%) and systematically higher Cr\textsubscript{2}O\textsubscript{3} (0.7%). Uncorrected Fe\textsuperscript{3+}/ΣFe ratios determined using the PAP procedure are 0.001 to 0.015 lower than those ratios determined using the ZAF procedure, and the difference in Fe\textsuperscript{3+}/ΣFe ratio by these two matrix corrections is correlated with Cr# ($r^2 = 0.975$). Despite this systematic offset, the magnitude of the difference in uncorrected Fe\textsuperscript{3+}/ΣFe ratios is small, even in Al-rich samples, compared to the variation caused by session-to-session differences in the primary standardization. After correcting the Fe\textsuperscript{3+}/ΣFe ratios using the W&V89 method, the PAP and ZAF procedures yield differences in Fe\textsuperscript{3+}/ΣFe (ZAF-PAP) between –0.002 and 0.001. When the W&V89 correction is used, effects of the matrix correction on the Fe\textsuperscript{3+}/ΣFe ratio are negligible.

Calculation of $f_{O_2}$ from the analyses of spinel, olivine, and orthopyroxene

Ultimately, the goal of determining the Fe\textsuperscript{3+}/ΣFe ratios of spinels from peridotites is to estimate the $f_{O_2}$ of equilibration. We calculate $f_{O_2}$ following Mattioli and Wood (1988) and Wood and Virgo (1989) using the following equation for log$f_{O_2}$:

$$\log\left( f_{O_2} \right)_{\text{P},T} = \frac{-24222}{T} + 8.64 + \frac{0.0567p}{T} - 12\log(1 - \text{Mg#}^{\text{ol}}) - \frac{2620}{T}\left(\text{Mg#}^{\text{ol}}\right)^2 + 3\log\left( X_{\text{Fe}}^{\text{ol}}, X_{\text{Fe}}^{\text{spl}} \right)^{\text{ops}} + 2\log(a_{\text{Fe}^{\text{pol}}}) \quad (4)$$

where $P$ is pressure in bars, $T$ is temperature in K, Mg#\textsuperscript{ol} = $X_{\text{Mg}}^{\text{ol}}$/($X_{\text{Mg}}^{\text{ol}} + X_{\text{Fe}}^{\text{ol}}$) and $X_{\text{Fe}}^{\text{pol}}, X_{\text{Fe}}^{\text{spl}}$ are the mole fractions of Mg and Fe in olivine, $X_{\text{Fe}}^{\text{ol}}, X_{\text{Fe}}^{\text{spl}}$ are the mole fractions of Fe in the two orthopyroxene octahedral sites calculated following Wood and Banno (1973), and $a_{\text{Fe}^{\text{pol}}}$ is the activity of the magnetite component in spinel. We discuss the calculation of $a_{\text{Fe}^{\text{pol}}}$ in the following section. Temperature and pressure are required to calculate $f_{O_2}$. We calculate temperature using the spinel-olivine Fe-Mg exchange thermometer of Li et al. (1995) and, unless otherwise specified, we follow Bryndzia and Wood (1990) and Wood et al. (1990) in assuming a pressure of 1.5 GPa.

Equation 4 does not appear in the above form in any of the Wood group papers, and there is some confusion in the literature about how different versions of the formula arose. Commonly, the version given in Wood et al. (1990) and Wood (1991) is cited, which includes a term for the $f_{O_2}$ of the quartz-fayalite-magnetite (QFM) buffer:

$$\log\left( f_{O_2} \right)_{\text{QFM}} = \frac{-220}{T} + 0.35 - \frac{0.0369p}{T} - 12\log(1 - \text{Mg#}^{\text{ol}}) - \frac{2620}{T}\left(\text{Mg#}^{\text{ol}}\right)^2 + 3\log\left( X_{\text{Fe}}^{\text{ol}}, X_{\text{Fe}}^{\text{spl}} \right)^{\text{ops}} + 2\log(a_{\text{Fe}^{\text{pol}}}) \quad (5)$$

As discussed by Herd (2008), this version of the $f_{O_2}$ equation requires the QFM formulation of Myers and Eugster (1983):

$$\log\left( f_{O_2} \right)_{\text{QFM}} = \frac{-24441.9}{T} + 8.29 \quad (6)$$

(Subtracting Eq. 6 from the first two terms in Eq. 4 yields the second two terms in Eq. 5.) Herd (2008) also suggests that the proper way to calculate absolute $f_{O_2}$ from Equation 5 is to use Equation 6 as written, without a pressure term, to calculate log$f_{O_2}$ (QFM)\text{p,T}. This is incorrect because the pressure term in Equation 5 is derived from the difference between the pressure dependences of the spinel-olivine-orthopyroxene buffer and QFM. Mattioli and Wood (1988) describe a method by which the pressure dependence of the spinel-olivine-orthopyroxene buffer can be approximated from standard state molar volumes of the phases by assuming Mg# = 0.90 in each of the silicates and a magnetite proportion of 0.02 in spinel. The resulting coefficient $\Delta P/(2.303 - R) = 0.0567$ appears in both Wood and Virgo (1989) and Bryndzia and Wood (1990). From this, we can determine the $P/T$ coefficient in Equation 5 by subtracting the pressure dependence of the QFM buffer [$\Delta P/(2.303 - R) = 0.0936$, using the standard state molar volumes given in Robie et al. (1995)] from Equation 4.

Using Equation 6 to calculate log$f_{O_2}$ (QFM)\text{p,T} for use in Equation 5 with no pressure term leads to a 0.6 log unit underestimate of absolute $f_{O_2}$ at 1150 °C and 1 GPa. Substituting
a parameterization of QFM into Equation 5 other than that of Myers and Eugster (1983) leads to systematic errors in \( f_{O_2} \). For example, replacement with O’Neill (1987) results in a 0.15 log unit underestimation of absolute \( f_{O_2} \) at 1150 °C and 1 GPa. We avoid this confusion by using Equation 4 to calculate log(\( f_{O_2} \)) before calculating \( f_{O_2} \) relative to the QFM reference buffer. Except where otherwise indicated, we report oxygen fugacity relative to QFM using the parameterization of Frost (1991):

\[
\log f_{O_2}(QFM)_T = \frac{-25096.3}{T} + 8.735 + \frac{0.11(P-1)}{T}.
\]

We calculate magnetite activity in spinel, \( a_{Fe^{3+}}^{pl} \), using the MELTS Supplemental Calculator (Sack and Ghiorso 1991a, 1991b; http://melts.ofm-research.org/CalcForms/index.html) with a slight modification to the calculation of spinel components. We describe this modification and justify our choice of the MELTS Supplemental Calculator for calculating \( a_{Fe^{3+}}^{pl} \) in the Supplementary Material.

**Uncertainty in the \( f_{O_2} \) calculation contributed by the EPMA analysis**

Uncertainty in \( f_{O_2} \) calculated from spinel peridotite oxybarometry depends on the accuracy and precision of the three compositional variables in Equation 4, \( Mg^{#}^{Opx} \), \((X_{Fe^{3+}}^{Opx}X_{Fe^{3+}}^{Opx})^{Opx} \), and \( a_{Fe^{3+}}^{pl} \), resulting from analysis by EPMA as well as on the uncertainty in the temperature and pressure of equilibration. We estimated uncertainty contributed by the compositional terms from repeated analysis of secondary standards. The uncertainty in \( f_{O_2} \) from the olivine analysis increases with \( Mg^{#}^{Opx} \) from ±0.04 log units at \( Mg^{#}^{Opx} = 0.85 \) to ±0.14 log units at \( Mg^{#}^{Opx} = 0.95 \), and the orthopyroxene analysis contributes an additional ±0.04 log units. We provide a complete description of how these uncertainties were calculated in the Supplementary Material.

We are able to relate uncertainty in the calculation of spinel Fe\(^{3+}\)/Fe ratio to uncertainty in log(\( a_{Fe^{3+}}^{pl} \)) calculated from the MELTS Supplemental Calculator through a logarithmic relationship described in the Supplementary Material (Supplementary Fig. S4). Following Parkinson and Arculus (1999) and Ballhaus et al. (1991), Figure 9a shows the relationship between log(\( a_{Fe^{3+}}^{pl} \)) and relative \( f_{O_2} \), and Figure 9b shows how relative \( f_{O_2} \) varies with spinel Fe\(^{3+}\)/Fe ratio. The uncertainty in relative \( f_{O_2} \) contributed by the spinel analysis is asymmetrical and increases with decreasing Fe\(^{3+}\)/Fe ratio. At Fe\(^{3+}\)/Fe = 0.10 the error in \( f_{O_2} \) is (+0.3/–0.4) log units (1σ), while at Fe\(^{3+}\)/Fe = 0.35 the error is ±0.1 log units (Fig. 9b). Figure 9 also shows an error envelope for the precision of the Fe\(^{3+}\)/Fe ratio measurement with no correction (dotted lines). Uncertainty in log(\( a_{Fe^{3+}}^{pl} \)) approximately doubles for spinel analyses that have not been corrected using the W&V89 method. This is particularly important for spinels with Fe\(^{3+}\)/Fe ratios <0.10, which may have uncertainties in \( f_{O_2} \) in excess of a log unit when uncorrected.

Temperature and pressure both enter into the calculation of \( f_{O_2} \) from spinel-olivine-orthopyroxene equilibria and must be determined through thermobarometry, or some suitable temperature and pressure must be assumed. We have calculated equilibration temperatures of the Hawaiian xenoliths using the spinel-olivine Fe-Mg exchange thermometer of Li et al. (1995), and we assume a pressure of 1.5 GPa. Li et al. (1995) did not evaluate the standard error of their thermometer using an independent validation data set, so we estimated uncertainty from the standard deviation in our own measurements of the Hawaiian xenoliths. For each Hawaiian xenolith, we calculated temperatures from the average spinel composition from each analytical session (Supplementary Table S2) and the sample average olivine compositions in Table 3. The standard deviation in calculated temperature for these samples varies from 25 to 82 °C. To be conservative, we used ±80 °C as our temperature uncertainty to explore the effects of temperature error on the \( f_{O_2} \) calculation.

The effect of temperature on calculated \( f_{O_2} \) is compositionally dependent as temperature enters into the \( f_{O_2} \) calculation both explicitly in Equation 4 and in the calculation of \( a_{Fe^{3+}}^{pl} \). Increasing temperature leads to a decrease in calculated \( f_{O_2} \) relative to QFM, but this effect is greater when spinel Cr# is lower (Supplementary Fig. S5). The magnitude of uncertainty due to temperature is also a function of temperature, such that samples with colder equilibration temperatures have greater uncertainty in \( f_{O_2} \). The temperature uncertainty of ±80 °C contributes about ±0.1 log units of uncertainty to the \( f_{O_2} \) calculated for low-Cr# sample 114923-41 at its calculated equilibration temperature (1118 °C). Temperature uncertainty for a similar peridotite with
a colder equilibration temperature of 700 °C (e.g., as appropriate for supra-subduction zone peridotites; Parkinson and Pearce 1998), would contribute >0.2 log units of uncertainty to the $f_{\text{O}_2}$ calculation.

Pressure is not well constrained for spinel peridotites due to the absence of a strongly pressure dependent reaction (MacGregor 2015). It is common for spinel peridotite oxybarometry studies to assume a single pressure for the $f_{\text{O}_2}$ calculation (e.g., Bryndzia and Wood 1990; Wood et al. 1990; Ballhaus 1993). We follow Wood et al. (1990) in choosing 1.5 GPa, which is roughly the center of the pressure range of spinel stability. Log $f_{\text{O}_2}$ decreases linearly with increasing pressure (Eq. 4), and each 0.25 GPa of pressure uncertainty leads to about ±0.1 log units uncertainty in $f_{\text{O}_2}$.

**Hawaiian xenolith $f_{\text{O}_2}$**

The replicate analyses of the Hawaiian xenoliths allow for an additional check on our estimated uncertainty in the $f_{\text{O}_2}$ calculation. Figure 10 shows Fe$^{3+}$/ΣFe ratios, $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$, and $f_{\text{O}_2}$ relative to QFM calculated for each individual analysis of each of the Hawaiian spinels. We calculated $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ and $f_{\text{O}_2}$ using the spinel-olivine exchange temperature particular to each spinel analysis. For each sample, measurements of relative $f_{\text{O}_2}$ from each analytical session fall well within the estimated error from all other measurements of that sample (Fig. 10a). This broad overlap is partly due to the use of only a single measurement of olivine and orthopyroxene from each sample, eliminating two sources of potential variation. Figure 10b, which shows variation in the calculated $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ shows that error bars in log $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ for all measurements of a given sample are also overlapping. This suggests that we have suitably propagated uncertainty in spinel Fe$^{3+}$/ΣFe ratios to uncertainty in $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$. Although samples with greater spinel Fe$^{3+}$/ΣFe ratios also record greater $f_{\text{O}_2}$ relative to QFM, estimates of $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ based on independent measurements of any given sample can increase, decrease, or remain constant with increasing spinel Fe$^{3+}$/ΣFe ratio (Fig. 10b). This highlights that the temperature estimation contributes significantly to the calculation of $f_{\text{O}_2}$.

The four Hawaiian xenoliths analyzed in this study record relative oxygen fugacities between QFM+0.15 (+0.34/−0.37) and QFM+0.98 (+0.24/−0.25) (Table 5, Fig. 10) at their equilibration temperatures and 1.5 GPa, which is slightly more oxidized than the mean $f_{\text{O}_2}$ recorded by abyssal peridotites from spreading centers (Bryndzia and Wood 1990; Wood et al. 1990). These relative oxygen fugacities also depend on temperature and pressure, and the quoted uncertainties do not reflect the additional uncertainties associated with our choice of pressure and temperature. Further contextualization of these results is beyond the scope of this communication, and will be discussed along with a larger data set in a future publication.

**Comparison of the Wood (1991) and Ballhaus et al. (1991) parameterizations of the spinel peridotite oxybarometer**

Although we have chosen to use the Wood (1991) version of the spinel-olivine-orthopyroxene oxybarometer to calculate $f_{\text{O}_2}$ (Eq. 4), numerous other studies use the Ballhaus et al. (1991) version of the oxybarometer. These two parameterizations are commonly considered to be interchangeable (e.g., Woodland et al. (1991) formulations of the spinel-olivine-orthopyroxene oxybarometer. Log $f_{\text{O}_2}$ (ΔQFM; a) and log $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ (b), calculated from corrected Fe$^{3+}$/ΣFe ratios, for each session in which a given spinel was analyzed (Supplementary Table S4 and S5). The olivine and orthopyroxene compositions in Table 3 were used for all $f_{\text{O}_2}$ calculations. Uncertainty in log $f_{\text{O}_2}$ (ΔQFM) includes contributions from analytical uncertainty on each phase (a). Uncertainty in log $a_{\text{Fe}_{3}O_{4}}^{\text{pl}}$ was determined as described in the Supplementary material. Uncertainty in corrected Fe$^{3+}$/ΣFe ratios was calculated using Equation 4. Error using the Ballhaus et al. (1991) method was estimated by propagating through the Ballhaus et al. (1991) oxybarometer our estimates of uncertainty in spinel Fe$^{3+}$/ΣFe ratio and olivine Mg$^{2+}$. 

![Figure 10](image-url)
al. 1992; Ballhaus 1993; Canil et al. 2006). Herd (2008) demonstrated that relative $f_{O_2}$ calculated using the Ballhaus et al. (1991) method is systematically lower than relative $f_{O_2}$ calculated with the Wood (1991) method. Luhr and Arrańa-Gómez (1997) similarly found that $f_{O_2}$ calculated using Ballhaus et al. (1991) was on average 0.8 log units below those calculated using Wood (1991). We compare the two parameterizations in Figure 10c using the Hawaiian xenolith data. Results from the two methods are correlated ($r^2 = 0.82$). Consistent with Herd (2008), relative $f_{O_2}$ calculated using the Ballhaus et al. (1991) method is 0.7 to 1.3 log units lower than results from the Wood (1991) method. The two methods cannot be considered directly comparable, and comparisons of peridotite $f_{O_2}$ data between studies using different $f_{O_2}$ parameterizations requires that sufficient analytical data be provided to allow for recalculation using either method.

**IMPLICATIONS**

The precision of $f_{O_2}$ calculated from spinel peridotite oxybarometry is chiefly limited by the precision of the measurement of spinel $Fe^{3+}/ΣFe$ ratios. We have shown that flaws in the primary standardization are the greatest source of imprecision in spinel $Fe^{3+}/ΣFe$ ratios determined by EPMA and that maximizing the precision of spinel $Fe^{3+}/ΣFe$ ratios requires the use of correction standards with independently measured $Fe^{3+}/ΣFe$ ratios. The W&V89 correction leads to a twofold improvement in precision of $Fe^{3+}/ΣFe$ ratios for most spinels measured by EPMA, and further improvements are possible if common minor elements such as V, Co, and Zn are also analyzed.

The $f_{O_2}$ recorded by peridotites offers insight into $f_{O_2}$ conditions prevalent in Earth’s upper mantle. If spinel peridotite oxybarometry is used to detect $f_{O_2}$ variations between different tectonic environments (e.g., Ballhaus 1993) or between different samples from a local environment, then measurements that allow the $f_{O_2}$ recorded by peridotites to be calculated must be more precise than the range of $f_{O_2}$ recorded by these samples. Uncertainty in calculated $f_{O_2}$ contributed by uncorrected EPMA analyses of spinel $Fe^{3+}/ΣFe$ ratios may be greater than ±1 log units (1σ) at $f_{O_2}$ less than about QFM-1 (Fig. 9). For comparison, the entire abyssal peridotite suite of Bryndzia and Wood (1990) varies in $f_{O_2}$ by only ±0.7 log units (1σ). We recommend that future studies that present EPMA measurements of spinel $Fe^{3+}/ΣFe$ ratio use the W&V89 method, or at least include analyses of spinel standards with independently measured $Fe^{3+}/ΣFe$ ratios so that precision may be estimated. Publication of complete EPMA data sets collected on unknowns and standards should become standard practice for spinel oxybarometry studies.

We have also provided methods for quantifying the contributions to total uncertainty in calculated $f_{O_2}$ from each parameter in the oxybarometer. For spinels with relatively low $Fe^{3+}/ΣFe$ ratios, the greatest contribution to this uncertainty comes from the calculation of $Δ_{Fe^{3+}}$, which is directly tied precision of measured $Fe^{3+}/ΣFe$ ratios in spinel. This precision depends on the total concentration of Fe in the spinel and on the $Fe^{3+}/ΣFe$ ratio itself. The difference in uncertainty in calculated $f_{O_2}$ from corrected spinel analyses compared to uncorrected analyses is lower by >0.5 log units for spinels with $Fe^{3+}/ΣFe$ ratios < 0.10.

Several studies have found evidence for differences in $f_{O_2}$ recorded by peridotites from different tectonic environments. Wood et al. (1990) found that the average $f_{O_2}$ recorded by continental xenoliths was about one order of magnitude greater than the average of abyssal peridotites (QFM-1: Bryndzia and Wood 1990). Ballhaus (1993) found that xenoliths from OIB localities were also on average about one log unit more oxidized than abyssal peridotites. Parkinson and Arculus (1999) showed that subduction-related peridotites record average $f_{O_2}$ of approximately QFM+1, about 2 log units more oxidized than abyssal peridotites. These differences of 1–2 log units are small enough that uncorrected EPMA data or calculations of $f_{O_2}$ using different formulations, may be too imprecise to resolve them.

Analysis of peridotite $f_{O_2}$ provides an alternative perspective on the $f_{O_2}$ prevalent in different upper mantle settings that complements the variations in $f_{O_2}$ revealed by analyses of basaltic glasses (Kelley and Cottrell 2012). In tectonic settings where $f_{O_2}$ has been estimated from both peridotites and glasses the results can be incongruent, which may indicate that, in addition to inherent differences between tectonic settings, $f_{O_2}$ records are subject to petrological processes in the upper mantle (e.g., Birner et al. 2016). For example, abyssal peridotites suggest a MORB source region with average $f_{O_2}$ of QFM-1 (Bryndzia and Wood 1990), but MORB glasses suggest a more oxidized MORB source with average $f_{O_2}$ of QFM (Cottrell and Kelley 2011). Future measurements of $f_{O_2}$ of mid-ocean ridge peridotites will need to use the W&V89 correction to achieve sufficient precision to allow an investigation of the potential petrological causes for this incongruence.

Finally, the greatest advantage that EPMA holds over Mössbauer analysis is that it allows spinel $Fe^{3+}/ΣFe$ ratios to be easily measured at the micrometer scale. As we try to connect $f_{O_2}$ measurements in peridotites to petrological processes, it may become necessary to investigate variations in spinel $Fe^{3+}/ΣFe$ ratios at the grain scale. Changes in the $Fe^{3+}/ΣFe$ ratio between spinel cores and rims, for example, can be observed by accurate and precise EPMA measurements.

**ACKNOWLEDGMENTS**

The authors thank Bernard Wood for providing spinel samples. We thank Leslie Hale for assisting with access to the Hawaiian xenolith samples from the National Rock and Ore Collection at the National Museum on Natural History (NMNH) in Washington, D.C. Chris MacLeod and Sherm Bloomer are thanked for providing access to the Tonga sample. We also wish to thank Tim Gooding and Tim Rose for assistance with sample preparation and for providing expertise and maintaining the electron microprobe lab at NMNH. This paper was improved by constructive reviews from B. Wood and an anonymous reviewer. F.D. received support from the Smithsonian Peter Buck Fellowship. S.B. received support from the Stanford Graduate Fellowship and McGee Grant. O.L. received support from the Natural History Research Experiences NSF REU program (EAR-1062692). We gratefully acknowledge funding from NSF award OCE-1433212 (to E.C.) and OCE-1454199 (to J.W.).

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Manuscript accepted august 29, 2016
Manuscript received april 23, 2016
Manuscript handled by M. Darby Dyar