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## <sup>57</sup>Fe Mössbauer spectroscopy analysis of spinels: Fe<sup>3+</sup>/Fe<sub>tot</sub> quantification accuracy and consequences on *f*<sub>O<sub>2</sub></sub> estimate

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**ABSTRACT.** — In this study spinel data from literature were treated in order to highlight the influence of Fe<sup>3+</sup>/Fe<sub>tot</sub> quantification accuracy on estimate of upper mantle *f*<sub>O<sub>2</sub></sub>. Particular regard was given to the importance of using recoil-free fraction *f* on Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios quantification derived from <sup>57</sup>Fe Mössbauer spectroscopy analysis (MS). For this aim Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios obtained by <sup>57</sup>Fe Mössbauer spectroscopy at 298 K (*RT*) were corrected with *f* values calculated by De Grave and Van Alboom (1991). Uncorrected and corrected Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios allowed to calculate *f*<sub>O<sub>2</sub></sub> by using oxygen geobarometric method. Oxygen fugacities derived by the uncorrected ratios are revealed systematically higher than those derived by corrected ones, with a difference up to 0.7 log *f*<sub>O<sub>2</sub></sub> units. By using chemical data from two literature works it was highlighted that *f*<sub>O<sub>2</sub></sub> overestimate is not dependent neither on rock chemical composition nor on the equilibrium phases involved in the calculation, but only on the Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios quantification accuracy.

**RIASSUNTO.** — In questo studio sono stati elaborati dati di letteratura relativi agli spinelli, in modo da far

risaltare l'influenza dell'accuratezza della quantificazione di Fe<sup>3+</sup>/Fe<sub>tot</sub> sulla stima di *f*<sub>O<sub>2</sub></sub> del mantello superiore. Particolare attenzione è stata posta all'utilizzo della frazione di atomi senza rinculo *f* sulla quantificazione dei rapporti Fe<sup>3+</sup>/Fe<sub>tot</sub> ottenuti mediante analisi spettroscopica Mössbauer <sup>57</sup>Fe (MS). Per questo scopo i rapporti Fe<sup>3+</sup>/Fe<sub>tot</sub> ottenuti mediante spettroscopia Mössbauer <sup>57</sup>Fe a 298 K (*RT*) sono stati corretti con i valori di *f* calcolati da De Grave e Van Alboom (1991). I rapporti Fe<sup>3+</sup>/Fe<sub>tot</sub> corretti e gli stessi rapporti non corretti hanno permesso di calcolare la *f*<sub>O<sub>2</sub></sub> mediante metodo geobarometrico per l'ossigeno. Le fugacità d'ossigeno derivate da rapporti non corretti si sono rivelate sistematicamente più alte di quelle derivate da rapporti corretti, con una differenza di valori di *f*<sub>O<sub>2</sub></sub> fino a 0,7 unità logaritmiche. Attraverso l'utilizzo di dati chimici provenienti da due lavori di letteratura è stato evidenziato che la sovrastima di *f*<sub>O<sub>2</sub></sub> non dipende né dalla composizione chimica della roccia né dalle fasi coinvolte nel calcolo all'equilibrio, ma dall'accuratezza nella quantificazione dei rapporti Fe<sup>3+</sup>/Fe<sub>tot</sub>.

**KEY WORDS:** *Spinel, Mössbauer spectroscopy, Fe<sup>3+</sup>/Fe<sub>tot</sub> quantification, oxygen fugacity, geothermobarometry.*

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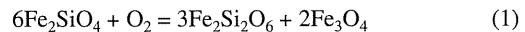
## INTRODUCTION

Spinel group minerals have general formula  $T(A_{1-i} B_i)M(A_i B_{2-i})O_4$ , cubic close packing structure,  $Fd\bar{3}m$  space group. In each unit cell, 8 of the 64 tetrahedral sites (T) and 16 of 32 octahedral sites (M) are occupied by divalent and trivalent A and B cations, respectively, and the parameter  $i$  accounts for cation disorder. In the  $(Mg, Fe^{2+})(Al, Fe^{3+}, Cr)_2O_4$  system, Mg, Fe and Al are disordered between T and M sites, whereas Cr is ordered in M site, due to its octahedral site preference energy (O'Neill and Navrotsky, 1984). Spinel mineral group exhibits a wide range of solid solutions, the thermodynamics of which has been extensively studied (Mattioli and Wood, 1988; Sack and Ghiorso, 1991). Compositions of spinels belonging to igneous and metamorphic rocks are closely related to different tectonic settings (Dick and Bullen, 1984). Spinel is generally associated with upper mantle derived rocks, as peridotites and serpentinites. They usually belong to ophiolitic sequences and are considered to be valuable petrogenetic indicators of the formation environment (Sack, 1982; Dick and Bullen, 1984; Sack and Ghiorso, 1991). Several studies were carried out to obtain estimates of intensive parameters  $T$ ,  $P$ , oxygen fugacity ( $f_{O_2}$ ), their changes in the geological setting, and host rocks chemical evolution (Irvine, 1967; Evans and Frost, 1975). In particular, Fe-spinels find importance for estimate of the upper mantle oxidation state and its variations with time and space, which are among the most important petrologic problems. This results from the fact that the composition of the fluid phases attending magmatic and metasomatic processes strongly depends on the oxidation state, and this may substantially affect the nature of primary melts. It is generally accepted that mantle fluids are dominated by the C-H-O system, given the common occurrence of carbonaceous material in mantle peridotites (Mathez *et al.*, 1984). Consequently,  $f_{O_2}$  either controls or reflects the composition of any volatile phase inside this system. Therefore, the fluids consist mainly of

$CO_2$  and  $H_2O$  under relatively oxidizing conditions close to fayalite-magnetite-quartz (FMQ) buffer,  $H_2O$  and  $CH_4$  under moderately oxidizing condition between FMQ and iron-wustite (IW) buffer, and  $CH_4$  below IW (Wood and Virgo, 1989).

There are currently two methods for the quantitative estimate of upper mantle oxidation state: experimental by electrochemical measurements of the intrinsic oxygen fugacity (Ulmer *et al.*, 1976; Arculus and Delano, 1981; Arculus *et al.*, 1984) and geothermobarometric one considering equilibrium among phases of variable  $Fe^{3+}/Fe_{tot}$  ratios. Spinel potentially contribute to latter method and many models involving spinel phase are proposed for both temperature estimate (Roeder *et al.*, 1979; Fabriès, 1979; O'Neill and Wall, 1987; Ballhaus *et al.*, 1991) and oxygen fugacity estimate of the upper mantle (Mattioli and Wood, 1986; O'Neill and Wall, 1987; Wood *et al.*, 1990; Ballhaus *et al.*, 1990; Ballhaus *et al.*, 1991).

Geothermometric and oxygen geobarometric models are generally based on heterogeneous equilibrium as follows:



The estimate of  $f_{O_2}$  is given through quantification of  $Fe^{3+}/Fe_{tot}$  ratio and experimentally calibrated activity-composition relationships of equilibrium mineral phases, at given pressure-temperature conditions. Nevertheless, small errors in the  $Fe^{3+}/Fe_{tot}$  ratio measurements were proved to produce large errors in  $f_{O_2}$  estimate (Wood and Virgo, 1989). Electron microprobe analysis (EMPA) is commonly used to investigate mineral composition, but this technique cannot determine multiple oxidation states of transition metals, and an indirect quantification of  $Fe^{3+}/Fe_{tot}$  ratio by EMPA is affected by large systematic errors.  $^{57}Fe$  Mössbauer spectroscopy (MS) is the most reliable method to investigate iron oxidation state in minerals. An important and frequent application of this method is the determination of highly accurate  $Fe^{3+}/Fe_{tot}$  ratios and the attribution of  $Fe^{2+}$  and  $Fe^{3+}$  to structural sites.

### Calculation of Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios

<sup>57</sup>Fe Mössbauer spectroscopy gives Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios by measuring absorption areas of Fe<sup>2+</sup> and Fe<sup>3+</sup> subspectra. These areas are proportional to the product of the number of absorption nuclei times the recoil-free fraction *f*. The *f* factor is determined by lattice vibrations of the probe atoms and then may suffer for temperature influence (Sawatzky *et al.*, 1969; De Grave and Van Alboom, 1991; Eeckhout and De Grave, 2003). Moreover, *f* factors for Fe<sup>2+</sup> (*f*<sub>2</sub>) and Fe<sup>3+</sup> (*f*<sub>3</sub>) are not equal, but, in spite this, are commonly assumed to be equal at room temperature (*RT*) for a given compound. De Grave and Van Alboom (1991) according to measurements on many phases of known composition, noticed that the assumption of equality of *f*<sub>2</sub> and *f*<sub>3</sub> would cause an error of about 15% in Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio for *RT* spectra, leading to an overestimate of Fe<sup>3+</sup> content. On the contrary, the difference between *f*<sub>2</sub> and *f*<sub>3</sub> values, was found to be negligible at low temperature (*LT*).

In absence of *LT* data, it is possible to minimize systematic errors due to temperature by applying empiric, correction factors to *RT* data. In this work, the Fe<sup>3+</sup>/Fe<sub>tot</sub> and Fe<sup>2+</sup>/Fe<sub>tot</sub> ratios derived from spectral areas, Fe<sup>3+</sup><sub>MS</sub> and Fe<sup>2+</sup><sub>MS</sub> respectively, were corrected to new ratios, (Fe<sup>3+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup> and (Fe<sup>2+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup> respectively, as described below:

$$\frac{\text{Fe}^{3+}_{MS}/\text{Fe}^{2+}_{MS} \times (1/C)}{(\text{Fe}^{3+}/\text{Fe}_{tot})^{\text{Corr}}/(\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}}} = \quad (2)$$

with the *C* factor defined as *f*<sub>3</sub>/*f*<sub>2</sub> by Dyar *et al.* (1993).

From Eqn (2) it derives that

$$\frac{(\text{Fe}^{3+}/\text{Fe}_{tot})^{\text{Corr}}}{\text{Fe}^{3+}_{MS}/\text{Fe}^{2+}_{MS} \times (1/C) \times (\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}}} = \quad (3)$$

Since

$$(\text{Fe}^{3+}/\text{Fe}_{tot})^{\text{Corr}} = 100 - (\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}} \quad (4)$$

the substitution of (Fe<sup>3+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup> into Eqn (3) yields

$$100 - (\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}} = \frac{\text{Fe}^{3+}_{MS}/\text{Fe}^{2+}_{MS} \times (1/C) \times (\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}}}{\text{Fe}^{3+}_{MS}/\text{Fe}^{2+}_{MS} \times (1/C) \times (\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}}} \quad (5)$$

so that

$$\frac{(\text{Fe}^{2+}/\text{Fe}_{tot})^{\text{Corr}}}{100 / [(\text{Fe}^{3+}_{MS}/\text{Fe}^{2+}_{MS} \times 1/C) + 1]} = \quad (6)$$

and (Fe<sup>3+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup> is obtained from Eqn (4).

## RESULTS

In order to evaluate the influence of iron quantification accuracy on calculated *f*<sub>O<sub>2</sub></sub>, chemical data from literature were considered. In particular, the work of Votyakov *et al.* (1998) was considered, because iron quantification for spinel was obtained by Mössbauer spectroscopy at *RT* condition with *f* factors for Fe<sup>2+</sup> (*f*<sub>2</sub>) and Fe<sup>3+</sup> (*f*<sub>3</sub>) assumed to be equal. In the present study, data of Votyakov *et al.* (1998) were corrected with *f* factors calculated by De Grave and Van Alboom (1991) for *RT* conditions: *f*<sub>2</sub> = 0.687 and *f*<sub>3</sub> = 0.887. The application of De Grave and Van Alboom (1991) corrections led to new Fe<sup>3+</sup>/Fe<sub>tot</sub> ratios, (Fe<sup>3+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup>, that are listed in Table 1. Notably, Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios obtained from *RT* spectra corrected with *f* factors differ by about 30% relative to those directly evaluated from the spectral areas. In order to quantify changes in iron contents derived from the use of correction factors, EMPA data were elaborated with (Fe<sup>3+</sup>/Fe<sub>tot</sub>)<sup>Corr</sup> ratios. As a consequence, a systematic decrease of Fe<sup>3+</sup> contents was highlighted (Table 1 and Fig. 1).

In order to evaluate the influence of Fe changes on *f*<sub>O<sub>2</sub></sub> estimate, rock chemical data of the same samples were used to calculate *f*<sub>O<sub>2</sub></sub> by using oxygen geobarometric method. Chemical data of Votyakov *et al.* (1998) samples were introduced into the oxygen geobarometric model of Ballhaus *et al.* (1990). This model works for spinel-olivine assemblages and was proved to be reliable for its applicability to the entire spectrum of spinel compositions (see appendix 1). Olivine data and spinel uncorrected data

TABLE 1

$Fe^{3+}/Fe_{tot}$  ratio and  $Fe^{3+}$  content (apfu) for literature spinel samples:  $Fe^{3+}/Fe_{tot}$  = ratio resulted from MS uncorrected data,  $Fe^{3+}$  = content derived from EMPA + MS uncorrected data,  $(Fe^{3+}/Fe_{tot})^{Corr}$  = ratio resulted from MS corrected data,  $(Fe^{3+})^{Corr}$  = content derived from EMPA + MS corrected data.

| Sample provenance work        | Rock including spinel sample | $Fe^{3+}/Fe_{tot}$ | $Fe^{3+}$ | $(Fe^{3+}/Fe_{tot})^{Corr}$ | $(Fe^{3+})^{Corr}$ |
|-------------------------------|------------------------------|--------------------|-----------|-----------------------------|--------------------|
| Votyakov <i>et al.</i> (1998) | 422                          | 0.17               | 0.056     | 0.14                        | 0.046              |
|                               | 481                          | 0.18               | 0.103     | 0.15                        | 0.086              |
|                               | 517                          | 0.25               | 0.072     | 0.21                        | 0.061              |
|                               | 7641                         | 0.20               | 0.146     | 0.16                        | 0.117              |
| Wood and Virgo (1989)         | KLB8311                      | 0.21               | 0.076     | 0.17                        | 0.062              |
|                               | KLB8316                      | 0.25               | 0.091     | 0.21                        | 0.076              |
|                               | MBR8307                      | 0.25               | 0.067     | 0.21                        | 0.056              |
|                               | MBR8309                      | 0.29               | 0.075     | 0.24                        | 0.063              |

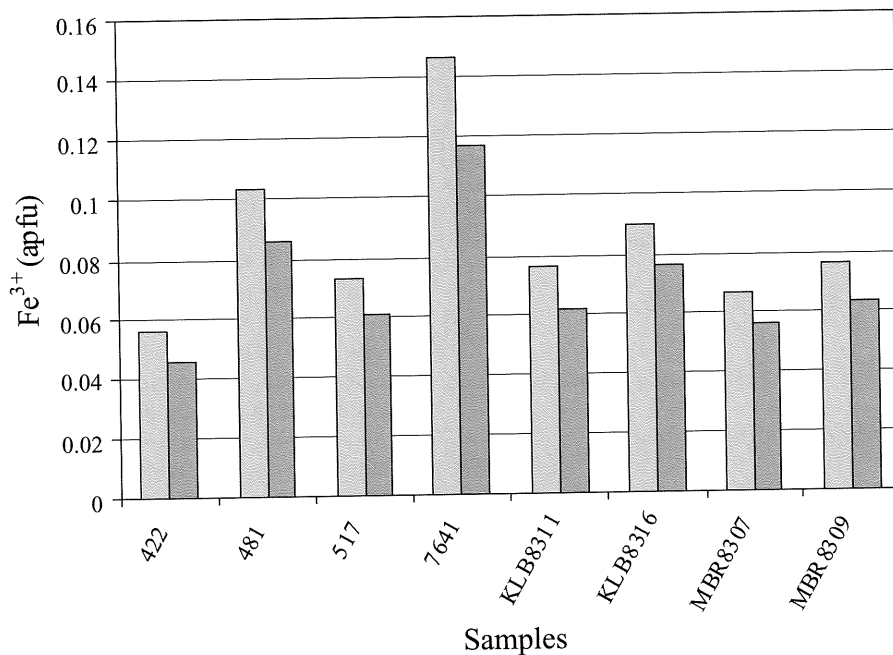


Fig. 1 – Comparison between the two sets of spinel  $Fe^{3+}$  contents (in atoms per formula unit, apfu) for literature samples: light grey columns =  $Fe^{3+}$  contents from uncorrected, room temperature MS data; dark grey columns =  $Fe^{3+}$  contents from corrected MS data.

were introduced into the model at  $T = 1273$  K and  $P = 1.5$  GPa and a first set of  $f_{O_2}$  was obtained. Then, spinel data corrected with  $f$  factors were re-introduced into the model at the same  $T$ - $P$  conditions and a second set of  $f_{O_2}$  was obtained. Both oxygen fugacity sets obtained were calculated in terms of  $\Delta \log (f_{O_2})_{FMQ}$  and results are listed in Table 2. Oxygen fugacities derived by using spinel corrected data are systematically lower than those derived by using spinel uncorrected data with an average difference of 0.5 and a maximum difference of 0.7 log ( $f_{O_2}$ ) units (Fig. 2).

A second set of literature data, spinel-olivine-pyroxene assemblages from Wood and Virgo (1989), was also considered. Also in Wood and Virgo (1989) iron quantification for spinel was obtained by Mössbauer spectroscopy at  $RT$  condition with  $f_2$  and  $f_3$  assumed to be equal. Wood and Virgo (1989) MS corrected data were elaborated following the previously described procedure and results are shown in Table 1. Also in this case a systematic decrease of Fe<sup>3+</sup> contents was highlighted (Fig. 1). Chemical data of Wood and Virgo (1989) samples were then introduced into the oxygen geobarometric model of Mattioli and Wood (1988), that works for spinel-olivine-pyroxene assemblages, and was

proved to be reliable for rock samples with low chromium concentration (see appendix 1). Chemical data of olivine, spinel and pyroxene were introduced into the model at  $T = 1273$  K and  $P = 15000$  bars and a first set of  $f_{O_2}$  was obtained. Then, spinel data corrected with  $f$  factors were re-introduced into the model at the same  $T$ - $P$  conditions and a second set of  $f_{O_2}$  was obtained. Both oxygen fugacity sets were calculated in terms of  $\Delta \log (f_{O_2})_{FMQ}$  and results are listed in Table 2. Also in this case, oxygen fugacities derived from spinel corrected data are systematically lower than those derived from spinel uncorrected data, with a constant difference of 0.5 log ( $f_{O_2}$ ) units (Fig. 2).

A further investigation by using the same literature works samples was done in order to evaluate the influence of iron quantification on equilibrium temperature calculated by thermometric method. Chemical data of both Votyakov *et al.* (1998) and Wood and Virgo (1989) samples were introduced into the geothermometer of Ballhaus *et al.* (1991) at a pressure of 1.5 GPa and a first set of temperatures was obtained. Spinel data were then corrected with  $f_2$  and  $f_3$  factors and re-introduced into the model at the same pressure condition. A second set of equilibrium temperatures was obtained. The two

TABLE 2

Results of oxygen fugacity in terms of  $\Delta \log (f_{O_2})_{FMQ}$  values for literature rock samples.

$\Delta \log (f_{O_2})_{FMQ}$  is calculated by using spinel  $Fe^{3+}/Fe_{tot}$  ratios;  
 $\Delta \log (f_{O_2})_{FMQ}^*$  is calculated by using spinel  $(Fe^{3+}/Fe_{tot})^{Corr}$  ratios.

| Sample provenance work        | Sample  | $\Delta \log (f_{O_2})_{FMQ}$ | $\Delta \log (f_{O_2})_{FMQ}^*$ | Oxygen geobarometer           |
|-------------------------------|---------|-------------------------------|---------------------------------|-------------------------------|
| Votyakov <i>et al.</i> (1998) | 422     | -0.2                          | -0.9                            | Ballhaus <i>et al.</i> (1990) |
|                               | 481     | +0.4                          | 0.0                             |                               |
|                               | 517     | +0.1                          | -0.3                            |                               |
|                               | 7641    | +1.5                          | +1.0                            |                               |
| Wood and Virgo (1989)         | KLB8311 | +0.5                          | 0.0                             | Mattioli and Wood (1988)      |
|                               | KLB8316 | +0.9                          | +0.4                            |                               |
|                               | MBR8307 | +1.1                          | +0.6                            |                               |
|                               | MBR8309 | +1.1                          | +0.6                            |                               |

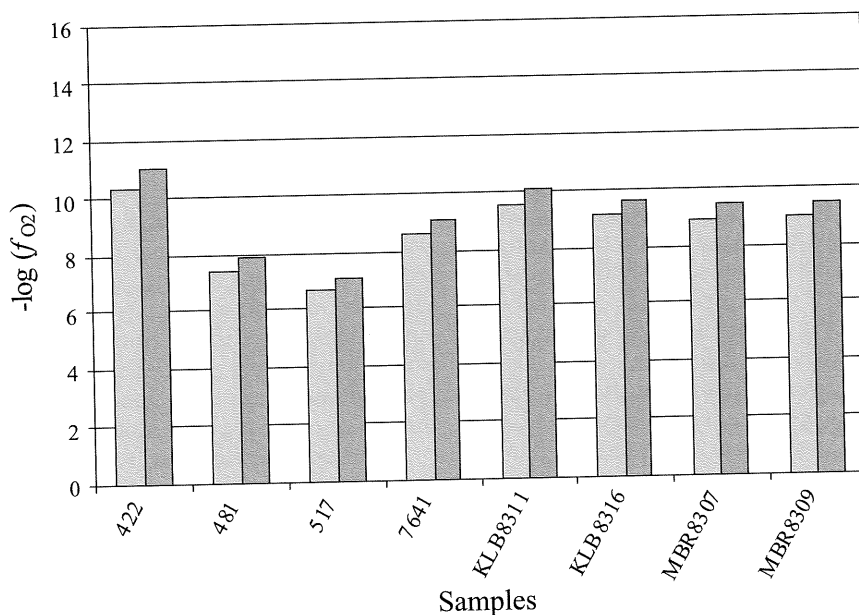


Fig. 2 – Comparison between the two sets of oxygen fugacities obtained for literature samples: light grey columns =  $-\log(f_{O_2})$  values calculated by using the spinel uncorrected  $Fe^{3+}$  contents; dark grey columns =  $-\log(f_{O_2})$  values calculated by using the spinel corrected  $Fe^{3+}$  contents.

equilibrium temperature sets revealed to be very similar for all samples considered. This result allowed to ascertain the small influence of iron quantification accuracy on the equilibrium temperature estimate.

#### CONCLUSIONS

In this work it was highlighted that errors on  $Fe^{3+}/Fe_{tot}$  ratios quantification accuracy should be taken into account since they may produce errors on mantle parameters evaluation and could seriously affect petrologic interpretations. In fact, this study allowed to quantify systematic errors due to the assumption of equality of recoil-free fraction  $f$  for  $Fe^{2+}$  and  $Fe^{3+}$  for spectra collected at  $RT$  condition and to verify its affection on mantle parameters estimate by using geothermobarometric models.  $Fe^{2+}/Fe^{3+}$  ratios corrected with  $f$  factors differ by about 30%

with respect to those directly evaluated from the spectral areas.  $Fe^{2+}/Fe^{3+}$  uncorrected ratios, in fact, lead to a constant  $Fe^{3+}$  overestimate that affects results by a systematic error. Oxygen fugacities derived by uncorrected data revealed to be systematically higher than those derived by corrected data with an average difference of 0.5  $\log f_{O_2}$  units. However, it must be remembered that  $Fe^{2+}$  and  $Fe^{3+}$  contents obtained from Mössbauer spectra collected at liquid nitrogen temperature do not suffer from  $f$  factors effect. These contents, and  $f_{O_2}$  values derived from them, can therefore be considered reliable. Furthermore, by using data from two literature works it was highlighted that  $f_{O_2}$  overestimate is not dependent neither on rock chemical composition nor on the equilibrium phases involved in the calculation, but only on  $Fe^{3+}/Fe_{tot}$  ratios quantification accuracy. On the contrary, the two equilibrium temperature sets revealed to be very similar for all samples so that it was possible to affirm that iron

quantification accuracy has a small influence on equilibrium temperature estimate.

$$a^{Ol}(\text{Fe}_2\text{SiO}_4) = \frac{X^{Ol}(\text{Fe}_2\text{SiO}_4)}{(X^{Ol}(\text{Fe}_2\text{SiO}_4))^2} \exp[(1006 (X^{Ol}(\text{Mg}_2\text{SiO}_4))^2/T] \quad (8)$$

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$$a^{Opx}(\text{Fe}_2\text{Si}_2\text{O}_6) = (X^{M1}_{\text{Fe}} \times X^{M2}_{\text{Fe}})^{Opx} \quad (9)$$

where in Eqn (8)  $X^{Ol}(\text{Fe}_2\text{SiO}_4)$  and  $X^{Ol}(\text{Mg}_2\text{SiO}_4)$  refer to mole fractions of  $\text{Fe}_2\text{SiO}_4$  and  $\text{Mg}_2\text{SiO}_4$  in olivine, and in Eqn (9)  $X^{M1}_{\text{Fe}}$  and  $X^{M2}_{\text{Fe}}$  are the atomic fractions of iron in the orthopyroxene M1 and M2 sites.

In the composition range of 0.01 to 0.10  $X^{\text{Sp}}(\text{Fe}_3\text{O}_4)$ , magnetite activities are then given by

$$a^{\text{Sp}}(\text{Fe}_3\text{O}_4) = -0.0299 X^{\text{Sp}}(\text{Fe}_3\text{O}_4) + 2.878 [X^{\text{Sp}}(\text{Fe}_3\text{O}_4)]^2 + 206.9 [X^{\text{Sp}}(\text{Fe}_3\text{O}_4)]^3 - 1463 [X^{\text{Sp}}(\text{Fe}_3\text{O}_4)]^4 + 2843 [X^{\text{Sp}}(\text{Fe}_3\text{O}_4)]^5 \quad (10)$$

Resulting oxygen fugacity is calculated as follows:

$$\log (f_{\text{O}_2})_{P,T} = -24222/T + 8.64 - 6 a^{Ol}(\text{Fe}_2\text{SiO}_4) + 3 a^{Opx}(\text{Fe}_2\text{Si}_2\text{O}_6) - 2\log a^{\text{Sp}}(\text{Fe}_3\text{O}_4) + 0.00567P/T \quad (11)$$

where  $T$  is in K and  $P$  in bars.

The thermometer of Ballhaus *et al.* (1991) consists of a simplified and improved version of the O'Neill and Wall (1987) model and was verified to give accurate results for equilibrium involving olivine and spinel phases (Ballhaus *et al.*, 1991; Votyakov *et al.*, 1998). Equilibrium temperature is given by

$$T = [(6530 + 280P + 7000 + 108P)(1 - 2 X^{Ol}(\text{Fe}) - 1960 (X^{\text{Sp}}(\text{Mg}) - X^{\text{Sp}}(\text{Fe}^{2+}) + 16150 X^{\text{Sp}}(\text{Cr}) + 25150 (X^{\text{Sp}}(\text{Fe}^{2+}) + \text{Ti}) / [\text{R} \ln K_D + 4705]) \quad (12)$$

Where  $T$  is in K,  $P$  in GPa,  $X^{\text{Sp}}(\text{Mg})$  is the  $\text{Mg}/(\text{Fe}^{2+} + \text{Mg})$  cation ratio in spinel,  $X^{\text{Sp}}(\text{Cr})$  is the  $\text{Cr}/\Sigma\text{R}^{3+}$  ratio in spinel,  $\text{Ti}$  is the titanium cations in spinel to four oxygens,  $K_D$  the ratio  $[X^{Ol}(\text{Mg}) \times X^{\text{Sp}}(\text{Fe}^{2+}) / X^{Ol}(\text{Fe}) \times X^{\text{Sp}}(\text{Mg})]$  with  $X^{Ol}(\text{Mg})$  the  $\text{Mg}/(\text{Fe}^{2+} + \text{Mg})$  cation ratio in olivine and all other notation as above.

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#### APPENDIX I

##### Geothermobarometers used

The olivine-spinel oxygen geobarometer proposed by Ballhaus *et al.* (1990) is demonstrated to be good for the reduced number of parameters occurring in calculations and its applicability to the entire spectrum of spinel compositions occurring in mantle rocks and mantle-derived melts at temperatures as low as 800°C. Ballhaus *et al.* (1990) made a comparison between  $f_{\text{O}_2}$  values retrieved by using various models (Wood *et al.*, 1990; Mattioli and Wood, 1988; O'Neill and Wall, 1987; Ballhaus *et al.*, 1990). Application of different models to spinel peridotite xenoliths worldwide showed similar but not equal results in terms of  $\log f_{\text{O}_2}$  units from FMQ buffer. Oxygen fugacity values obtained by using Ballhaus *et al.* (1990) model were demonstrated to be intermediate with respect to those obtained by using other models. Oxygen fugacity is calculated relatively to the FMQ buffer (O'Neill, 1987) as follows:

$$\Delta \log (f_{\text{O}_2})_{P,T} = 0.27 + 2.505/T - 400 P/T - 6\log X^{Ol}(\text{Fe}) - 3.200(1 - [X^{Ol}(\text{Fe})])^2/T + 2\log X^{\text{Sp}}(\text{Fe}^{2+}) + 4\log X^{\text{Sp}}(\text{Fe}^{3+}) + 2.630 [X^{\text{Sp}}(\text{Al})]^2/T \quad (7)$$

where  $T$  is in K,  $P$  in GPa,  $X^{Ol}(\text{Fe})$  is the  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$  cation ratio in olivine,  $X^{\text{Sp}}(\text{Fe}^{2+})$  is the  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$  cation ratio in spinel,  $X^{\text{Sp}}(\text{Fe}^{3+})$  and  $X^{\text{Sp}}(\text{Al})$  are the  $\text{Fe}^{3+}/\Sigma\text{R}^{3+}$  and  $\text{Al}/\Sigma\text{R}^{3+}$  ratios in spinel respectively ( $\Sigma\text{R}^{3+}$  is the total content of trivalent ions).

The olivine-spinel-pyroxene oxygen geobarometer proposed by Mattioli and Wood (1988) requires a projection from the complex spinel system onto the simple  $\text{MgAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$  binary join. Even if compositional restrictions must be counted, the model is considered reliable at low chromium concentration, where magnetite activity results a very strong function of  $X^{\text{Sp}}(\text{Fe}_3\text{O}_4)$ , that is the end-member magnetite mole fraction (Wood and Virgo, 1989). Activities of  $\text{Fe}_2\text{SiO}_4$  in olivine and activities of  $\text{Fe}_2\text{Si}_2\text{O}_6$  in orthopyroxene are given by

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