1 Spinel-Olivine-Pyroxene Equilibrium Iron Isotopic Fractionation 2 and Applications to Natural Peridotites

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20 **Keywords:** Iron, Isotopes, Redox, Spinel, NRIXS, Geothermometer

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22 In Prep. for *Geochimica et Cosmochimica Acta*

24 Abstract

25 Eight spinel-group minerals were synthesized by a flux-growth method
26 producing spinels with varying composition and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios. The mean force
27 constants of iron bonds in these minerals were determined by synchrotron
28 Nuclear Resonant Inelastic X-ray Scattering (NRIXS) in order to determine the
29 reduced isotopic partition function ratios (β -factors) of these spinels. The mean
30 force constants are strongly dependent on the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the spinel but are
31 independent, or weakly dependent on other structural and compositional
32 parameters. From our spectroscopic data, it is found that a single redox-
33 dependent calibration line accounts for the effects of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ on the β -factors of
34 spinels. This calibration successfully describes the equilibrium Fe isotopes
35 fractionation factors between spinels and silicates (olivine and pyroxenes). Our
36 predictions are in excellent agreement with independent determinations for the
37 equilibrium Fe isotopic fractionations for the magnetite-fayalite and the
38 magnetite-hedenbergite couples. Our calibration applies to the entire range of
39 $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios found in natural spinels and provides a basis for interpreting iron
40 isotopic variations documented in mantle peridotites. Except for a few exceptions,
41 most of the samples measured so far are in isotopic disequilibrium, reflecting
42 metasomatism and partial melting processes.

43 1. Introduction

44 Partitioning of ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron between different minerals
45 and melts can control redox conditions in igneous rocks. For example, the oxygen
46 fugacity ($f\text{O}_2$) of lithospheric mantle xenoliths decreases with the depth of provenance
47 (Woodland et al., 2003; McCammon and Kopylova, 2004; Yaxley et al., 2012), which
48 reflects the increasing abundance with depth of Fe^{3+} -bearing garnet that limits the
49 availability of oxygen for other redox-sensitive elements (Rorhbach et al., 2007; Stagno
50 et al., 2013). In other instances, iron partitioning between minerals can be used to trace
51 P-T- $f\text{O}_2$ conditions. For example, the olivine-spinel (O'Neill and Wall, 1987; Ballhaus et
52 al., 1991) and the orthopyroxene-spinel (Liermann and Ganguly, 2002, 2007) Fe-Mg
53 exchange reactions are well-established geothermometers, while the olivine-spinel-
54 orthopyroxene assemblage is frequently used as an oxybarometer (O'Neill and Wall,
55 1987; Wood, 1990).

56 The widespread occurrence and large compositional range of the spinel group
57 make it an important petrogenetic tracer. In addition to mineral-mineral partitioning,
58 the distribution of cations between different crystallographic sites within spinel has
59 been proposed as a potential geothermometer (*e.g.*, Della Giusta et al., 1996; Lucchesi et
60 al., 1998; Harrison et al., 1998; Uchida et al., 2005). Typically, the structure of spinel is
61 made up by a cubic close-packed array of oxygen atoms surrounding tetrahedral (T) and
62 octahedral (M) sites. In the so-called 2-3 spinels (studied here), these two non-
63 equivalent cation sites accommodate a large variety of divalent A cations (commonly
64 Mg, Fe^{2+}) and trivalent B cations (commonly Al, Fe^{3+} , Cr). The ideal configuration is
65 simply that A cations occupy T sites and B cations occupy M sites. However, this
66 configuration ($^{\text{IV}}(\text{A})^{\text{VI}}(\text{B})_2\text{O}_4$) is rarely obeyed. Some degree of octahedral-tetrahedral
67 disorder (degree of inversion) is generally observed: A in M sites and B in T sites.

68 Several studies reported that the degree of inversion strongly depends on the thermal
69 history of the spinels (O'Neill and Navrotsky, 1983; 1984; Andreozzi et al., 2001;
70 Andreozzi and Lucchesi, 2002). However, as the bulk composition of spinels exerts a
71 major control on this distribution, its use to derive thermal history is not
72 straightforward.

73 The Mg and Fe isotopic composition of spinels is emerging as a new petrogenetic
74 tracer. Young et al. (2009) and Liu et al. (2011) found significant Mg isotope
75 fractionation between olivine and spinel in mantle xenoliths that they showed scaled
76 with equilibration temperature. These results were then confirmed by both theoretical
77 (Schauble, 2011) and experimental (Macris et al., 2013) studies. The Fe isotope
78 composition of spinel group minerals (lato sensu, including the *ülvospinel*-magnetite
79 series) has also been the focus of much attention but data interpretation of spinel-
80 olivine and spinel-pyroxene fractionations are less straightforward than for Mg isotopes
81 (Beard and Johnson, 2004; Williams et al., 2004; 2005; Zhao et al., 2010; 2014) because
82 iron has multiple oxidation states. Interestingly, Williams et al. (2004; 2005) reported
83 correlations between the Fe isotope signatures of both clinopyroxenes and spinels with
84 several geochemical indices of melt extraction and oxidation, suggesting that iron
85 isotopic fractionation could be used as an oxybarometer. However, in those studies, the
86 effects of late disturbance and metasomatism on mineral-spinel Fe isotopic
87 fractionations, as initially described by Beard and Johnson (2004), could not be reliably
88 estimated.

89 Another limitation of the use of Fe isotopes as a thermo-oxybarometer is the lack
90 of mineral-spinel equilibrium fractionation factors for Fe isotopes. Only few
91 experimental and theoretical data are available. Polyakov and Mineev (2000)
92 demonstrated that the valence state of iron affects the reduced isotopic partition

function ratios (referred below as β -factor) of spinels. This implies that, all other things being equal during mineral-spinel equilibration, heavy Fe isotopes concentrate preferentially into Fe³⁺-bearing spinels. Shahar et al. (2008) studied the particular case of the equilibrium fractionation between fayalite and magnetite and found that magnetite is indeed enriched in heavy Fe isotopes relative to fayalite.

However, previous studies were restricted to magnetite, whereas both spinel bulk composition and structure may strongly affect the magnitude of the Fe isotope intermineral fractionation. In this study, the synchrotron technique of nuclear resonant inelastic X-ray scattering (NRIXS) is used to derive β -factors of iron isotopes by measuring the force constant of iron bonds (Seto et al., 1995; Sturhahn et al. 1995; Dauphas et al., 2012, 2014). Monocrystals of different compositions, (Mg, Fe)(Al, Cr, Fe)₂O₄ and redox states are explored. Using our spectroscopic data, a positive trend between the β -factors and the redox state is observed and parameterized. We show in particular that our model can account for the measured equilibrium fractionation between magnetite and fayalite (Shahar et al., 2008) and between magnetite and hedenbergite (Dauphas et al., 2007). Therefore, our model can be used to determine the inter-mineral equilibrium partitioning between spinel-group minerals and coexisting silicates over a range of compositions and the full range of redox states. Finally, as a case study, we compare our predictions to available data on natural peridotites.

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2. Experimental procedures and methods

2.1. Spinel synthesis

Spinel were synthesized in Pt-crucibles using high-purity oxides and FeO with 94% ^{57}Fe (Cambridge Isotope Laboratory). For NRIXS spectroscopic studies, it is mandatory to avoid any Fe-bearing impurities that would contribute to the collected signal. Therefore, a flux growth method was used because it produces large, euhedral, homogeneous spinels, free of any inclusions that would be produced by other conventional solid-state methods (Andreozzi, 1999; Lenaz and Skogby, 2003). Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) was used as flux. The oxides and flux mixtures were melted at 1200 °C for 12 to 24 hours, and then cooled at 4 °C/hour to allow nucleation and growth of single crystals. Mixtures of CO_2 and H_2 diluted with Ar flowing past the sample were used to control the oxygen fugacity (Table 1). Samples are labeled as $\text{Fe(III)}_x\text{(II)}_y$, where x refers to the atomic percentage of iron in the trivalent sites and y refers to the atomic percentage of iron present in the divalent sites of the spinel. High values of $(x+y)$ therefore refer to spinels rich in iron. After each run, the experimental charges were soaked in 1 M HCl overnight at ~50 °C to dissolve sodium borate glasses and to recover euhedral spinels. Unanticipated and sudden gas shortages complicated the run for spinels of intermediate redox state $[\text{Fe(III)}_{41}\text{(II)}_{21}$, $\text{Fe(III)}_{31}\text{(II)}_{32}$ and $\text{Fe(III)}_{25}\text{(II)}_{39}$].

2.2. Compositional and redox characterizations of synthetic spinels

All the spinels were examined under a microscope and observed to be euhedral (Fig. 1). Eight grains from each run were picked, polished, and analyzed using a Cameca SX-50 electron probe at the University of Chicago (15 kV, 40 nA). The homogeneity and

the lack of any inclusion were confirmed, except for runs Fe(III)41(II)21, Fe(III)31(II)32, Fe(III)25(II)39 as mentioned before (Table 2).

Spinels in Fe(III)41(II)21, Fe(III)31(II)32, Fe(III)25(II)39 come from the same experimental run with gas shortage toward the end of the run. These samples cover a large range of compositions and redox ratios ($\text{Fe}^{3+}/\text{Fe}_{\text{tot}} \sim 0.4$ to 0.7). However, the composition and the resulting redox ratio determined by stoichiometry were homogeneous within each of these small grains recovered (Table 2).

Besides these three small grains, the spinels were crushed into powders and the purity of these samples was further checked using a Bruker D8 Discover X-ray diffractometer equipped with a microfocus tube (Cu, 50 kV, 1 mA). All detected peaks corresponded to spinel and no impurities were found in all powders. Finally, Mössbauer spectroscopy was performed on these homogeneous powders (~ 10 - $20 \mu\text{m}$ thickness on Kapton tape) to determine the redox ratios ($\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$). The Mössbauer spectra were collected with a ^{57}Co source in a Pd matrix, using constant acceleration mode. The zero velocity point was adjusted to coincide with the isomer shift of α -iron to be zero. A VORTEX silicon drift detector was used with an energy resolution of 200 eV at 14.4 keV, providing excellent background rejection. All data presented here were taken at room temperature. No Mössbauer spectra were collected for Fe(III)41(II)21, Fe(III)31(II)32, Fe(III)25(II)39 due to their small sizes. For these samples, the redox ratios were calculated from chemical analyses by electron probe. When available, $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios obtained by Mössbauer and electron probe are in good agreement.

2.3. NRIXS spectroscopy

Details on the NRIXS (Nuclear Resonant Inelastic X-Ray Scattering) technique are available in Chumakov and Sturhahn (1999), Sturhahn et al. (1995), and Seto et al.

(1995). This technique was first applied to isotope geochemistry by Polyakov et al. (2005; 2007), who calculated β -factors for Sn and Fe using previously published partial PDOS, $g(E)$. The partial PDOS, $g(E)$ is itself derived from the measured phonon excitation probability density function $S(E)$ using a Fourier-Log inversion. More recently, Dauphas et al. (2012) and Hu et al. (2013) showed that β -factors could be calculated directly from $S(E)$, through the mean force constant, $\langle F \rangle$, of the bonds holding iron in position. At the high temperatures relevant to igneous and metamorphic geochemistry, the fractionation between ^{56}Fe and ^{54}Fe takes the form:

$$1000 \ln \beta_{56\text{Fe}/54\text{Fe}} \simeq 2853 \frac{\langle F \rangle}{T^2}, \quad (1)$$

where T is in K and $\langle F \rangle$ is proportional to the 3rd central moment of $S(E)$,

$$\langle F \rangle = \frac{M}{E_R \hbar^2} \int_{-\infty}^{+\infty} (E - E_R)^3 S(E) dE, \quad (2)$$

with M the mass of ^{57}Fe , $\hbar$ is the reduced Planck constant, and E_R is the free recoil energy. When the derived force constant is higher than 100 N/m, which is the case for most Fe-bearing oxides and silicates, equation (1) gives an approximation of the true β -factors with a precision better than 99% down to 300°C. At lower temperature, a more general equation applicable to all temperatures is,

$$1000 \ln \beta_{56\text{Fe}/54\text{Fe}} \simeq \frac{A_1}{T^2} + \frac{A_2}{T^4} + \frac{A_3}{T^6}, \quad (3)$$

where the coefficients A_1 , A_2 , and A_3 can be calculated from the moments of the phonon excitation probability density function $S(E)$ (Eq. 3 of Dauphas et al., 2012).

The NRIXS measurements were performed at beamline 3-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory. The storage ring was operated in top-up mode with 24 bunches separated by 153 ns. Two APD detectors positioned at 180° from each other and perpendicular to the incident X-ray beam direction were used. The sample was positioned in between those two detectors. Because spinels have cubic

structures, crystallographic orientation has no effect on the NRIXS spectrum. This is confirmed by the fact that the same force constants were derived whether analysis was done using single grains or powders of the same sample. As the signal was the greatest when single crystals were used, analyses were performed mostly using single crystals. The average energy resolution (full width at half maximum -FWHM) was 1.33 meV. The monochromator was tuned from ~ -130 meV to $\sim +130$ meV (-150 meV to $+150$ meV for Fe(III)O(II)₂₇) with a step size of 0.25 meV and a collection time of 2-3 s per step. The number of scans collected per sample depends on its ⁵⁷Fe content, and it ranges from 2 to 12 scans. All data were acquired at room pressure and room temperature (299±1 K). Data reduction was done with a Mathematica software (SciPhon 1.0) described in Dauphas et al. (2014). Its main features are that it calculates all the parameters needed for iron isotope geochemistry, and it propagates all sources of errors (*i.e.*, counting statistics, baseline subtraction, energy scaling) on the derived parameters.

3. Results

3.1 Spinel compositions and structures

The spinels have very similar chemical and structural properties to those obtained by others using the same synthesis method (Andreozi 1999, 2001; Lenaz and Skogby, 2003; Halenius et al. 2002; Lenaz et al. 2006). Table 3 summarizes the chemical and structural characteristics of spinels synthesized for this study and those from the literature: structural formula, the experimental degree of inversion (i_{exp}), bond distances (T-O and M-O), the oxygen positional parameter (u) and the cell edge (a). Table 4 summarizes available Mossbauer data (literature available for similar spinels and our own data) and derived properties such as redox state and site occupancy.

As detailed below, the Fe^{3+}/Fe_{total} ratio is the main property affecting the iron force constant of spinels. Particular attention was thus paid to the determination of this ratio. When possible, redox states were determined by Mössbauer spectroscopy (Fig. 2 and table 4) and electron probe (using oxide stoichiometry; Table 3). Within uncertainty (± 0.11 in Fe^{3+}/Fe_{total} for EMPA determination and ± 0.06 for Mössbauer determination), all redox ratios computed by stoichiometry are in excellent agreement with redox derived from Mössbauer spectroscopy with the exception of $Fe(III)_4(II)_0$. Still, for this spinel, our Mössbauer data are in complete agreement with data of Lenaz et al. (2006). The very low iron content and the relatively large uncertainties on the determination of chemical compositions make determining the Fe^{3+}/Fe_{total} ratio by stoichiometry difficult for $Fe(III)_4(II)_0$. As a consequence, when available, the redox ratios determined by Mössbauer spectroscopy were preferred over chemical compositions.

In addition to the highly variable redox state, the total iron content, the degree of inversion, the cell parameters, T-O and M-O mean distances, the oxygen positional parameter (u) and the cation distribution over tetrahedral and octahedral sites vary

significantly from one sample to another (Tables 3 and 4). Our spinels thus document a large array of chemical and structural properties though the analysis of these parameters is beyond the scope of this article (see Andreozzi et al. 2001, Halenius et al. 2002 and Lenaz et al. 2006 for in depth discussions of these aspects).

3.2 Force constants and other parameters derived from NRIXS

The phonon density of states $g(E)$ are derived from the phonon excitation probability density function $S(E)$ measured by NRIXS, (Fig. 3 and Fig. A1). Systematic changes as a function of the redox ratio and of the total iron content are expected. For spinels containing only Fe^{3+} (ferric iron), a strong contribution at 29 meV continuously increases as the Fe content increases. This band originates from the vibrations of Fe atoms at the tetrahedral sites (Handke et al., 2005). This contribution is associated with a long tail and a high-energy contribution centered at 73 meV and also observed in pure magnetite (Handke et al., 2005). When ferrous iron is progressively added to the spinel structure, these features vanish and the contribution at 29 meV turns to a broad shoulder. Finally, for pure Fe^{2+} -bearing spinels, this contribution is very weak and no tail extends to energies higher than 40 meV. Several parameters that can be calculated from $S(E)$ and $g(E)$ are compiled in Table A1. This compilation includes estimates of the Lamb-Mössbauer factor, kinetic energy per atom, force constant, internal energy, vibrational specific heat, vibrational entropy, critical temperature and velocities (Debye, p-wave and s-wave). As the present paper essentially focuses on high temperature isotopic fractionation, only the mean force constant of the iron bonds given by the 3rd moment of $S(E)$ is discussed in detail (Table 5). The calculations of the β -factors are then straightforward at temperature above 300°C and using equation (1). For the calculation of β -factors at temperatures below ~300 °C, higher order moments of $S(E)$ are needed

(Eq. 3; Dauphas et al., 2012, Hu et al., 2013) and those terms are also compiled in Table A1.

The force constants of the eight spinels vary from 207 ± 14 to 307 ± 17 N/m. These force constants correlate with the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio (Fig. 4). A linear regression through the Al-bearing spinels gives a slope of 104 ± 17 N/m and a force constant of 196 ± 12 N/m at $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0$. There is no significant correlation between force constants and the total amount of iron present in the spinels (Table 3). Nonetheless, the Cr-bearing spinel shows a force constant significantly lower than other ferric spinels. This may be due to its extremely low iron content. However, as discussed below, this could also be related to the large chromium content of this spinel. The site distribution of ferric iron has no measurable effect. For instance, it varies significantly among the three oxidized spinels (between 14 and 35 % of tetrahedral ferric iron, Table 4), yet they share the same force constant (Table 3). The degree of inversion (evaluated from previously published crystallographic studies) does not appear as a dominant parameter affecting the force constant either. In detail, from the eight spinels analyzed, only the pure Cr-bearing spinel $\text{Fe(III)}_4\text{(II)}_0$ plots significantly off of the main correlation (Fig. 4). Its force constant (244 ± 22 N/m) is significantly lower than similarly oxidized Cr-free spinels (296 ± 18 N/m). This is most likely due to the effect of the complete substitution of Cr for Al in the octahedral sites. Mantle spinels contain typically 50 to 60 % Al_2O_3 and 15-20 % Cr_2O_3 . Therefore, the calibration established on MgFeAl spinels is the one that should be used for application to natural spinels.

4. Discussion

4.1 Comparison with existing data

Polyakov and Mineev (2000) reported β -factors for spinel ($\text{Mg}_{0.9}\text{Fe}_{0.1}\text{Al}_2\text{O}_4$), magnetite (Fe_3O_4), ferrochromite (FeCr_2O_4) and a Cr-ferrite ($\text{MgCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$). These factors were determined from the second order Doppler (SOD) shift in Mössbauer spectroscopy. However, the determination of the SOD shift using conventional Mössbauer spectra is fraught with difficulties. The positions of the absorption lines shift as a function of temperature for a variety of reasons. Additional complications also arise when a distribution of hyperfine field parameters is caused by changes of chemical or magnetic nature, which is the case in some spinel minerals. For example the β -factors for magnetite proposed by Polyakov and Mineev (2000) were later proven to be inaccurate when NRIXS and new Mössbauer data were made available (Polyakov et al., 2007; Mineev et al., 2007; Dauphas et al., 2012).

Magnetite is the only spinel mineral extensively and carefully studied using NRIXS spectroscopy by Polyakov et al. (2007) and Dauphas et al. (2012). While Polyakov and coworkers used data from Seto et al. (2003) collected on a slightly over-oxidized magnetite, Dauphas and coworkers used unpublished data from APS. Within error bars, the β -factors estimated from these two studies agree. In the present work, we did not analyze pure magnetite. Nonetheless, Fe(III)41(II)21 has the same $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ (66%) as magnetite but with an FeO content of only 28 wt%. The mean force constant for $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0.66$ is 264 ± 6 N/m based on our regression for Al-bearing spinels, the force constant for magnetite derived from Polyakov et al., (2007) is 228 ± 15 N/m, and that of Dauphas et al. (2014) is 225 ± 16 . While the difference in composition may be the cause for the discrepancies in the force constants, we suggest that the reason may be due to the limited energy range over which previous data were collected (typically 80 meV

instead of 130 meV in the present study). Handke et al. (2005) collected nuclear inelastic scattering (NIS) spectra of magnetite single spectra and calculated the DOS *ab initio* within the density functional theory (DFT). Although they show the absence of single phonons above 90 meV, it does not mean that data can be safely truncated at this energy because multi-phonon processes spill into the 100-180 meV range and contribute to $S(E)$. Such high-energy tails have been observed in silicate glasses, silicate and oxide minerals analyzed by Dauphas et al., (2012; 2014) and are unambiguously observed in the present study (Fig. A1). These multi-phonon processes contribute significantly to the mean force constants and therefore, neglecting them leads to systematic underestimation of $\langle F \rangle$.

Our NRIXS measurements provide the most exhaustive and self-consistent dataset so far. They show a clear correlation between the redox states and force constants of spinels (Fig. 4). Literature data also show such a correlation but the trend is different and more scattered (Fig. 4). The Mg-ferrite studied by Polyakov and Mineev (2000) has a force constant similar to our oxidized Mg-spinel (336 vs. 307 ± 17 to 296 ± 18 N/m, respectively). Conversely, a large difference is found for reduced spinels. While our Fe^{2+} -bearing spinels have $\langle F \rangle$ values around ~ 196 N/m, Polyakov and Mineev (2000) reported values as low as 106 and 100 N/m for ‘spinel’ and ferrochromite, respectively. Such a difference is not related to composition because the Fe contents were similar in the two studies. This is more likely related to the spectroscopic method employed (SOD shift vs. NRIXS spectroscopy). Such disagreement is also found between the force constants derived from SOD shift by Polyakov and Mineev (2000) and by NRIXS by Dauphas et al. (2014) for olivine (133 vs. 197 ± 10 N/m respectively). The same is found for Fe^{2+} -bearing pyroxenes (108 N/m derived from SOD shift vs. 195-165 N/m derived from NRIXS by Jackson et al., 2009). Finally, Mineev et al. (2007) proposed a revised $\langle F \rangle$

value for magnetite (199 N/m) derived from the SOD shift. The difference between the values proposed by Polyakov et al., (2007) and Mineev et al., (2007; 228 N/m and 199 N/m, respectively) was attributed to the slightly over-oxidized nature of the magnetite used in Polyakov et al. (2007). This is indeed possible but in that case the redox-dependence of the force constant of spinel would be extreme since the oxidation of the magnetite reported in Polyakov et al., (2007) is only slightly higher than for stoichiometric magnetite (Fig. 4). Instead, one can hypothesize that the $\langle F \rangle$ derived by SOD shift for Fe²⁺-rich minerals (including magnetite) is systematically underestimated. The reason for this is unclear and this question should be addressed in future studies. But if $\langle F \rangle$ values derived from SOD shifts for Fe²⁺-silicates were correct, then metal-silicate partitioning of iron isotopes should lead to significant enrichments of light Fe isotopes in silicates. This is not observed in experimental studies and in natural samples for which metal-silicate equilibrium was assessed (Roskosz et al., 2006; Poitrasson et al., 2009; Hin et al., 2012; Jordan and Young, 2014; Shahar et al., 2015).

4.2 Equilibrium fractionation factors between spinels and olivines.

Large Fe isotopic variations in spinels (lato sensu, including magnetite) have been reported in igneous rocks and peridotites (*e.g.* Beard and Johnson, 2004, Williams et al., 2004; 2005; Johnson et al., 2010; Zhao et al., 2010; 2015) and in metamorphic rocks (Dauphas et al., 2007; Frost et al., 2007; Valaas Hysolp et al., 2008). However, the origin of these variations is generally unclear. In particular, the effects of equilibrium and kinetic fractionations cannot be easily disentangled. The redox calibration presented here can help interpreting such dataset. In particular, a straightforward use of the β -factors determined from our spectroscopic results is the development of geothermometers based on the equilibrium fractionation of Fe isotopes between spinels

and other minerals ($\Delta^{56}\text{Fe}_{\text{Sp-Min}}$). This fractionation corresponds to the difference in δ -values of two coexisting phases at equilibrium. It is also related to the difference between the β -factors of the coexisting phases through:

$$\Delta^{56}\text{Fe}_{\text{Sp-Min}} \approx 1000 \cdot \ln \alpha_{\text{Sp-Min}} = 1000 \cdot (\ln \beta_{\text{Sp}} - \ln \beta_{\text{Min}}) = \frac{2853}{T^2} (F_{\text{Sp}} - F_{\text{Min}}), \quad (4)$$

where T is in Kelvin. In the following sections we test our redox-dependent calibration of spinel β -factors on two particularly well-documented inter-mineral isotopic fractionations: the spinel-olivine and the spinel-pyroxene systems.

Shahar et al. (2008) calibrated experimentally equilibrium isotopic fractionation between magnetite and fayalite (Fig. 5). In Figure 5, we compare the predicted equilibrium fractionation using our redox-dependent calibration for a spinel containing 66% Fe^{3+} with the experimental determination of Shahar et al. (2008). A good agreement is found (Fig. 5). Based on the Mössbauer dataset of De Grave and Van Alboom (1991), Polyakov and Mineev (2000) estimated the β -factor for olivine (unknown composition). Combining this with the β -factor of magnetite also derived from Mössbauer spectroscopy (Mineev et al., 2007), the equilibrium fractionation factor between magnetite and olivine can be calculated. The estimate based on Mössbauer SOD shift also agrees with experimental data (Fig. 5). Therefore, it seems that despite the differences between SOD shift- and NRIXS-derived force constants for Fe^{2+} -bearing minerals, the inter-mineral fractionation factors are satisfactorily determined by both approaches. The situation may be different however if metallic iron is involved in the equilibrium as already mentioned.

4.3 Equilibrium fractionation factors between spinels and pyroxenes.

The same approach was followed for the spinel-pyroxene geothermometer. Again, we considered a spinel lying on the redox trend defined by our whole dataset and containing 66% Fe³⁺. The force constants of Fe²⁺-bearing pyroxenes were taken from NRIXS data for three orthoenstatites from Jackson et al. (2009). The reason for the significant scatter of these data is unclear but may, once again, result from the truncation of the NRIXS spectra at 80 meV. We thus report the three predictions (one for each pyroxene analyzed by Jackson and coworkers). Here, our predictions are compared to the magnetite-hedenbergite fractionation measured in an equilibrated, fine grain quartz-pyroxene rock sample from the island of Akilia (West Greenland), which experienced granulite facies metamorphism at about 750°C (Griffin et al., 1980; Dauphas et al., 2004, 2007). For the spinel-pyroxene thermometer, a good agreement is found between our predictions and the data collected on the natural samples (Fig. 5). Inter-mineral Fe isotopic fractionations derived from SOD shift for hedenbergite (Polyakov and Mineev, 2000) and for magnetite (Mineev et al., 2007) also provide an excellent agreement with data collected on natural samples (Fig. 5). As already pointed out for the olivine-magnetite couple, it seems that the differences between the force constants determined from the SOD shift and NRIXS spectra do not affect the quality of the inter-mineral fractionation factors.

The agreement between our prediction and data collected on experimental and natural samples indicates that the compositional dependence of this isotopic thermometer is weak. Furthermore, hedenbergite is a clinopyroxene whereas Jackson et al., 2009 reported data for orthoenstatite. This suggests that everything else being comparable (only Fe²⁺, lack of trivalent cations in pyroxenes), the nature of the pyroxene (ortho vs. clino) may not a key parameter affecting the Fe isotopes partitioning. Of course, the fact that clinopyroxenes generally contains much more ferric iron than

coexisting orthopyroxene (*e.g.*, Canil and O'Neill, 1996) must however have a small effect, that may explain why the clinopyroxenes are generally slightly heavier than orthopyroxene and olivines in natural peridotites (Williams et al., 2005; Huang et al., 2011).

Iron is found as Fe²⁺ and Fe³⁺ in mantle-derived pyroxenes (*e.g.*, Canil and O'Neill, 1996). Therefore, unlike the spinel-olivine couple for which only the Fe³⁺/Fe_{tot} ratio of the spinel needs to be considered, the Fe³⁺/Fe_{tot} of pyroxenes must also be known to readily use this thermometer. In the absence of significant amount of ferric iron in pyroxene, our calibration can be directly applied. When significant ferric iron is present in pyroxene, a correction must be applied. To date, there is no systematic NRIXS study of pyroxenes with varying Fe³⁺/Fe_{tot}. However, it is interesting to note that the trend defined by spinels is very similar to the trends defined by natural glass analogues studied elsewhere (Dauphas et al., 2014). For (1) spinels, (2) basaltic (including andesitic and dacitic) and (3) rhyolitic glasses, $\frac{\partial \langle F \rangle}{\partial (Fe^{3+}/Fe_{tot})} = 104 \pm 17, 152 \pm 40$ and 144 ± 32 N/m respectively. It is therefore reasonable, as a first approximation, to consider a similar redox-dependence for pyroxenes and spinels.

4.4 Iron isotopes and spinel oxybarometry

The oxygen fugacity of mantle peridotites can be estimated by studying ferrous and ferric iron distribution in spinel, olivine, and pyroxene. An important assumption in the application of spinel-based oxybarometers is that all the phases are in thermodynamic equilibrium but iron isotope measurements have revealed that this is often not the case. A related issue is that interpretations of iron isotopes in the presence of metasomatism and partial melting effects are hampered by a poor knowledge of equilibrium fractionation factors. For instance, Williams et al. (2004; 2005) found

correlations between spinel iron isotopic compositions and tracers of partial melting and oxygen fugacity but had to make important assumptions regarding inter-mineral isotopic fractionation factors to model their results. The mean force constants measured here remedy this problem and provide a framework with which to interpret iron isotopic analysis of spinel-bearing rocks and their melting products. The iron isotopic compositions of spinel-olivine and spinel-pyroxene mineral pairs can be used in principle to understand the petrogenesis of mantle rocks but the determination of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of pyroxene from their bulk composition is notoriously inaccurate (Canil and O'Neill, 1996). For this reason, we only examine the simpler case of the spinel-olivine oxybarometer.

Our NRIXS data were used to predict the effect of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the spinels on the equilibrium fractionation between spinel and olivine at a given temperature and pressure (Fig. 6). As expected, it depends linearly on the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the spinel. Moreover, up to 1500 K, a significant enrichment of spinels in heavy isotopes is expected. Also, even when ferric iron is not present in the system, the fractionation is never negative (Fig. 6). This result is opposite to previous estimates based on data from Polyakov and Mineev (2000) used in previous studies (Beard and Johnson, 2004; Zhao et al., 2010). The negative values predicted by this previous model are very rarely measured in nature (Fig. 6) and when measured, likely reflect metasomatic overprints (Beard and Johnson, 2004; Johnson et al., 2010).

Turning to the hypothetical effect of pressure, Huang et al. (2013) have recently shown that Mg isotope fractionations at 1200 K changes by about 0.1‰ from 0 to 3 GPa when Mg occupies different sites in coexisting minerals (6-fold coordination in olivines and pyroxenes vs. 8-fold coordination in pyrope and majorite). They also found a negligible effect of pressure when magnesium occupies the same site in coexisting

minerals. Similar pressure-dependence have not been measured or calculated for Fe isotopes so far. Nonetheless, in the geological context of our work, an effect of pressure should not be analytically resolvable. First the smaller mass difference between Fe isotopes (56 vs. 54 for Fe and 26 vs. 24 for Mg) should lead to a smaller variability of the equilibrium fractionation factors. Second, iron is both 4- and 6-fold coordinated in natural spinels and pyroxenes and is 6-fold coordinated in olivine. Therefore, the possible effect of coordination chemistry should be tempered by the coexistence of two coordinations in the mineral of interest. Consequently, the dominant factors controlling Fe isotopes fractionation between spinel, olivine and pyroxenes are temperature and the redox state. In this context, the coupled study of Fe and Mg isotopes, on the same grains, could bring converging and independent information on P, T and fO_2 that prevailed during the mineral equilibration.

Our predictions are compared to available data for natural peridotites and igneous rocks for which petrological description of coexisting minerals (including spinel ferric/ferrous ratios) were available (Beard and Johnson, 2004; Williams et al., 2004, 2005; Johnson et al., 2010; Zhao et al., 2010; 2015; Fig. 6). The scatter in the data set indicates, as pointed out by most authors, that isotopic equilibrium is rarely observed. From all these samples, only the Mg-peridotites from Yangyuan, (China) show limited variation in the degree of partial melting and of silicate melt metasomatism (Zhao et al., 2015). These samples fall close to the spinel-olivine equilibrium isotopic fractionation line predicted by the NRIXS results presented here. Figure 6 is drawn for an equilibrium temperature of 1000°C, as determined from petrological thermometers (Zhao et al., 2015). In any case, it is clear from this data compilation that Mg-peridotites from Yangyuan are indeed in isotopic equilibrium whereas other samples from various studies show a lot more scatter, suggesting disequilibrium possibly associated with

metasomatic and partial melting events as initially suggested by Beard and Johnson (2004).

Finally, the calibration presented here rules out the initial assertion that isotopic data from Williams et al., (2004; 2005) may reflect the redox state of the host mantle prevailing during the equilibration of the samples. Indeed, the results reported in those studies do not align along any redox-dependent trend, at any temperature. The very large fractionation observed for relatively reduced spinel could not result from isotopic equilibration in a closed system. These data essentially records complex and highly variable metasomatic episodes as alternatively proposed in Williams et al. (2005). Iron isotopic analyses of mineral separates and bulk rocks of peridotites thus provide a new tracer of the petrogenesis of mantle-derived rocks.

5. Conclusion

NRIXS spectroscopy offers the opportunity to calibrate equilibrium Fe isotopic fractionation between minerals and melts without the need for experimental equilibrations in extreme P, T, fO_2 conditions, which can easily be compromised by kinetic isotope fractionations. Nonetheless, this method still needs to be tested against independently determined inter-mineral isotopic fractionation data in order to demonstrate its accuracy. In this work, such comparison was carried out, with success, for the spinel-olivine and spinel-pyroxene systems.

The β -factors determined by NRIXS show moderate yet significant discrepancies with previous estimates from Mössbauer measurements. While more work is needed to fully demonstrate the advantage of NRIXS over Mössbauer on determining β -factors, a consistent NRIXS dataset can already be used to explain Fe isotopic variations in natural rocks (Dauphas et al., 2014; this study).

The proposed calibration is particularly useful in recognizing disequilibrium between coexisting minerals, caused by metasomatic and partial melting events. In this respect, the use of the spinel-olivine assemblage is important because these minerals are ubiquitous in rocks from planetary mantles. The experimental calibration of equilibrium iron isotopic fractionation between those two minerals shows that the redox state of the spinel is the main mineralogical parameter controlling the magnitude of the inter-mineral fractionation (on top of the usual temperature dependence). Except in rare case of an extensive substitution of Cr for Al (and potentially of Zn for Mg), no significant correction is needed to account for the compositional variability of natural mantle spinels. The same remark also holds for olivine and pyroxenes.

The spinel β -factors reported here are applied to published data of inter-mineral iron isotopic fractionations and it is shown that except for the Mg-fertile peridotites

505 from China, most samples studied thus far display evidence for isotopic disequilibrium
506 between coexisting minerals, indicating overprint by metasomatism and partial melting
507 processes. Iron isotopes are thus powerful tracers of the petrogenesis of mantle rocks
508 and their melt products. The results presented here are only relevant to the spinel
509 stability field and it is currently unknown to what extent iron isotopes can be
510 fractionated between minerals and melts at higher pressure in the garnet stability field.

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6. Acknowledgment

We thank Ian Steele (University of Chicago) for assistance in performing the electron probe analyses and Séverine Bellayer (UMET, ENSCL, Université Lille 1) for additional electron microprobe analysis. Jonathan Giencke (Bruker AXS) performed the XRD analysis. We thank Dr. X.M. Zhao for sharing her data on the peridotites from Yangyuan, North China Craton with us. The thoughtful reviews of three anonymous reviewers and the handling by S. Weyer deeply improved the quality of this work. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. This work was supported by an ANR grant (2011JS56 004 01; FrIHIDDA) to MR; grants from NSF Petrology and Geochemistry (EAR1144429), NASA Cosmochemistry (NNX12AH60G), LARS (NNX14AK09G) and FACCTS programs to ND; a Chateaubriand Fellowship to CKS.

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8. Figure captions

Figure 1: Micrographs of some euhedral spinels synthesized for this study. (a): $\text{Fe(III)}_{20}\text{(II)}_0$, (b): $\text{Fe(III)}_0\text{(II)}_{27}$, (c): $\text{Fe(III)}_{14}\text{(II)}_0$, (d): $\text{Fe(III)}_{32}\text{(II)}_0$.

Figure 2: Conventional Mössbauer spectra collected on the synthetic spinels at ambient temperature. The best fits to the data are shown as continuous lines. The fit procedure is given in section 2.2 and fit parameters are provided in table 4.

Figure 3: Partial phonon density of states of analyzed spinels.

Figure 4: Iron force constants of spinels as a function of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. The regressions were calculated using the Isoplot software on the Al-bearing spinels only. The orange envelope corresponds to the 2 SD of the linear fit to the data (best fit in red). The black dotted lines (large dots) are the best fit to the force constants of basaltic, andesitic and dacitic glasses on one hand and of rhyolitic glasses on the other hand as a function of the redox ratio (Dauphas et al., 2014). The dotted line (small dot) is a guide for the eyes through the data sets of P&M. Literature data are from: P&M: Polyakov and Mineev, 2000; P: Polyakov et al., 2007; M: Mineev et al., 2007; D: Dauphas et al., 2012.

Figure 5: Equilibrium fractionation as a function of temperature for the couples spinel-olivine and spinel-pyroxene. In order to compare our predictions to available data, the spinel has the same redox ratio as magnetite and all the pyroxenes considered here are pure ferrous end-members. The envelope correspond to the typical 2 SD on the slope of

the predicted trend from this study (using the NRIXS data of Jackson et al., 2007 for En 93). Literature data are from: P&M: Polyakov and Mineev, 2000; M: Mineev et al., 2007.

Figure 6: Equilibrium fractionation between spinel and olivine as a function of the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the spinels. The envelope corresponds to the 2 SD on our linear calibration of the oxybarometer at 1000°C.

Figure A1: Two measured phonon excitation probability density function $S(E)$ of a fully oxidized and a fully reduced spinel. Both spectra show unambiguous signal at energies higher than 90 meV.

Table 1: Synthesis conditions.

Sample	Starting mix (mg)					Run duration at 1200 °C (hours)	T _{quench} ^(a) (°C)	Gas flows (l _n /min)
	MgO	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	Flux (Na ₂ B ₄ O ₇)			
Fe(III)14(II)0	367	64	771	-	1747	24	40	Air
Fe(III)32(II)0	241	121	458	-	1067	24	40	Air
Fe(III)20(II)0	196	76	370	-	866	24	40	Air
Fe(III)41(II)21	36	69	111	-	289	12	900	3.4% H ₂ :CO ₂ (0.02:0.15)
Fe(III)31(II)32	36	69	111	-	289	12	900	3.4% H ₂ :CO ₂ (0.02:0.15)
Fe(III)25(II)39	36	69	111	-	289	12	900	3.4% H ₂ :CO ₂ (0.02:0.15)
Fe(III)0(II)27	16.8	95.9	102.2	-	391.4	12	910	10% H ₂ :CO ₂ (0.15:0.03)
Fe(III)4(II)0	130.3	52.4	-	444.4	1377	12	40	Air

(a): Temperature at which the samples were quenched in air

Table 2: Spinel compositions determined by electron microprobe for samples Fe(III)41(II)21, Fe(III)31(II)32 and Fe(III)25(II)39.

Sample #	FeO	MgO	Al ₂ O ₃	Total	Fe ³⁺ /Fe _{tot}
Fe(III)41(II)21	28.2	19.8	50.5	98.5	0.66
	27.8	19.8	50.9	98.4	0.65
	28.2	19.8	50.5	98.6	0.66
	28.0	19.7	50.6	98.3	0.65
	28.4	19.8	50.3	98.6	0.66
	28.2	19.6	50.3	98.1	0.66
	27.6	19.7	50.4	97.8	0.66
	27.6	19.7	50.8	98.1	0.65
	27.4	19.8	50.2	97.5	0.66
	27.3	19.9	50.8	98.0	0.66
	27.2	20.0	50.4	97.6	0.67
	27.3	19.9	51.1	98.3	0.65
	27.8	20.1	51.0	98.9	0.66
	27.6	19.7	50.8	98.1	0.65
	27.8	19.8	50.2	97.8	0.66
	28.4	19.9	50.3	98.6	0.67
	28.2	19.6	50.3	98.0	0.66
	28.1	19.7	50.3	98.1	0.66
	28.1	19.8	50.4	98.3	0.66
	28.3	19.8	50.8	98.9	0.66
Fe(III)31(II)32	27.8	17.6	54.9	100.4	0.49
	28.7	17.3	53.0	99.1	0.52
	28.4	17.2	53.4	99.1	0.50
	27.6	17.4	54.3	99.3	0.49
	28.2	17.2	53.9	99.2	0.49
	27.3	17.5	54.2	99.0	0.49
	28.4	17.3	53.9	99.6	0.50
	28.2	17.2	53.5	99.0	0.50
	28.7	17.2	52.8	98.7	0.52
	28.0	17.3	53.9	99.2	0.50
	27.6	17.3	53.5	98.4	0.50
	27.8	16.8	54.7	99.3	0.46
	27.9	17.0	53.8	98.7	0.48
	28.7	16.9	53.7	99.3	0.49
	28.4	16.9	53.8	99.1	0.48
	28.4	17.1	54.1	99.6	0.49
	28.0	17.0	54.4	99.4	0.48
	28.4	17.1	54.1	99.6	0.49
	28.0	17.2	54.5	99.7	0.48
	28.3	17.0	53.6	98.9	0.49
Fe(III)25(II)39	28.3	15.5	55.7	99.6	0.39
	28.8	15.3	54.9	99.0	0.40
	28.1	15.3	55.0	98.4	0.39
	28.9	15.2	55.2	99.3	0.39
	28.3	15.2	55.2	98.7	0.39
	29.0	15.1	55.2	99.4	0.39
	29.3	15.0	55.4	99.7	0.39
	28.6	15.1	55.3	99.0	0.39
	28.3	15.5	55.8	99.6	0.39
	28.2	15.4	55.7	99.3	0.39
	28.6	15.4	55.1	99.2	0.40
	28.6	15.7	55.2	99.5	0.41

28.9	15.3	55.0	99.2	0.40
29.1	15.6	55.1	99.8	0.42
29.0	15.2	54.9	99.1	0.40
28.9	15.3	55.2	99.4	0.40
28.3	15.2	55.2	98.7	0.39
28.3	15.6	55.2	99.2	0.41
28.3	15.4	55.4	99.1	0.39
29.1	15.5	55.3	100.0	0.41

Table 3: Compilation of compositional and structural data on spinels prepared in comparable conditions (Data from Andreozzi et al., 2001 a, b, c and Lenaz et al., 2006). The main properties of our spinels are provided when available.

Published data on similar spinels														
	He4b/d	Fe3-10	Fe3-20	MgF1aa	MgF1a	MgF1b	Fe(II)0(U)27	Fe(II)4(U)0	Fe(II)14(U)0	Fe(II)20(U)0	Fe(II)32(U)0	Fe(II)41(U)21	Fe(II)31(U)32	Fe(II)25(U)39
Composition (Wt%)														
MgO	19.3 (2)	19.4 (2)	20.5 (3)	28.2 (2)	27.3 (2)	26.9 (2)	19.45	19.4	27.38	26.55	25.97	19.8	17.18	15.35
FeO	13.7 (3)	0	0	0	0	0	13.54	2.19	7.22	10.76	16.1	27.87	28.14	28.65
Fe2O3	0	2.4 (1)	4.1 (1)	7.9 (5)	10.8 (2)	18.0 (4)	0	0	0	0	0	0	0	0
Al2O3	66.8 (2)	0	0	64.4 (6)	61.7 (3)	55.1 (5)	66.89	0.0	64.79	61.62	56.57	50.55	53.9	55.25
Cr2O3	0	76.5 (3)	75.2 (9)	0	0	0	0	78.03	0	0	0	0	0	0
Stoichiometry based on 4 oxygens														
Mg	0.726(6)	0.95	0.991	1.020 (3)	1.011 (5)	1.015 (5)	0.73	0.96	0.99	0.98	0.98	0.79	0.68	0.61
Fe ²⁺	0.274 (6)	0	0.007	0	0	0	0.27	0.04	0.01	0.02	0.02	0.21	0.32	0.39
Al	1.984 (5)	0	0	1.843 (6)	1.791 (6)	1.646 (13)	1.98	0	1.86	1.8	1.68	1.59	1.69	1.74
Fe3+	0.016 (5)	0.06	0.098	0.144 (5)	0.202 (5)	0.344 (12)	0.01	0.03	0.14	0.2	0.32	0.41	0.31	0.25
Cr	0	1.99	1.903	0	0	0	0	1.98	0	0	0	0	0	0
Redox state														
Fe ²⁺ /Fe _{tot} (EMP)	0.94	-	0.07	-	-	-	0.95	1	0.04	0.09	0.07	0.4	0.49	0.66
Fe ²⁺ /Fe _{tot} (MS)	0.96	0.07	0.07	0	0	0	1	0.09	0	0	0	-	-	-
Site occupancy														
T site														
Mg	0.514	-	0.986 (12)	-	0.728 (8)	-								
Fe2+	0.272	-	0.007 (1)	-	0	-								
Al	0.214	-	0	-	0.181 (7)	-								
Fe3+	0	-	0.007 (1)	-	0.091 (7)	-								
M site														
Mg	0.213	-	0.005 (1)	-	0.272 (7)	-								
Fe2+	0.004	-	0	-	0	-								
Al	1.769	-	0	-	1.617 (9)	-								
Fe3+	0.015	-	0.091 (3)	-	0.111 (7)	-								
Cr	0	-	1.903 (12)	-	0	-								
Crystal data														
a	8.1071 (3)	-	8.3410 (1)	-	8.1174 (3)	-								
u	0.26278 (5)	-	0.26128 (8)	-	0.26187 (5)	-								
T-O	1.9347 (4)	-	1.968 (1)	-	1.9244 (7)	-								
M-O	1.9287 (4)	-	1.996 (1)	-	1.9378 (4)	-								
i _{exp}	0.22 (1)	0	0	-	0.27	-								

Andreozzi, 2001; Lenaz 2001; Andreozzi, 2000; Andreozzi, 2001a

Table 4: Mössbauer fit parameters from literature data for similar spinels (L., 2006: Lenaz et al., 2006; A., 2001: Andreozzi et al., 2001; H.,2002: Halenius et al., 2002) and from our own fit to our data.

Sample	Sites	Centroid shift (mm/s)	Quadrupole splitting (mm/s)	Relative area
Fe3-10 (L., 2006)	VI Fe3+	0.34	0.38	93
	IV Fe2+	0.91	-	7
MgF1aa (A., 2001)	VI Fe3+	0.29	0.87	56
	IV Fe3+	0.19	0.5	44
MgF1b (A., 2001)	VI Fe3+	0.29	0.84	55
	IV Fe3+	0.22	0.48	45
	VI Fe3+	0.32	0.81	4
He4b (at 80K. H., 2002)	IV Fe2+(1)	1.03	2.8	28
	IV Fe2+(2)	1.03	2.48	25
	IV Fe2+(3)	1.03	1.99	31
	IV Fe2+	1.03	1.29	12
Fe(III)4(II)0	VI Fe3+	0.31	0.4	91
	IV Fe2+	0.97	0	9
Fe(III)14(II)0	VI Fe3+	0.3	0.85	65
	IV Fe3+	0.22	0.64	35
Fe(III)20(II)0	VI Fe3+	0.27	0.66	86
	IV Fe3+	0.16	0.59	14
Fe(III)32(II)0	VI Fe3+	0.3	0.67	77
	IV Fe3+	0.16	0.59	23
Fe(III)0(II)27	IV Fe2+(1)	1.08	1.75	100

Table 5: Force constants derived from NRIXS spectra. From these values fractionation factors can be determined down to 300°C by equation (1): $1000 \ln \beta_{56\text{Fe}/54\text{Fe}} \approx 2853 \frac{\langle F \rangle}{T^2}$, where T is in Kelvin. See text for more details.

Sample	<F>	error
Fe(III)4(II)0	244	22
Fe(III)14(II)0	296	18
Fe(III)32(II)0	305	16
Fe(III)20(II)0	307	17
Fe(III)0(II)27	207	14
Fe(III)31(II)32	240	13
Fe(III)25(II)39	222	14
Fe(III)41(II)21	250	14
Olivine ^a	197	10
Enstatite 93 ^b	195	15
Enstatite 87 ^b	170	15
Enstatite 80 ^b	165	15

a: from Dauphas et al., 2014

b: From Jackson et al., 2009

Table A1: NRIXS dataset for the eight spinels analyzed in this study.

	Fe(III)O(II)27			Fe(III)31(II)32			Fe(III)25(II)39			Fe(III)41(II)21			Fe(III)20(II)0			Fe(III)4(II)0			Fe(III)32(II)0			Fe(III)14(II)0		
Total energy range:	-149,637	to	149,843	-129,489	to	130,012	-129,391	to	130,229	-129,566	to	130,044	-129,103	to	130,087	-129,421	to	129,48	-129,486	to	129,994	-129,492	to	130,138
Energy cutoff (left and right in meV):	49	and	24	43,6	and	22,8	29	and	24	32,6	and	29,6	20,6	and	24,8	40,2	and	25,6	29,8	and	23,6	38,4	and	26,2
Baseline subtracted:																								
a=	-5,16E-05	±	5,11E-04	6,79E-04	±	5,98E-04	-2,98E-04	±	6,54E-04	-5,30E-05	±	6,55E-04	2,87E-03	±	9,98E-04	1,71E-04	±	7,69E-04	1,40E-03	±	9,54E-04	7,26E-04	±	6,83E-04
b=	3,94E-01	±	6,65E-02	4,27E-01	±	6,70E-02	3,43E-01	±	7,63E-02	4,23E-01	±	7,51E-02	9,28E-01	±	1,18E-01	7,90E-01	±	8,66E-02	8,86E-01	±	1,11E-01	5,13E-01	±	7,75E-02
-----From S-----																								
lamb-mossbauer factor from S:	0,7440	±	0,0025	0,7706	±	0,0021	0,7647	±	0,0026	0,7832	±	0,0024	0,8207	±	0,0025	0,7958	±	0,0064	0,8171	±	0,0026	0,8169	±	0,0036
Internal energy/atom from S (meV):	28,69	±	0,73	29,15	±	0,69	28,93	±	0,73	29,32	±	0,74	30,07	±	0,80	29,27	±	1,25	30,04	±	0,75	29,92	±	0,83
Kinetic energy/atom from S (meV):	14,35	±	0,36	14,58	±	0,34	14,46	±	0,36	14,66	±	0,37	15,04	±	0,40	14,63	±	0,62	15,02	±	0,38	14,96	±	0,41
Force constant from S (N/m):	207	±	14	240	±	13	222	±	14	250	±	14	307	±	17	244	±	32	305	±	16	296	±	18
-----beta-value coefficients from S-----																								
1000 ln beta 56Fe/54Fe=A1/T^2+A2/T^4+A3/T6 (T in K)																								
A1:	5,89E+05	±	3,92E+04	6,84E+05	±	3,60E+04	6,33E+05	±	3,89E+04	7,14E+05	±	3,93E+04	8,77E+05	±	4,98E+04	6,96E+05	±	9,03E+04	8,72E+05	±	4,47E+04	8,44E+05	±	5,06E+04
A2:	-4,52E+09	±	8,07E+08	-4,94E+09	±	5,69E+08	-4,08E+09	±	5,96E+08	-4,67E+09	±	5,60E+08	-6,56E+09	±	8,37E+08	-3,72E+09	±	1,41E+09	-6,61E+09	±	7,16E+08	-6,17E+09	±	7,66E+08
A3:	9,60E+13	±	3,03E+13	9,20E+13	±	1,62E+13	6,75E+13	±	1,62E+13	7,13E+13	±	1,41E+13	1,10E+14	±	2,46E+13	4,34E+13	±	3,74E+13	1,12E+14	±	2,00E+13	1,01E+14	±	2,04E+13
1000 ln beta 56Fe/54Fe=B1<F>/T2-B2<F>^2/T^4 (T in K)																								
B1:	2,85E+03			2,85E+03			2,85E+03			2,85E+03			2,85E+03			2,85E+03			2,85E+03			2,85E+03		
B2:	8,17E+04			6,87E+04			6,81E+04			6,24E+04			5,70E+04			5,47E+04			5,79E+04			5,81E+04		
-----From g-----																								
lamb-mossbauer factor from g:	0,7419			0,7699			0,7640			0,7820			0,8201			0,7951			0,8165			0,8161		
lamb-mossbauer factor at T=0 from g:	0,9106			0,9176			0,9160			0,9206			0,9289			0,9228			0,9283			0,9279		
Critical temperature (K):	1092			1263			1224			1351			1717			1461			1675			1671		
Resilience (N/m):	80			93			90			99			126			107			123			123		
Internal energy/atom from g (meV):	28,70			29,16			28,93			29,32			30,08			29,27			30,05			29,93		
Kinetic energy/atom from g (meV):	14,35			14,58			14,47			14,66			15,04			14,63			15,02			14,96		
Kinetic energy/atom at T=0 from g (meV):	6,56			7,21			6,98			7,45			8,32			7,52			8,27			8,16		
Vibrational entropy (kb/atom):	1,16			1,08			1,10			1,04			0,94			1,02			0,95			0,96		
Vibrational specific heat (kb/atom):	0,90			0,89			0,89			0,88			0,86			0,88			0,86			0,86		
Force constant from g (N/m):	207			240			222			251			308			244			306			296		
-----beta-value coefficients from g-----																								
1000 ln beta 56Fe/54Fe=A1/T^2+A2/T^4+A3/T6 (T in K)																								
A1:	5,90E+05			6,84E+05			6,33E+05			7,15E+05			8,78E+05			6,96E+05			8,73E+05			8,45E+05		
A2:	-4,53E+09			-4,99E+09			-4,11E+09			-4,74E+09			-6,65E+09			-3,74E+09			-6,70E+09			-6,26E+09		
A3:	9,73E+13			9,72E+13			7,06E+13			7,71E+13			1,19E+14			4,47E+13			1,21E+14			1,10E+14		
-----Velocities from g-----																								
Input density (g/cc):	3,5			3,5			3,5			3,5			3,5			3,5			3,5			3,5		
Input bulk modulus (GPa):	100			100			100			100			100			100			100			100		
Debye velocity (m/s):	5133	±	117	5306	±	60	5301	±	269	5359	±	160	5701	±	105	6355	±	1368	5513	±	75	5614	±	68
p-wave velocity (m/s):	7577	±	90	7713	±	47	7710	±	209	7756	±	125	8035	±	86	8592	±	1196	7880	±	60	7963	±	55
s-wave velocity (m/s):	4651	±	112	4816	±	57	4812	±	256	4867	±	152	5195	±	100	5826	±	1302	5015	±	72	5111	±	65
Poisson ratio:	0,198			0,181			0,181			0,175			0,141			0,074			0,160			0,150		
Comparison 1000 lnβ for 56Fe/54Fe at 300K																								
from A1-A3 S coefficients (‰):	6,12			7,11			6,62			7,45			9,08			7,34			9,02			8,75		
from A1-A3 g coefficients (‰):	6,12			7,12			6,63			7,46			9,10			7,34			9,04			8,77		
from kinetic energy from S (‰):	6,10			7,10			6,61			7,45			9,07			7,34			9,01			8,74		
from kinetic energy from g (‰):	6,12			7,11			6,62			7,46			9,08			7,34			9,02			8,76		

Figure

Fig.1

Figure

Figure

Figure

Figure

Figure

Fig. A1