# Estimating the iron oxidation state of serpentinite using X-ray absorption fine structure spectroscopy

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### ABSTRACT

Iron can exist in serpentinite in various oxidation states. Changes in the oxidation state of Fe play a crucial role in geological processes, including supporting diverse biological systems on the ocean floor and the redox states of aqueous fluids released in subduction zones. Synchrotron X-ray absorption near-edge structure (XANES) spectroscopy has been used to measure the oxidation state of Fe in serpentine minerals; however, a general scheme for estimating the oxidation state of Fe in serpentinite composed of several Fe-bearing minerals has not been established. We evaluated the accuracy of using XANES spectra to estimate the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio (molar ratio of Fe<sup>3+</sup> to total Fe) of physical olivine-magnetite mixtures and serpentinites. Two approaches were tested: (1) linear combination fitting (LCF) and (2) pre-edge peak analysis of XANES spectra. Estimating Fe<sup>3+</sup>/ $\Sigma$ Fe using analysis of the pre-edge peaks was not always suitable when magnetite was included. Using LCF, XANES spectra are well fitted by the optimal combination of Fe-bearing minerals, even for mixtures of magnetite and Fe-bearing silicate minerals (i.e., serpentine and olivine). The Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of the serpentinites were estimated with a root mean squared error (RMSE) of 0.14 with LCF. These results demonstrate that LCF of XANES spectra is useful for estimating the oxidation state of Fe in serpentinites.

Keywords: Serpentinite, iron oxidation state, X-ray absorption near edge structure, Oman ophiolite

### INTRODUCTION

Serpentinization of the mantle peridotite is an important process that changes the oxidation state of Fe to produce H<sub>2</sub> and hydrocarbons (Klein et al. 2009; Preiner et al. 2020), potentially supplying energy that sustains biological communities of the seafloor, submarine hydrothermal systems, and subduction zones (Sleep et al. 2004; Schrenk et al. 2013; Plümper et al. 2017). In addition, changes in the redox state can lead to the formation of organic matter through interactions between ultramafic rocks and water under anoxic conditions, a process that may have contributed to the emergence of life on Earth and may be responsible for life on other planets (Ménez et al. 2018; Steele et al. 2022). A quantitative assessment of the oxidation state of Fe in natural serpentinites would provide significant constraints on these processes (Klein et al. 2009; Andreani et al. 2013; Ellison et al. 2020).

The simplified reaction for the serpentinization of mantle peridotite is as follows:

Because one of the most important host minerals of  $Fe^{3+}$  in serpentinite is magnetite, H2 production is thought to be related to the amount of magnetite produced (Malvoisin et al. 2012; McCollom and Bach 2009). However, previous studies have shown that Fe<sup>3+</sup> is hosted not only by magnetite, but also by serpentine (O'Hanley and Dyar 1993; Klein et al. 2009; Marcaillou et al. 2011; Andreani et al. 2013; Bonnemains et al. 2016; McCollom et al. 2016; Ellison et al. 2020). The mantle redox state and  $Fe^{3+}/\Sigma Fe$  ratio (molar ratio of  $Fe^{3+}$  to total Fe) of serpentine are controlled by various factors, including pressure, temperature, water-rock ratio, silica activity, and redox state of subducting sediments (Klein et al. 2009; Andreani et al. 2013; Debret et al. 2014; Eberhard et al. 2023; Clift 2017; Padrón-Navarta et al. 2023; Oyanagi and Okamoto 2024). Therefore, the determination of the  $Fe^{3+}/\Sigma Fe$  ratio of serpentine minerals is important for understanding the spatial and temporal variations in Fe partitioning and H<sub>2</sub> generation during the complex serpentinization histories of the oceanic lithosphere and subduction zone. The oxidation state of Fe in serpentinized peridotites has

In Equation 1, H<sub>2</sub> is formed by the reduction of H<sub>2</sub>O due to the oxidation of ferrous iron (Fe<sup>2+</sup>) to ferric iron (Fe<sup>3+</sup>).

been determined using Mössbauer spectroscopy (O'Hanley and Dyar 1993; Klein et al. 2009) and wet chemical analyses (e.g., Evans 2008). These analyses require at least several tens to hundreds of milligrams of sample to determine the bulk-rock

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 $Fe^{3+}/\Sigma Fe$  ratio. Electron energy loss spectroscopy is also employed to determine the  $Fe^{3+}/\Sigma Fe$  ratio using small samples (van Aken and Liebscher 2002). However, this technique requires a great deal of sample preparation, and the measurements must be performed under a high vacuum.

X-ray absorption near edge structure (XANES) spectroscopy is a technique for analyzing absorption spectra obtained by irradiating a sample with X-rays. Detailed analysis of the spectra in the region near the absorption edge provides information on the chemical state (oxidation and coordination) of the element of interest (Henderson et al. 2014). XANES measurements can be performed under atmospheric pressure; consequently, they can be applied to various sample forms (e.g., powder, thin section, and solution). Moreover, XANES measurements can be carried out on samples ranging from a few to several tens of milligrams in the case of powder samples, although the amount of sample required depends on the element of interest and its abundance. XANES has been extended to in situ analyses and two-dimensional imaging, linking the redox state of Fe and the microstructure of minerals in volcanic rocks (Yoshida et al. 2023b), serpentinite (Marcaillou et al. 2011; Andreani et al. 2013; Muñoz et al. 2013; Debret et al. 2014; Ellison et al. 2020), and iron ore sinters (Kimura et al. 2018).

In XANES spectra, changes to the coordination and oxidation state of an element are reflected in the shape and location of the pre-edge peak (Wilke et al. 2001) and the region near the absorption edge (Waychunas et al. 1983; Bianconi et al. 1985). XANES has been used for in situ analyses of the oxidation state of Fe in various minerals (Wilke et al. 2001; Dyar et al. 2002; Andreani et al. 2013; Muñoz et al. 2013; Sutton et al. 2017; Ellison et al. 2020). Determining the oxidation state of iron in rock-forming minerals commonly involves using the centroid position energy and integrated intensity of the pre-edge peak (Bajt et al. 1994; Wilke et al. 2001; Marcaillou et al. 2011). However, the pre-edge peaks are much smaller than the main absorption peak, thereby requiring a spectrometer with high energy resolution and a high signal-to-noise ratio for accurate measurements (Debret et al. 2014).

Linear combination fitting (LCF) of the XANES spectra has been widely used for quantitative estimation of the chemical states of elements in meteorites, clays, and Fe oxides (Sutton et al. 2017; Husain et al. 2020; Honty et al. 2021). LCF assumes that the XANES spectrum of an element in the target material can be reconstructed as a linear combination of spectra from standard samples and that the chemical state can be described as a mixture of the chemical states of the elements in the reference material (Ravel and Newville 2005; Tabuchi et al. 2020). This method has been applied successfully to determine the bulk-rock  $Fe^{3+}/$  $\Sigma$ Fe ratio of chondrites (Sutton et al. 2017). Marcaillou et al. (2011) analyzed the proportion of each mineral in an experimental reactant and product mixture of serpentine, olivine, pyroxene, and magnetite using LCF. However, they did not estimate the bulk  $Fe^{3+}/\Sigma Fe$  ratio using the LCF method, instead using the pre-edge peak. There are few examples of the LCF method being adapted to evaluate the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of natural rocks, and its applicability to natural serpentinites has not been validated.

Accurate estimation of the  $Fe^{3+}/\Sigma Fe$  ratio using LCF requires appropriate mineral standards for the end-members in the sample, and it is preferable to use a serpentine standard for estimating the  $Fe^{3+}/\Sigma Fe$  ratio of serpentinite. However, it is difficult to prepare natural or synthetic samples of pure serpentine end-members with various oxidation states. In this study, we tested various combinations of available Fe<sup>2+</sup>- and Fe<sup>3+</sup>-bearing minerals other than serpentine as standards and validated the use of LCF to estimate the  $Fe^{3+}/\Sigma Fe$  ratio of serpentinite. First, to verify the accuracy of the estimation of the  $Fe^{3+}/\Sigma Fe$  ratio using the pre-edge peak and LCF, the  $Fe^{3+}/\Sigma Fe$  ratios of olivine-magnetite mixtures with known bulk  $Fe^{3+}/\Sigma Fe$  ratios were estimated using the pre-edge peak and LCF. We investigated the optimal combination of mineral standards to increase the accuracy of the estimated  $Fe^{3+}/\Sigma Fe$  ratio. Then, LCF was applied to natural serpentinite from the Oman ophiolite to determine the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio, which was compared with the results of wet chemical analysis (titration). The advantages and limitations of LCF of XANES spectra from serpentinites are discussed by comparing LCF with pre-edge peak analysis and titration methods.

### METHODS

### Analyzed samples

Two sample groups were used for estimating  $Fe^{3+}/\Sigma Fe$  ratios: (1) olivinemagnetite mixtures and (2) natural serpentinites from the Oman ophiolite. The olivine-magnetite mixtures were made from olivine with  $X_{Mg}$  (molar ratio of Mg to Mg + Fe<sup>2+</sup>) of 0.90 and magnetite powders (FUJIFILM Wako Pure Chemical Corporation, purity >95%). The olivine powder was made by crushing the olivine sand in a tungsten mortar. Assuming theoretical structural formulas, the  $Fe^{3+}/\Sigma Fe$  ratios of olivine and magnetite are 0 and 0.67, respectively. Bulk mineral powders with a broad range of  $Fe^{3+}/\Sigma Fe$  ratios (0.09–0.59; Table 1) were prepared by mixing various amounts of olivine and magnetite.

The natural serpentinite samples were taken from drill core from sites CM1A (22°54.435'N, 58°20.149'E) and CM2B (22°54.660'N, 58°20.149'E) of the Oman ophiolite onshore drilling project (Kelemen et al. 2020). Hole CM1A has a total depth of 404.15 m, penetrating from the lower crust to the upper mantle portions of the ophiolite, and CM2B has a total depth of 300.0 m, from the crust-mantle boundary to the upper mantle. Detailed descriptions of CM1A and CM2B have been presented previously (Katayama et al. 2020; Kelemen et al. 2020; Kourim et al. 2022; Yoshida et al. 2020, 2023a). We analyzed eight samples of completely serpentinized durite from the crust-mantle transition zone and 10 samples of partly serpentinized harzburgite from the upper mantle (Table 2).

The serpentinized dunites analyzed in this study are composed of serpentine, brucite, magnetite, and Cr-spinel, with no relic olivine or orthopyroxene (Online Materials<sup>1</sup> Fig. S1a) (Yoshida et al. 2023a). The host rock serpentine is mainly lizardite (Lz;  $X_{Mg}$  = 0.96–0.97), with minor veins of antigorite (Atg) + chrysotile (Ctl) (Yoshida et al. 2023a). The sample has a mesh texture, with cores of serpentine, brucite, and fine-grained (1–2 µm) magnetite. Magnetite veins occur in the

TABLE 1. Olivine-magnetite ratios, bulk-rock FeO and Fe2O3 contents(wt%), and Fe3+/ $\Sigma$ Fe ratios calculated from EPMA data ofolivine and stoichiometric magnetite (Fe3O4) compositionfor the olivine-magnetite mixtures

Magnetite (mg)	Fe <sub>2</sub> O <sub>3</sub> *	FeO	Fe <sub>2</sub> O <sub>3</sub>	$Fe^{3+}/\Sigma Fe$	
9.6	12.2	10.0	1.1	0.09	
11.4	14.2	10.5	2.5	0.18	
14.4	17.0	11.1	4.6	0.27	
13.3	21.6	12.2	8.1	0.37	
26.3	30.1	14.2	14.4	0.48	
81	52.2	19.2	30.8	0.59	
	Magnetite (mg) 9.6 11.4 14.4 13.3 26.3 81	Magnetite (mg) Fe2O3*   9.6 12.2   11.4 14.2   14.4 17.0   13.3 21.6   26.3 30.1   81 52.2	Magnetite (mg) Fe2O3* FeO   9.6 12.2 10.0   11.4 14.2 10.5   14.4 17.0 11.1   13.3 21.6 12.2   26.3 30.1 14.2   81 52.2 19.2	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

Note: Total Fe contents (Fe\_2O\_3\*; wt%) were calculated using Fe\_2O\_3\* = Fe\_2O\_3 + 1.11  $\times$  FeO.

Analytical method		XRF	Titration			TG		
Sample name	Lithology	Fe <sub>2</sub> O <sub>3</sub> *	FeO	Fe <sub>2</sub> O <sub>3</sub>	$Fe^{3+}/\Sigma Fe$	Srp	Brc	Srp+Brc
C5707A 79Z3 40-45	Dunite	10.9	3.5	7.0	0.64	76.7	11.1	87.8
C5707A 107Z2 5-10	Dunite	10.4	2.6	7.5	0.72	83.0	4.8	87.8
C5708B 15Z3 7-12	Dunite	9.1	2.8	6.1	0.66	79.7	12.1	91.7
C5708B 15Z3 38-43	Dunite	9.2	2.7	6.2	0.67	78.9	10.8	89.7
C5708B 16Z2 30-35	Dunite	9.2	2.9	5.9	0.64	79.2	11.9	91.1
C5708B 52Z3 16-21	Dunite	12.8	3.1	9.4	0.73	77.3	8.6	85.9
C5708B 59Z4 11-16	Dunite	8.7	2.5	5.9	0.68	80.7	13.3	94.0
C5708B 63Z3 37-42	Dunite	9.7	2.4	7.1	0.73	80.1	13.4	93.5
C5707A 144Z2 24-32	Harzburgite	6.9	2.2	4.5	0.65	83.0	7.8	90.8
C5707A 179Z3 18-26	Harzburgite	7.5	2.1	5.2	0.69	87.6	4.2	91.8
C5708B 68Z1 27-31	Harzburgite	7.3	2.4	4.7	0.64	82.9	7.4	90.3
C5708B 77Z4 70-75	Harzburgite	7.7	3.5	3.7	0.49	60.9	6.3	67.2
C5708B 86Z3 10-15	Harzburgite	7.4	2.6	4.6	0.62	77.6	8.4	86.1
C5708B 90Z3 40-45	Harzburgite	7.6	3.1	4.2	0.55	64.9	7.5	72.4
C5708B 99Z2 68-73	Harzburgite	7.9	3.5	4.0	0.51	59.2	6.5	65.7
C5708B 100Z2 80-85	Harzburgite	8.2	3.2	4.7	0.57	69.4	7.9	77.2
C5708B 106Z3 16-21	Harzburgite	7.1	2.6	4.2	0.59	87.0	6.9	93.9
C5708B 11072 7-12	Harzburgite	77	3.8	35	0.45	520	5 /	583

TABLE 2. Bulk-rock Fe chemistry and mass fraction of serpentine and brucite of the studied serpentinites

Notes: Total Fe contents ( $Fe_2O_3^*$ ) were determined using WDXRF (wt%). FeO was determined using potassium dichromate titration (wt%).  $Fe_2O_3$  contents were calculated using  $Fe_2O_3 = Fe_2O_3^* - 1.11$  FeO.  $Fe^{3+}/\Sigma$ Fe ratios were calculated from the FeO and  $Fe_2O_3$  contents. The mass fraction of serpentine and brucite was determined by thermogravimetric (TG) analysis (wt%).

mesh rims, and the rims of Cr-spinel are partly altered to magnetite. The partly serpentinized harzburgite is composed of olivine, orthopyroxene, Cr-spinel, and secondary serpentine (Lz + Ctl), brucite, and magnetite with a mesh texture (Online Materials<sup>1</sup> Fig. S1b). The degree of serpentinization of the harzburgite is 60-90% (Table 2). Olivine is more serpentinized than orthopyroxene (Online Materials<sup>1</sup> Fig. S1b). The serpentinized harzburgite contains less magnetite and brucite than the serpentinized dunite. The brucite in the serpentinized dunites and harzburgites are partly weathered to form reddish minerals.

### Analytical methods

Raman spectroscopy was carried out to identify the minerals using a Horiba XploRA PLUS at Tohoku University, Sendai, Japan. Raman spectra were collected in three accumulations with an integration time of 3 s and a grating with 1800 grooves/mm. Denoising and background subtraction for the Raman spectra were carried out using the software provided with the spectrometer (LabSpec 6). The chemical compositions of the minerals were determined using an electron probe microanalyzer (EPMA; JEOL JXA-8200) at Tohoku University. Mineral reference standards [wollastonite (Si, Ca), rutile (Ti), corundum (Al), hematite (Fe), manganosite (Mn), periclase (Mg), albite (Na), K-feldspar (K), and eskolaite (Cr)] were used for calibration. The accelerating voltage was 15.0 kV, and the probe current for quantitative analyses was 12 nA.

Bulk-rock major element compositions, including total Fe contents, of serpentinite samples were determined using a wavelength-dispersive X-ray fluorescence (WDXRF) (Rigaku ZSX Primus IV) at Tohoku University (Yamasaki et al. 2023). The accelerating voltage was 75 kV, and the beam current was 8 mA. Fine-grained powdered samples were heated at 105 °C for 2 h, then heated in a furnace at 950 °C for 2 h to obtain loss on ignition values. Glass disks were prepared by heating 5.4 g of flux (49.75 wt% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 49.75 wt% LiBO<sub>2</sub>, and 0.50 wt% LiBr) and 0.6 g of sample in a muffle furnace at 1050 °C. Bulk-rock total Fe contents were calculated as Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>\*).

The FeO content of serpentinite was determined using potassium dichromate titration at Palynosurvery (Fujioka, Japan). Powdered samples were digested using a mixture of sulfuric and hydrofluoric acid until no residue remained (Geological Survey of Japan 1978). The Fe<sub>2</sub>O<sub>3</sub> content was calculated by subtracting FeO from total Fe (Fe<sub>2</sub>O<sub>3</sub> = Fe<sub>2</sub>O<sub>3</sub> + -1.11 FeO). Bulk-rock Fe<sup>3+</sup>/ $\Sigma$ Fe ratios were calculated by dividing the Fe<sup>3+</sup> content by the total Fe content.

The mass fraction of hydrous minerals was measured by thermogravimetry (TG, Rigaku Thermo Plus EVO II TG 8120) at Tohoku University. Powdered samples were weighed (20–25 mg) and placed in a platinum container, and the temperature was raised from room temperature (~20 °C) to 1050 °C at a rate of 10 °C/ min in an Ar atmosphere. On the TG curves, mass loss between 250 and 450 °C was attributed to the decomposition of brucite, and mass loss between 450 and 750 °C was attributed to the decomposition of serpentine (Okamoto et al. 2011, 2024).

## X-ray absorption fine structure measurement and evaluation of the Fe oxidation state

XANES spectra from mineral standards, olivine-magnetite mixtures, and natural serpentinites were measured at beamlines BL-12C and BL-9C of the Photon Factory at the High Energy Accelerator Research Organization, Tsukuba, Japan. A pellet of 10 mm in diameter was prepared by pressing mixed fine-grained rock or mineral (10-30 mg) and boron nitride (100 mg) powders for quick X-ray absorption fine structure (XAFS) transmission analyses. A Si (111) double crystal monochromator and focusing mirror were installed upstream on the beamline. The ring energy was 2.5 GeV and the current was 450 mA. Measurements were performed using an energy of 6600-8200 eV and an energy width of 0.4 eV. Pre-edge regions (7095-7125 eV) were measured separately with energy steps of 0.1 eV at beamline BL-9C. The pre-edge measurement time was  $\sim 10$  min. The beam size was  $0.6 \times 0.6$  mm. The photon flux was  $2.5 \times 10^{11}$  photons/s/mm<sup>2</sup> (at 8 keV), and the measurement time was 5-10 min per sample. The photo-oxidation of serpentine minerals during XAFS measurement may cause a slight overestimation of Fe3+/2Fe ratio of 0.05-0.1 (Debret et al. 2014), but the photon flux is much lower, and the measurement time is shorter than the previous study. We confirmed that there was no significant change in the XANES spectra due to photo-oxidation even when the measurement duration was varied up to ~15 min. The X-ray energy calibration was based on the first inflection point of the absorbance at the K edge of Fe metal foil at 7112.0 eV (Bearden and Burr 1967). Measured XANES spectra were normalized and flattened using Larch software version 0.9.70 (Newville 2013). The normalization range was adjusted by ensuring that the absorption before the pre-edge (7000-7050 eV) and post-edge (7200-7400 eV) regions was flattened to 0 and 1, respectively.

The Fe<sup>3+</sup>/ $\Sigma$ Fe ratios were estimated from the XANES spectra using LCF and standard spectra, which is similar to the method of Sutton et al. (2017). In LCF, a spectrum from an unknown sample is modeled as a linear combination of spectra from standard samples, and the combined spectrum is optimized using a nonlinear least-squares method. For LCF, we used SciPy, an open-source Python library (Virtanen et al. 2020). The spectrum between 7110 and 7150 eV was used for fitting. The Fe<sup>3+</sup>/ $\Sigma$ Fe ratio was calculated by summing the Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of each standard sample multiplied by each weight calculated using LCF and dividing by the total weight. The goodness of fit to the XANES spectra was evaluated using the root mean squared error (RMSE) as follows:

$$RMSE = \sqrt{\frac{\sum_{i}^{n} (y_i - f_i)^2}{n}}$$
(2)

where *n* is number of data points,  $y_i$  is the measured intensity, and  $f_i$  is the predicted intensity of the XANES spectra.

We prepared eight mineral standards with variable Fe oxidation states and coordination, including octahedrally coordinated ferrous iron ( $^{VI}Fe^{2+}$ )-bearing minerals (olivine and enstatite), octahedrally coordinated ferric iron ( $^{VI}Fe^{3+}$ )-bearing

minerals (andradite, aegirine, and clinozoisite), tetrahedrally coordinated ferrous iron (<sup>IV</sup>Fe<sup>2+</sup>)-bearing mineral (staurolite), tetrahedrally coordinated ferric iron (<sup>IV</sup>Fe<sup>3+</sup>)-bearing mineral (sanidine), and magnetite (Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>O<sub>4</sub>), which contains VIFe<sup>2+</sup>, VIFe<sup>3+</sup>, and <sup>IV</sup>Fe<sup>3+</sup> in a ratio of 1:1:1 (Online Materials<sup>1</sup> Table S1). The EPMA data of the standard minerals used in this study indicate that andradite  $[Ca_{3.0}Fe_{2.0}^{3+}(SiO_4)_3]$  and aegirine  $(Na_{11}Fe_{0.9}^{3+}Si_2O_6)$  have compositions close to the end-members (Online Materials<sup>1</sup> Table S2). Olivine has a composition of (Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>SiO<sub>4</sub>, enstatite has a composition of (Mg<sub>0.9</sub>Fe<sub>0.1</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, and clinozoisite has a composition of Ca2.0Fe3+Al2.6(Si2O7)(SiO4)O(OH). Staurolite shows small concentrations of Mg and Ti:  $(Fe_{1,7}^{2+}Mg_{0,4})Al_{9,0}O_6(Si_{3,9}Ti_{0,1}O_4)_4(O,OH)_2$ , and sanidine has a small amount of Na and Fe: (K<sub>4.0</sub>Na<sub>0.1</sub>)(Al<sub>3.8</sub>Fe<sup>3+</sup><sub>0.2</sub>)Si<sub>12</sub>O<sub>32</sub>. The composition of these minerals is spatially uniform, and they contain no impurities except staurolite (Online Materials<sup>1</sup> Fig. S2). Although staurolite contains quartz inclusions, the effect on Fe K-edge XANES spectra is negligible because the concentration of iron in the quartz is low. LCF was conducted for all combinations of 2 to 8 standard samples to identify the optimal combination. The Akaike information criterion (AIC) (Akaike 1973) was used to assess the validity of the LCF model with each combination of standard samples, and the LCF model with the lowest AIC value was considered optimal.

Fe<sup>3+</sup>/ $\Sigma$ Fe ratios were also calculated using the integrated pre-edge peak intensity and pre-edge peak centroid position following the empirical calibration diagram of Wilke et al. (2001). For pre-edge extraction, the background was subtracted from the normalized XAFS spectra by fitting a Lorentz function plus a linear function in the region a few electron volts before and after the pre-edge. The centroid position energy and the integrated intensity of the pre-edge peaks were obtained using numerical integration similar to that used in Ellison et al. (2020). The data points were interpolated using cubic splines, and Simpson's rule was used for numerical integration. The Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of a sample was obtained by interpolation from the empirically derived calibration grid obtained from XANES spectra of mechanical mixtures of the three mineral standards (olivine for <sup>VI</sup>Fe<sup>2+</sup>, sanidine for <sup>IV</sup>Fe<sup>3+</sup>, and andradite for <sup>VI</sup>Fe<sup>3+</sup>) Wilke et al. (2001).

### RESULTS

## XANES spectra from typical Fe<sup>2+</sup>- and Fe<sup>3+</sup>-bearing minerals

XANES spectra from the mineral standards and magnetite are shown in Figure 1. XANES spectra are characterized by the absorption edge energy (energy at half absorption), edge crest (point of maximum absorption), and trough (first minimum after the edge crest), which vary with the coordination number and oxidation state (Fig. 1) (Waychunas et al. 1983; Guda et al. 2021). The edge crests are around 7127-7140 eV in all spectra, and there is a small pre-edge peak at 7112-7115 eV. The absorption edge energies of octahedrally coordinated Fe-bearing minerals (olivine, enstatite, clinozoisite, aegirine, and andradite) are 0.4-1.4 eV higher than those of tetrahedrally coordinated Febearing minerals with the same oxidation state (staurolite and sanidine; Fig. 1), consistent with the results of Waychunas et al. (1983). For minerals with the same coordination number, the edge energy is 4-5 eV higher for Fe<sup>3+</sup>-bearing minerals than Fe<sup>2+</sup>-bearing minerals. The energies of the troughs for tetrahedrally coordinated Fe-bearing minerals are 8-11 eV higher than those for octahedrally coordinated Fe-bearing minerals. Andradite has an edge energy that is 1.3–1.4 eV higher than the other two <sup>VI</sup>Fe<sup>3+</sup>-bearing minerals (aegirine and clinozoisite). Despite having the same oxidation state (Fe<sup>2+</sup>) and coordination number (octahedral), the spectrum for enstatite differs from that of olivine. This difference can be because the six-coordinated octahedral structure of the M2 site that hosts Fe in enstatite is distorted compared to olivine (Closmann et al. 1996). The edge energy of magnetite containing both  $Fe^{3+}$  and  $Fe^{2+}$  is between the edge energies of Fe<sup>2+</sup> and Fe<sup>3+</sup>-bearing minerals. The pre-edge peak



FIGURE 1. (a) XANES spectra from typical  $Fe^{2+}$  and  $Fe^{3+}$ -bearing minerals. Arrows indicate the pre-edge peaks, circles indicate the edges, diamonds represent the edge crests, and squares represent the troughs. (b) Extracted pre-edge peaks for each mineral. OI = olivine ( $^{VI}Fe^{2+}$ ); En = enstatite ( $^{VI}Fe^{2+}$ ); Adr = andradite ( $^{VI}Fe^{3+}$ ); Aeg = aegirine ( $^{VI}Fe^{3+}$ ); Czo = clinozoisite ( $^{VI}Fe^{3+}$ ); St = staurolite ( $^{IV}Fe^{2+}$ ); Sa = sanidine ( $^{IV}Fe^{3+}$ ); Mag = magnetite ( $^{VI}Fe^{2+}$ : $^{VI}Fe^{3+}$ : $^{VV}Fe^{3+}$  = 1:11).

of magnetite is relatively large compared to <sup>VI</sup>Fe-bearing minerals because of the iron in the tetrahedral site.

### Estimated $Fe^{3+}/\Sigma Fe$ ratios of olivine-magnetite mixtures

**XANES analytical results.** Figure 2 shows XANES spectra for mixtures with different proportions of olivine and magnetite. As the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio increases from 0.09 to 0.59, the edge energy increases from 7120.4 to 7122.5 eV, the trough energy increases from 7151.2 to 7160.2 eV, and the edge crest intensity decreases from 1.64 to 1.43. No systematic relationship was found between the trough intensity and Fe<sup>3+</sup>/ $\Sigma$ Fe ratio. These results support the previously reported correlations between Fe<sup>3+</sup>/ $\Sigma$ Fe ratios and edge energies (Guda et al. 2021).

Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of olivine-magnetite mixtures estimated using pre-edge spectra. The pre-edge intensity increases with increasing Fe<sup>3+</sup>/ $\Sigma$ Fe ratio due to the tetrahedrally coordinated Fe<sup>3+</sup> in magnetite (Fig. 2a). The pre-edge peak gradually shifts



FIGURE 2. (a) XANES spectra from olivine-magnetite mixtures. (b) Pre-edge peaks from the olivine-magnetite mixtures. (c) Pre-edge centroid energy vs. integrated pre-edge area. The area surrounded by the dotted line shows the applicable range of the empirical calibration curve by Wilke et al. (2001) for the quantification of  $Fe^{3+}/\Sigma Fe$ . Solid symbols indicate data that plot within the diagram area and open symbols indicate data that plot outside the diagram area enclosed by dotted line. (d)  $Fe^{3+}/\Sigma Fe$  ratios estimated from the pre-edge centroid energy and integrated pre-edge area.

toward higher energies with increasing proportions of magnetite (Fig. 2b; Online Materials<sup>1</sup> Table S3). The olivine-magnetite mixtures with Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of 0.09, 0.18, and 0.27 plot outside of the empirically derived triangular field with olivine (<sup>VI</sup>Fe<sup>2+</sup>), andradite (<sup>VI</sup>Fe<sup>3+</sup>), and sanidine (<sup>IV</sup>Fe<sup>3+</sup>) endmembers on the diagram proposed by Wilke et al. (2001) (Fig. 2c). For cases with higher Fe<sup>3+</sup>/ $\Sigma$ Fe ratios that plot inside the triangular field (Fig. 2c), the RMSE for the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio is 0.12 (Fig. 2d), which is similar to values (±0.1) reported in previous studies on Fe bearing minerals (Wilke et al. 2001; Ellison et al. 2020).

Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of olivine-magnetite mixture estimated using LCF. LCF was applied to XANES spectra of the olivinemagnetite mixtures (Fe<sup>3+</sup>/ $\Sigma$ Fe = 0.09–0.59) with all combinations of eight minerals (olivine, enstatite, andradite, clinozoisite, aegirine, staurolite, sanidine ± magnetite) used as end-members in the fitting models. Figure 3 shows representative observed and calculated spectra for the case where the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio is 0.27. When magnetite is included as an LCF end-member, two end-members (olivine and magnetite) are sufficient to reproduce the spectrum of the olivine-magnetite mixture (Fig. 3a; RMSE = 0.003). Increasing the number of end-members results in almost no change in the fitted spectrum (Fig. 3b). Next, to investigate the effect of unknown minerals in the sample, magnetite was treated as an unknown mineral and fitting was performed using the seven end-members without magnetite. When magnetite is not included as an end-member, the spectra fitted using fewer end-members (N < 3) deviate clearly from the shape of the edge crest and subsequent trough (Fig. 3c; RMSE = 0.017), but the position of the edge crest is well reproduced using five end-members (Fig. 3d; RMSE = 0.010).

The RMSE between the measured and modeled XANES spectra of six olivine-magnetite mixtures were compared using LCF models that either included or did not include magnetite XANES spectra. Figure 4 shows the RMSE between the measured XANES spectra and the LCF, the AIC, and the RMSE of the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio. For LCF models including magnetite, the RMSEs of the LCFs are almost constant with the number of end-members (RMSE = 0.003–0.004, Fig. 4a). The AIC has a minimum at four end-members, with a combination of olivine,



FIGURE 3. XANES spectra and linear combination fitting for an olivine-magnetite mixture with a  $Fe^{3+}/\Sigma Fe$  ratio of 0.27 using (a) olivine and magnetite; (b) olivine, enstatite, sanidine, and magnetite; (c) olivine and aegirine; and (d) olivine, enstatite, aegirine, andradite, and sanidine as standards. Open circles are XANES spectra, red lines are the results of linear combination fitting, and black lines are the residuals. Ol=olivine; Mag=magnetite; En=enstatite; Adr= andradite; Aeg=aegirine; Sa=sanidine.

enstatite, sanidine, and magnetite (Fig. 4b). The  $Fe^{3+}/\Sigma Fe$  ratios obtained using LCF are in good agreement with the theoretical values obtained from the mixing ratio, and almost constant with number of endmembers (RMSE of the  $Fe^{3+}/\Sigma Fe = 0.01$ ; Fig. 4c; Online Materials<sup>1</sup> Fig. S3a). Even with an increase in the number of end-members, the contribution of end-members other than olivine and magnetite was small (Fig. 4d). When magnetite is not included in the set of standard spectra, the RMSE and AIC of the LCF were minimized when five end-members were used (RMSE = 0.01; Figs. 4a and 4b), a combination of olivine, enstatite, aegirine, andradite, and sanidine (Fig. 4e). The RMSE between  $Fe^{3+}/\Sigma Fe$  ratios determined by the mixing ratios and LCF decreases as the number of end-members increases and becomes almost constant (RMSE of the  $Fe^{3+}/\Sigma Fe = 0.03$ ) when the number of end-members is five or more (Fig. 4c). The LCF value is slightly overestimated compared to the theoretical value  $(Fe^{3+}/\Sigma Fe = 0.04; Online Materials^1 Fig. S3b)$ . To estimate the uncertainty of the Fe<sup>3+</sup>/ $\Sigma$ Fe estimation with LCF, we investigated the relationship between the fitting error and the estimation error for all combinations of LCF performed for the olivine-magnetite mixture (Online Materials<sup>1</sup> Fig. S3c). The relationship between the fitting errors (RMSE of the LCF) and the errors of the estimated Fe<sup>3+</sup>/ $\Sigma$ Fe ratios indicates that the larger the fitting error, the larger the error in the estimation of the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio. From this relationship, when the RMSE of LCF is 0.01, the accuracy of Fe<sup>3+</sup>/ $\Sigma$ Fe can be estimated as ± 0.05 (Online Materials<sup>1</sup> Fig. S3d).

### Estimated $Fe^{3+}/\Sigma Fe$ ratios of natural serpentinites

Natural serpentinites from the Oman ophiolite. To investigate the applicability of XAFS to the measurement of the oxidation state of iron in natural serpentinites, the  $Fe^{3+}/\Sigma Fe$  of serpentinized dunites and harzburgites were examined using titration and XRF. The  $Fe_2O_3^*$  (all iron as  $Fe_2O_3$ ) concentrations of the serpentinized dunite determined by XRF (8.7–12.8 wt%) are slightly higher than those of the serpentinized harzburgite (6.9–8.2 wt%; Table 2). The range of  $Fe^{3+}/\Sigma Fe$  ratios of the serpentinized dunite and harzburgite samples determined by titration are 0.64–0.73 and 0.45–0.69, respectively. The  $Fe^{3+}/\Sigma Fe$  ratio of the harzburgite increases with increasing amounts of serpentine, from 0.45 at 52.9 wt% serpentine (C5708B-119Z2-7-12) to 0.69 at 87.6 wt% serpentine (C5707A-179Z3-18-26; Table 2).



FIGURE 4. Number of end-members vs. (a) root mean squared error (RMSE), (b) Akaike's information criterion (AIC), and (c) RMSE of the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of the olivine-magnetite mixtures. Plots with orange and black indicate LCF with eight end-members including magnetite, an LCF with seven end-members without magnetite, respectively. All combinations are tested for each number of end-members, and the plot shows the cases with the minimum RMSE between the measured XANES spectra and the linear combination fit. The weights of end-members used for LCF with (d) eight standards (including magnetite) and (e) seven standards (excluding magnetite). The color in (d) and (e) indicates the weight of each standard sample. Ol = olivine; En = enstatite; Aeg = aegirine; Adr = andradite; Czo = clinozoisite; St = staurolite; Sa = sanidine; Mag = magnetite.

 $Fe^{3+}/\Sigma Fe$  estimates from XANES spectra. We estimated the Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of natural serpentinites (serpentinized dunite and serpentinized harzburgite) from the Oman ophiolite using the LCF of the XANES spectra (Online Materials<sup>1</sup> Fig. S4). We investigated the optimal combination of standard spectra for LCF of the serpentinized dunites and harzburgites. The combination of four end-members (olivine, enstatite, and magnetite) has the lowest AIC and RMSE values (Online Materials<sup>1</sup> Figs. S5a and S5b). Although the LCF shows lower intensities than the data near the edge crest (~7130 eV), the XANES spectra of the serpentinized dunites (Fig. 5a) and harzburgites (Fig. 5b) are generally well fitted by LCF with the five end-members. Figure 5c shows the relationship between the Fe<sup>3+</sup>/ $\Sigma$ Fe ratios estimated by the best LCF model with five end-members (olivine, enstatite, andradite, aegirine, and sanidine) and titration. The  $Fe^{3+}/\Sigma Fe$  ratio of the serpentinite sample obtained using LCF shows a linear increase with the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio determined by titration, although the former is systematically lower. The  $Fe^{3+}/\Sigma Fe$  ratio estimated using LCF for the serpentinized dunites differs from the value obtained using titration by  $\sim 0.09-0.2$ , which is larger than the difference for the serpentinized harzburgites (~0.05–0.1). The RMSE of the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio between LCF and titration is 0.14 (Online Materials<sup>1</sup> Fig. S5c), which is slightly larger than the error in  $Fe^{3+}/\Sigma Fe$  estimated from the RMSE of LCF (0.12; Online Materials<sup>1</sup> Fig. S3d).

### DISCUSSION

The pre-edge method has been commonly used to estimate the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of silicate glasses and minerals (Wilke et al. 2001; Berry et al. 2003; Marcaillou et al. 2011; Andreani et al. 2013). However, its applicability to serpentinites, which are mixtures of Fe-bearing silicates and magnetite, is not clear. Some of our results for olivine-magnetite mixtures using the pre-edge method plot outside of the empirical diagram of Wilke et al. (2001) (Fig. 2c). This may be due to the large influence of the tetrahedrally coordinated Fe<sup>3+</sup> in magnetite on the pre-edge peak (Wilke et al. 2001). This suggests that the estimation of Fe<sup>3+</sup>/ $\Sigma$ Fe ratios using the pre-edge method is not suitable for magnetite-bearing samples.

On the other hand, the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of the olivine-magnetite mixture was estimated by LCF with high accuracy (RMSE of the Fe<sup>3+</sup>/ $\Sigma$ Fe = 0.03) compared to the pre-edge method (RMSE of the Fe<sup>3+</sup>/ $\Sigma$ Fe = 0.12; Fig. 2d) over a wide range of Fe<sup>3+</sup>/ $\Sigma$ Fe ratios (0.09–0.59), even when magnetite was not included in the standard spectrum. These results are consistent with the results of a previous study that showed that the estimation of Fe<sup>3+</sup>/ $\Sigma$ Fe ratios using LCF is less affected by the standard minerals used for fitting (Sutton et al. 2017) and suggested that the LCF method can be used to evaluate the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio, even for minerals that are not included in the standard spectrum. Therefore, LCF may be effective in cases where the pre-edge method is not applicable.



FIGURE 5. XANES spectra and linear combination fitting using olivine, enstatite, aegirine, andradite, and sanidine standards for (a) dunite and (b) harzburgite. (c)  $Fe^{3+}/\Sigma Fe$  ratios of serpentinized dunite and harzburgite samples estimated using linear combination fitting with olivine, enstatite, andradite, and magnetite.

In this study, the Fe<sup>3+</sup>/ $\Sigma$ Fe ratios of serpentinites estimated using LCF were systematically lower than those estimated using titration (Fig. 5c), even for olivine (Fe<sup>3+</sup>/ $\Sigma$ Fe = 0) and magnetite  $(Fe^{3+}/\Sigma Fe = 0.67)$ , where the  $Fe^{3+}/\Sigma Fe$  ratios of olivine and magnetite determined by titration were 0.13-0.17 and 0.78, respectively (Online Materials<sup>1</sup> Table S4). The  $Fe^{3+}/\Sigma Fe$  ratios of magnetite determined by titration are 16% higher than the true value defined by the stoichiometry of magnetite. Therefore, we consider that the discrepancy of Fe<sup>3+</sup>/ $\Sigma$ Fe ratios between LCF and titration method is mainly because of oxidation during titration. Similar results were also seen in a comparison of wet chemical analysis and the Mössbauer method (Canil et al. 1994). On the other hand, results from titration methods that have taken steps to prevent oxidation agree with XANES results to within the measurement error (Bézos et al. 2021). In our titration method, rock samples were dissolved using HF in air. Oxidation from  $Fe^{2+}$  to  $Fe^{3+}$  during dissolution easily occurs during or after dissolution of the sample powder (Andrade et al. 2002; Nakamura et al. 2020). Oxidation also may be enhanced in the presence of fluoride due to a decrease in the redox potential of Fe<sup>2+</sup>/Fe<sup>3+</sup>(Andrade et al. 2002), which may result in systematically higher  $Fe^{3+}/\Sigma Fe$  ratios.

On the other hand, the  $Fe^{3+}/\Sigma Fe$  ratio can be underestimated by LCF due to the presence of  $Fe^{3+}$  in the mineral used as a standard sample for the Fe<sup>2+</sup> end-members (olivine, enstatite, and staurolite). If we focus on olivine and enstatite, which were used to estimate the  $Fe^{3+}/\Sigma Fe$  of the Ol-Mag mixture and serpentinites, the  $Fe^{3+}$  in typical mantle olivine is close to or below the detection limit of Mössbauer spectroscopy (Fe<sup>3+</sup>/ $\Sigma$ Fe  $\leq$ 0.04; e.g., Duba et al. 1973; Canil et al. 1994). The exact location of the olivine from China used in this study is unknown. However, the  $X_{Mg}$  value of the olivine is 0.90, which is in the range of typical mantle olivine values ( $X_{Mg} = 0.86 - 0.94$ , Sobolev et al. 2007). Thus, it is likely that the olivine is of mantle origin, which has a low  $Fe^{3+}/\Sigma Fe$  ratio. Moreover, the  $Fe^{3+}$  content of enstatite is generally less than ~1% of the total Fe (Eftaxias and Vassilikou-Dova 1990), thus the effect on the estimation of  $Fe^{3+}/\Sigma Fe$  will be negligible when using the LCF method.

Natural Fe-bearing minerals are generally solid solutions, which may affect the estimation of the  $Fe^{3+}/\Sigma Fe$  ratio with

LCF. Of the standard minerals used in this study, andradite and aegirine have compositions close to the end-members. Olivine is a solid solution of forsterite-fayalite, enstatite is that of enstatite-ferrosilite, and clinozoisite is that of clinozoisiteepidote (Online Materials<sup>1</sup> Table S2). However, the valence and coordination of iron are the same in each of these solid solutions, and the effect on the XAFS spectrum and the estimation of the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio is considered insignificant.

The difference in the Fe<sup>3+</sup>/ $\Sigma$ Fe ratios determined by titration and by LCF is larger for dunite than harzburgite, which may reflect differences in the magnetite contents of these rocks. The dunite from the Oman ophiolite has a stronger magnetic susceptibility than the harzburgite, suggesting that it contains more magnetite (Hong et al. 2022). This difference between dunite and harzburgite in Fe<sup>3+</sup>/ $\Sigma$ Fe ratios measured by titration vs. LCF could be attributed to the titration method, since there was no significant difference between dunite and harzburgite in terms of LCF fitting (Figs. 5a and 5b). Our results suggest the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio may be overestimated if no special care is taken during the titration process, and under appropriate conditions where photo-oxidation does not occur, the XAFS method may be less affected by oxidation during analysis than the titration method.

### IMPLICATIONS

In contrast to conventional methods for estimating the bulkrock  $Fe^{3+}/\Sigma Fe$  ratio (e.g., titration and the Mössbauer method), XANES-based analyses have the advantage of being applicable to small samples (~30 mg) and in situ measurement, including redox state mapping. The advantages of XANES (small analytical spots and rapid measurements) mean that quantitative maps of the Fe redox state can be obtained, which could reveal relationships between rock microtexture and redox state. Serpentinites usually have complex textures, including mesh textures and multi-stage veining, which are related to the evolution of fluid flow, redox conditions, and water-rock reactions (Andreani et al. 2007, 2013; Rouméjon et al. 2015; Shimizu and Okamoto 2016; Yoshida et al. 2023a). Previous studies have made 2D images of the Fe oxidation state of serpentine mesh textures using the pre-edge peaks (Andreani et al. 2013; Ellison et al. 2020). Our results show that LCF can be used to estimate the oxidation state of iron with high accuracy even when the pre-edge method cannot be used, and that it can be applied to various serpentinite samples. Accordingly, LCF makes it possible to obtain more detailed quantitative maps of the Fe redox state, which can provide important insights into the evolution of serpentinization involving Fe partitioning and H<sub>2</sub> production. On the other hand, the crystallographic anisotropy of minerals may affect Fe<sup>3+</sup>/ΣFe mapping (Muñoz et al. 2013). However, at least in the case of the low-temperature serpentine analyzed in this study, it is common for the lizardite and chrysotile contained in it to exhibit crystal sizes smaller than the beam size of the mapping (several to  $20 \,\mu\text{m}$ ) and the thickness of the analyzed sample (Andreani et al. 2013). Thus, the effect of crystal orientation is expected to be small. Further research is needed on the effects of anisotropy when applying this LCF method to mapping serpentinite samples, including relatively coarse-grained serpentine.

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#### Endnotes:

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