

## Supplemental Material

### RAW DATA

Crystal-chemical, crystallographic and spectroscopic raw data of the reference materials studied in this article can be downloaded at DOI:10.5281/zenodo.5484779.

### PREPARATION AND CHARACTERIZATION OF THE MINERAL REFERENCES

#### Crystal-cell parameters, chemical compositions and local structure of the Nb references

The nature of the Nb reference materials was checked using single-crystal X-ray diffraction and electron microprobe analyzes. Supplemental Tables S1 and S2 summarize the chemical compositions and crystal-cell parameters of these minerals.

The local structure of Nb indicated in Table 1 for each Nb mineral comes from the following references: Perrault (1968) (fluorcalciopyrochlore), Bonazzi et al. (2006) (hydropyrochlore), Wenger et al. (1991) (columbite-(Mn)), Chakhmouadian and Mitchell (1998) (Nb perovskite), Melini (1982) (niocalite). The local structure of Nb, Fe, Ti and Ce in the synthetic samples comes from: Gouget et al. (2019) (lueshite), Meagher and Lager (1979) (rutile), Horn et al. (1972) (anatase), Blake et al. (1966) (hematite), Yang et al. (2006) (goethite), Wyckoff (1963) (cerianite), Jehng and Wachs (1991) (Nb<sub>2</sub>O<sub>5</sub>).

#### Detailed procedure of synthesis of Nb-substituted minerals

**Niobium-substituted Fe oxides (1 wt% Nb).** The synthesis of Nb-substituted iron oxides has been adapted from the procedure used to prepare Sc-substituted iron oxides (Chassé et al. 2017). A solution containing ca. 0.291 g of NbCl<sub>5</sub> was diluted in 37 wt% HCl. The pH of this acidic solution was raised to 3 by adding 10 M NaOH. This procedure is necessary to avoid Nb oxides precipitation. 4.5 g of Fe(NO<sub>3</sub>) · 9H<sub>2</sub>O were dissolved into 100 mL of 18.2 MW · cm deionized water. 10 mL of the NbCl<sub>5</sub> solution was withdrawn from solution and mixed with the Fe(NO<sub>3</sub>) · 9H<sub>2</sub>O solution. At the same time, 50 mL of 1.35 M NaOH were added raising the pH of the solution up to

13 and leading to the precipitation of ferrihydrite ( $\text{Fe}^{3+}\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ). The solution was then filled up to 1 L with 33 mM NaOH. The solution was heated at 70 °C in a water-bath under moderate stirring for 48 h and centrifuged 10 min at 8,000 rpm and 10 min at 10,000 rpm to separate the solid product from the supernatant. The solid was washed by adding 3 M  $\text{H}_2\text{SO}_4$  in order to remove potential adsorbed Nb species or poorly crystallized iron oxides. This solution was placed in ultrasonic bath and then in water bath for 2 h at 45 °C. After removing the supernatant by centrifugation at 10,000 rpm during 10 min, the solid was washed three times with 18.2 MW · cm deionized water. The solid was dried out for 24 h at 45 °C in autoclave giving 1 g of Nb-substituted goethite. Nb-substituted goethite was converted into Nb-substituted hematite through dehydration by heating in a furnace at 300 °C for 2 h.

**Niobium-substituted Ti oxides (5 wt% Nb).** 5.5 mL of  $\text{TiCl}_4$  were mixed in 44.5 mL of 3 M HCl in an ice bath under strong stirring. 675 mg of  $\text{NbCl}_5$  was diluted in 20 mL of 12 M HCl and added to the  $\text{TiCl}_4$  acid solution. 10 M NaOH was progressively added under strong stirring while measuring the pH. Once the pH reached ca. 3–4, 3 M NaOH was added dropwise up to pH ca. 5. 1 M NaOH was progressively added to increase the pH up to 6. The solution was then heated for 60 min in a microwave furnace at 800 W with a temperature ramp attaining 200 °C in 10 min. The solution was washed three times with deionized water and once with 3 M  $\text{HNO}_3$  in order to remove the amorphous phases. Before each centrifugation, the solution was placed in ultrasonic bath and then shaken using a vortex mixer. After each centrifugation, the supernatant was removed. Niobium-substituted anatase was finally dried out in an oven for 12 hours at 60 °C (Dufour et al. 2012). Niobium-bearing rutile (5 wt%) was obtained by heating Nb-bearing anatase (5 wt%) at 700 °C for 3h.

**Niobium-substituted cerianite. (1 wt% Nb).** 3 g of 1 wt% Nb-substituted cerianite was synthesized by homogenizing 2.97 g of  $\text{Ce}^{4+}\text{O}_2$  with 0.0132 g of  $\text{Nb}_2\text{O}_5$  and 0.0168 g of  $\text{Nd}_2\text{O}_3$  to satisfy charge balance in an agate mortar with ethanol. The synthesis was completed by heating the mixture at 1300 °C for six hours. A 10 °C · min<sup>-1</sup> temperature step was used up to 1000 °C followed

by a  $5\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$  temperature step up to  $1300\text{ }^{\circ}\text{C}$ . The operation was repeated three times after homogenization in an agate mortar for 30 min between each run.

### **X-ray diffraction patterns of the synthetic reference materials**

The successful completion of the syntheses was verified by powder X-ray diffraction analysis. Figures S1 and S2 show the X-ray diffraction patterns of the synthetic compounds. The main reflection peaks are noted in the Miller indices notation.  $\text{Nb}_2\text{O}_5$  reference consists of at least three polymorphs crystallizing in different systems with different Nb coordination number.

## **ANALYSES OF X-RAY ABSORPTION SPECTRA**

### **Normalization procedure**

The shape of the MBACK normalization function preserves the branching ratio between the  $L_3$ - and  $L_2$ -edges by applying a single smooth background function over the entire XANES spectra between 2350 and 2500 eV (Supplemental Fig. S3).

### **Deconvolution of niobium $L_{2,3}$ -edges XANES spectra**

Figures S4 and S5 show the deconvolution of the XANES spectra of all the reference materials into three pseudo-Voigts at the  $L_3$ - and  $L_2$ -edges. The continuum background was removed using an error function with arbitrarily fixed width (ca. 8 eV) and inflection points (2373.0 and 2467.0 eV) in order to obtain comparable fit results. The amplitude, center, width and intensity of the three pseudo-Voigts are given in Supplemental Table S3.

The deconvolution of the XANES spectra allows the comparison of the splitting between the A and B features ( $\Delta E$ ), the full width at half maximum of feature B with respect to feature A ( $\text{FWHM}_{\text{B/A}}$ ) and the intensity ratio ( $I_{\text{a}}/I_{\text{b}}$ ) between the  $L_3$ - and  $L_2$ -edges (Supplemental Fig. S6).  $\Delta E(L_2)$  and  $\Delta E(L_3)$ ,  $\text{FWHM}_{\text{B/A}}(L_2)$  and  $\text{FWHM}_{\text{B/A}}(L_3)$  as well as  $I_{\text{A/B}}(L_2)$  and  $I_{\text{A/B}}(L_3)$  exhibit strong correlations ( $R^2 = 0.94, 0.95, 0.93$ , respectively).

The branching ratio ( $I[L_3]/I[L_2]$ ) is determined based on features  $A_3$  and  $A_2$  because they are less subject to broadening than  $B_3$  and  $B_2$ . Instead of using the relative intensity of the features, we

consider their areas obtained by the fitting procedure which gives a better measure of their intensity (Scherz et al. 2005). The branching ratios range from 1.5 to 2.6 with an average of 1.87. The agreement of the branching ratio with the expected statistical value of 2 is also found for other  $4d$  elements such as  $Zr^{4+}$  and  $Mo^{6+}$  because the Slater-Condon integrals of  $4d$  elements are too small to influence the branching ratio of the  $L_3$  and  $L_2$ -edges (De Groot et al. 1994).

Contrary to what it is expected from the increase of the Auger decay at the  $L_2$ -edge that should enhance the broadening of the features, the widths of features  $A_2$  are smaller than  $A_3$  (2.0 and 2.4 eV, respectively) while those of  $B_2$  and  $B_3$  are more similar (3.53 and 3.67 eV, respectively). This trend results in the larger  $FWHM_{B/A}$  at the  $L_2$ -edge. This broadening is related to low intensity transitions accompanying the  $t_{2g}$  transition at the  $L_3$ -edge (Fig. S4 and S5). Despite such specificity is not often observed in the literature, larger widths of the  $L_3$ -edge features with respect to those at the  $L_2$ -edge have been mentioned in the case of Nb for  $Nb_2O_5$  (Sugiura et al. 1988) and other  $4d$  elements such as Sr, Zr, Ru, Rh, Pd (Schaaffs et al. 1957; Sugiura et al. 1987). This points out the differences in the core-hole created in  $2p_{1/2}$  and  $2p_{3/2}$  levels which cause different effects on the final states between the  $3d$  and  $4d$  elements.

## CALCULATIONS OF Nb $L_{2,3}$ -EDGES X-RAY ABSORPTION NEAR-EDGE STRUCTURE SPECTRA

### Crystal-field and ligand-field multiplet effects on Nb $L_{2,3}$ -edges spectra

**Step-by-step modeling of a Nb  $L_{2,3}$ -edges X-ray absorption spectrum.** The interpretation of the spectral features is influenced by the strong electronic interaction between the  $2p$  core wave function with the  $4d$  wave functions for a  $4d^n$  transition metal (De Groot 2005; Ikeno et al. 2011). However, atomic multiplet theory alone does not take into account the effects of the neighbors of the absorbing atom. Crystal-field multiplet (CFM) theory includes the symmetry effects induced by the ligands while ligand-field multiplet (LFM) theory considers two or more configurations to describe the ground and final state taking into account the ligand character of the valence band of the atom, for instance, the oxygen  $2p$  valence band for an oxide. In order to

interpret XANES spectra obtained on selected reference materials and relate the spectral features to Nb local environment, theoretical spectra are calculated with each parameter varying independently from the others. The calculation of a Nb  $L_{2,3}$ -edges spectrum based on the single-particle model gives a spectrum with a single feature at 2371 eV (Haverkort et al. 2012) (Supplemental Fig. S7a), the theoretical energy of the  $2p^64d^0 \rightarrow 2p^54d^1$  transition of  $\text{Nb}^{5+}$  ions. Experimental  $L_{2,3}$ -edges spectra exhibit additional features, not reproduced in the single-particle approximation, arising from crystal-field and ligand-field multiplet effects. The double-peaked edge feature is obtained by considering crystal-field effects (Supplemental Fig. S7b) simulating symmetry effects induced by the Nb neighbors. In this model, the absorbing transition metal is modeled in its crystal structure as a cation surrounded by an array of negative point charges representing the ligands. The five-fold degeneracy of the  $d$ -orbitals is removed with relative energies affected by the nature and oxidation state of the absorbing atoms and by the arrangement and nature of the surrounding ligands (Burns 1993). In the case of  $4d^0$  transition metals such as  $\text{Nb}^{5+}$ , multiplet effects also influence the spectral features (De Groot et al. 1994). The dipole selection rule implies that the final  $2p^5$  orbitals are split into two states ( $2p_{3/2}$  and  $2p_{1/2}$ ) due to the spin orbit coupling. The  $L_2$ -edge, with two features centered at ca. 2470 eV (Supplemental Fig. S7c), arises from the addition of this spin-orbit coupling between the  $4d$  and  $2p$  orbitals of Nb considering atomic values of 0.124 eV and 63.97 eV, respectively. Another multiplet effect results from electron-electron interactions. The Slater-Condon parameters  $F^2_{pd}$ , the radial part of the Coulomb repulsion, and  $G^1_{pd}$  and  $G^3_{pd}$ , the radial part of the Coulomb exchange interaction are used to take into account this effect. These parameters are scaled relatively to their Hartree-Fock values ( $F^2 = 2.680$  eV,  $G^1 = 1.627$  eV and  $G^3 = 0.946$  eV) by a reduction parameter (commonly 80 %) shifting in energy all the features and yielding variations in their relative intensities (Supplemental Fig. S7d).

The simulation of X-ray absorption spectra of covalent solids such as Nb minerals requires the addition of more than one configuration (Miedema and de Groot 2013). ligand-field multiplet theory solves this problem by adding a configuration  $4d^{n+1}\underline{L}$  to the  $4d^n$  ground state. In the case of a

Nb oxide, an electron has been moved from the oxygen  $2p$  valence orbitals to the  $4d$  orbitals of Nb with  $\underline{L}$  denoting a ligand hole. In order to accurately describe the energy levels, LFM calculations require the introduction of new parameters, i.e. the charge transfer energy between  $4d^n$  and  $4d^{n+1}\underline{L}$  ( $\Delta$ ) and the hopping integrals describing the mixing between  $4d^n$  and  $4d^{n+1}\underline{L}$  configurations ( $V_{eg}$  and  $V_{t2g}$ ). The C features are reproduced (Supplemental Fig. S7e) with the charge transfer parameters used for Ti compounds (Table 4, i.e.. Okada and Kotani 1993). The spectra are well reproduced when all these effects are considered (Supplemental Fig. S7f).

**Spectral effects of the atomic multiplets.** The transition from a spherical symmetry ( $SO_3$ ) to an octahedral symmetry ( $O_h$ ) splits both edges into the two features, with the energy splitting dependent on the  $10Dq$  crystal-field parameter (Supplemental Fig. S7b). Variation of the  $2p$  spin-orbit coupling has an influence on the energy position of the  $L_2$ -edge. We investigated the effects of the  $p-d$  electronic interactions defined by  $F^2$ ,  $G^1$  and  $G^3$ . Absorption spectra were calculated with Slater-Condon integrals rescaled between 50 and 100 % their atomic values with an interval of 10 %. The spectrum obtained with a reduction of 100 % is equivalent to the free ion case. The reduction of the Slater integrals leads to the increase in the  $I_A/I_B$  ratio at the  $L_3$ -edge (Supplemental Fig. S8a).  $A_3$  feature has a greater intensity than  $B_3$  only with a reduction of  $F^2$ ,  $G^1$  and  $G^3$  to 50 %. The same trend is observed at the  $L_2$ -edge with a sharp increase of the relative intensity ratio when the Slater integrals are reduced to ca. 50 %.

**Spectral effects of the crystal-field multiplets.** In these simulations,  $Nb^{5+}$  is six-fold coordinated ( $[^6]Nb$ ) by oxygen ligands in an octahedral symmetry, as it is the case in a large range of Nb minerals (Waroquiers et al. 2017). However,  $d^0$  transition metals in six-fold coordination such as  $Nb^{5+}$ ,  $Ti^{4+}$ ,  $V^{5+}$  and  $Mo^{6+}$  commonly constitute distorted octahedra (Kunz and Brown 1995; Piilonen et al. 2006). In order to investigate the influence of the distortion of the  $Nb^{5+}$  site on the spectral shapes, we simulated spectra considering the successive site symmetries: 1)  $SO_3 \supset O_h \supset T_d \supset C_{3v}$  and 2)  $SO_3 \supset O_h \supset D_{4h}$  resulting in different energy splittings of the d orbitals (Butler 1981). Elongation and compression along the z-axis as well as square plane cases have been approximated

in  $D_{4h}$  site symmetry.

In  $O_h$  and  $T_d$  geometries, one crystal-field parameter,  $10Dq$ , needs to be considered. Increasing the intensity of crystal-field effects leads to an increase in  $\Delta E$  (Supplemental Fig. S8b). However,  $10Dq$  is not equal to  $\Delta E$  (De Groot et al. 1990). Here,  $10Dq$  is greater than  $\Delta E$  by ca. 5–20 % when the input value of  $10Dq$  is  $< 2.5$  eV. The discrepancy between the theoretical and calculated values are under 5 % with an input value greater than 2.5 eV. Whereas the  $L_2$ -edge features have relative intensity ratios close to 1, those of the  $L_3$ -edge features increase from ca.0.6 to 1.0 with increasing  $10Dq$  parameters (Supplemental Fig. S8c).

Compared to a regular  $NbO_6$  octahedron, the spectrum of regular Nb tetrahedral site ( $T_d$ ) is characterized by low relative intensity ratios (0.4 and 0.73 at the  $L_3$ -edge and  $L_2$ -edge, respectively, Supplemental Fig. S9). When the symmetry is lowered to  $D_{4h}$ , four features are visible arising from three crystal-field parameters ( $Dq$ ,  $Ds$ ,  $Dt$ ) reflecting the energy differences between the four levels. The  $Dq$ ,  $Ds$ ,  $Dt$  parameters are related by the following set of equations (König and Kremer 1977):

$$E_{a_{1g}} = +6Dq - 2Ds - 6Dt \text{ (} d_{z^2} \text{ orbital)} \quad (1)$$

$$E_{b_{1g}} = +6Dq + 2Ds - Dt \text{ (} d_{x^2-y^2} \text{ orbital)} \quad (2)$$

$$E_{e_g} = -4Dq - Ds + 4Dt \text{ (} d_{xz}, d_{yz} \text{ orbital)} \quad (3)$$

$$E_{b_{2g}} = -4Dq + 2Ds - Dt \text{ (} d_{xy} \text{ orbital)} \quad (4)$$

The tetragonal elongation and the compression of the  $NbO_6$  octahedra both result in additional and broadened features induced by the splitting of the  $t_{2g}$  level into  $b_{2g}$  and  $e_g$  levels and the  $e_g$  level into  $a_{1g}$  and  $b_{1g}$ . The energy level of a specific orbital is distinct between the compression and the elongation of the octahedron. For the compression case,  $b_{1g}$  and  $e_g$  levels occupy the same wide feature (feature 4, Supplemental Fig. S9) due to their proximity in energy. The same occurs in the elongation case for the  $a_{1g}$  and  $b_{2g}$  levels (feature 3, Supplemental Fig. S9). In the case of square-plane geometry, corresponding to the infinite elongation of an octahedron

along the z-axis, the high energy feature ( $b_{1g}$  level) is of lesser intensity than the broad feature (feature 2, Supplemental Fig. S9) with a shoulder corresponding to the ( $e_g$ ,  $a_{1g}$ ) and  $b_{2g}$  levels. The additional features resulting from the Nb site distortion increase in intensity with higher distortion (Supplemental Fig. S9).

The trigonal distortion of  $\text{NbO}_6$  octahedra ( $C_{3v}$ ) calculated with  $Dq$ ,  $D\tau$  and  $D\sigma$  crystal-field parameters leads to the broadening of the low energy feature originating from the splitting of the  $t_{2g}$  levels into  $a_1$  and  $a_2$  (feature 1, Supplemental Fig. S9).

## FIGURE CAPTIONS

**Figure S1:** X-ray diffraction patterns with annotated Miller indices of (a) Nb-substituted Fe oxides, (b) Nb-substituted Ti oxides.

**Figure S2:** X-ray diffraction patterns with annotated Miller indices of the other synthetic references (a) lueshite, (b) Nb-substituted cerianite and (c)  $\text{Nb}_2\text{O}_5$ .

**Figure S3:** MBACK normalization method of  $\text{Nb}_2\text{O}_5$  Nb  $L_{2,3}$ -edges XANES spectrum (black line). The MBACK normalization curve (dashed red line) is dominated by a Legendre polynomial term with an additional error function term (Weng et al. 2005). The edge energy chosen as the input parameter of the MBACK function implemented in Larch is ca 2371 eV.

**Figure S4:** Deconvolution of the  $L_3$ -edge for the complete set of reference spectra with three pseudo-Voigts (PV1, PV2, PV3) and a step error function (ERF). The experimental (Exp.) and the fitted data (Fit.) are shown by the black and purple curves, respectively.

**Figure S5:** Deconvolution of the  $L_2$ -edge for the complete set of reference spectra with three pseudo-Voigts (PV1, PV2, PV3) and a step error function (ERF). The experimental (Exp.) and the fitted data (Fit.) are shown by the black and purple curves, respectively.



**Figure S6:** Binary plots of the correlation of (a)  $\Delta E$ , (b)  $I_A/I_B$  and (c)  $\text{FWHM}_{B/A}$  between the  $L_3$ - and the  $L_2$ -edges. Pearson's correlation coefficients are given after excluding lueshite data.

**Figure S7:** Theoretical spectra reproduce experimental spectra (such as the one of columbite here) when crystal-field and ligand-field multiplet effects are taken into account in the simulations. (a) Atomic spectrum for the  $2p^64d^0 \rightarrow 2p^54d^1$  transition of  $\text{Nb}^{5+}$  ions. (b) Addition of crystal-field effects with Nb occupying a regular octahedral site ( $O_h$ ).  $10Dq = 4.1$  eV was chosen in order to simulate the columbite spectrum. (c) Inclusion of  $2p$  (scale factor of 0.98) and  $4d$  spin-orbit coupling. (d) Inclusion of atomic multiplet effects with Slater-Condon integrals scaled to 80 % of their atomic values ( $F^2_{pd} = 1.972$  eV,  $G^1_{pd} = 1.627$  eV and  $G^3_{pd} = 0.946$  eV). (e) Inclusion of ligand-field multiplet effects involving the hybridization of the  $2p$  (O) and  $4d$  (Nb) orbitals. (f) Experimental spectrum of columbite. Experimental spectra must be normalized (MBACK curve, dashed line) and absorption background must be removed to be compared with theoretical spectra.

**Figure S8:** Binary plots of (a) the correlation between  $10Dq$  and  $\Delta E$ . (b) and (c)  $I_A/I_B$  ratio with respect to  $10Dq$  and Slater-Condon reduction factor.

**Figure S9:** Influence of the local symmetry of Nb site on the spectral Nb  $L_{2,3}$ -edges XANES features. (a)  $O_h$  symmetry (regular  $^{[6]}\text{Nb}$  octahedron). (b)  $T_d$  symmetry ( $^{[4]}\text{Nb}$ ). (c)  $D_{4h}$  symmetry (compressed  $^{[6]}\text{Nb}$  octahedron). (d)  $D_{4h}$  symmetry (elongated  $^{[6]}\text{Nb}$  octahedron). (e)  $D_{4h}$  symmetry ( $^{[4\text{-sq}]}\text{Nb}$  square plane). (f)  $C_{3v}$  symmetry (trigonal distortion of the  $^{[6]}\text{Nb}$  octahedron).

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