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21 The complexity of niobium (Nb) mineralogy, dominated by more than one hundred oxides of  
22 similar crystal chemistry, makes it particularly challenging to determine Nb speciation in minerals.  
23 Here, we describe the first Nb  $L_{2,3}$ -edges X-ray absorption near-edge structure (XANES) data on  
24 Nb-bearing minerals and synthetic oxides relevant to geological contexts. The interpretation of Nb  
25  $L_{2,3}$ -edges XANES spectra in light of crystal-field theory mirrors the sensitivity of spectra to the  
26 local site symmetry and the electronic configuration around Nb atoms. Crystal-field multiplet  
27 simulations give estimates of the  $10Dq$  crystal-field parameter of  $\text{Nb}^{5+}$ , ranging from 2.8 to 3.9 eV  
28 depending on Nb coordination and Nb–O distances. In particular, the  $10Dq$  vs.  $R^{-5}$  relationship  
29 (where R represents the average Nb–O bond distance) is observed for octahedrally-coordinated Nb,  
30 as expected in a point-charge model. Complementary ligand-field multiplet simulations provide  
31 evidence of charge transfer between Nb and O. The Nb–O bonds show an equivalent mixing  
32 between ionic and covalent character unlike more ionic  $3d$  metal–O bonds. These interpretations  
33 provide information on the mechanisms by which  $\text{Nb}^{5+}$  substitutes for  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$  or  $\text{Ce}^{4+}$  in oxides  
34 common in environmental contexts. Whereas the substitution of  $\text{Nb}^{5+}$  for  $\text{Ce}^{4+}$  does not modify the  
35 local structure of the cation site in cerianite, the substitution of  $\text{Nb}^{5+}$  for  $\text{Ti}^{4+}$  in rutile and anatase  
36 results in an increase of the cation-ligand distance and a decrease in the symmetry of the cation site.  
37 Conversely, the substitution of  $\text{Nb}^{5+}$  for  $\text{Fe}^{3+}$  in hematite and goethite results in a smaller cation site  
38 distortion. Our study demonstrates the usefulness of Nb  $L_{2,3}$ -edges XANES spectroscopy to  
39 constrain Nb speciation in minerals with direct relevance for understanding the processes that can  
40 concentrate this critical metal at economic levels.

41 **Keywords:** Niobium, XANES, multiplet,  $10Dq$ , local structure, speciation

45 Niobium (Nb) is a typical critical element (European Commission 2020). It is intensively  
46 used by industry to produce superalloys, superconducting magnets and catalysts (Schulz et al.  
47 2017). In the frame of the environmental transition, Nb-based materials are also valued for their  
48 large range of innovative properties that result from structural defects (Ismael 2020, Ma et al. 2020).  
49 This multitude of applications is expected to increase the demand in the coming years. This  
50 economic importance is combined with the scarcity of Nb deposits. The low concentration of Nb on  
51 Earth, ca. 12 ppm in the upper continental crust (Rudnick and Gao 2014), and its geochemical  
52 properties limit the incorporation of Nb into most common rock-forming minerals. Under oxygen  
53 fugacities relevant to lithospheric and surficial environments, Nb occurs only as Nb<sup>5+</sup> (Cartier et al.  
54 2015) with the electronic configuration [Kr] 4d<sup>0</sup>. Its high valence relative to its ionic radius (0.64 Å  
55 in octahedral coordination, i.e. Shannon 1976) makes Nb one of the high-field-strength elements  
56 (HFSE) along with Zr, Sn, Hf, Ta, Pb, Th and U. Niobium concentrates in silicic melts during  
57 partial melting and fractional crystallization until the late precipitation of Nb minerals of the  
58 pyrochlore and columbite supergroups (Linnen and Cuney 2005). During weathering, Nb is among  
59 the most immobile elements (Hill et al. 2000) due to the resistance of primary Nb minerals to  
60 alteration. It is consequently used for mass-balance calculations (Kurtz et al. 2000) and  
61 environmental studies (Nabi et al. 2021) although the presence of organic ligands, which can  
62 increase Nb solubility, challenges this approach (Friis and Casey 2018). Such geochemical behavior  
63 is basic to the formation of world-class lateritic Nb deposits, as a consequence of a significant  
64 residual enrichment during lateritic weathering of primary deposits, typically by an order of  
65 magnitude relative to the parent rock (Mitchell 2015).

66 Niobium is octahedrally coordinated with oxygen ligands in ca. 85 % of Nb minerals  
67 (Waroquiers et al. 2017). The most abundant phases are multicomponent oxides with the general  
68 formula AB<sub>2</sub>O<sub>6</sub> (columbite-group minerals: e.g. columbite, euxenite, aeschynite) and A<sub>2</sub>-  
69 <sub>x</sub>B<sub>2</sub>O<sub>7</sub> (pyrochlore-group minerals: pyrochlore, betafite, samarskite). The eight-fold coordinated A-

70 site, a square antiprism, is occupied by rare-earth elements (REE), Ca, U, Th, Fe, while the  
71 octahedral B-site is occupied by Ti, Nb, Ta and W and forms double chains in a zigzag pattern by  
72 sharing at least two edges with neighboring octahedra (Ewing 1975). Due to strong interionic  
73 repulsion, most NbO<sub>6</sub> octahedra are distorted (Kunz and Brown 1995). Metamictization is common  
74 due to the presence of radioactive elements (Zietlow et al. 2017). It can form local structures made  
75 of corner-sharing octahedra at the expense of the edge-sharing linkages observed in the crystalline  
76 oxides (Ewing 1975). Unambiguous identification of Nb minerals is needed to understand  
77 geological and geochemical processes concentrating Nb such as magmatic differentiation (Walter et  
78 al. 2018; Lee et al. 2006), metasomatic events (Wu et al. 2021) and supergene weathering  
79 (Lottermoser and England 1988; Wall et al. 1996). However, the similar crystal chemistry and  
80 metamictization of Nb minerals make the analysis of Nb speciation using X-ray diffraction analyses  
81 challenging.

82 Niobium is also found as a minor or trace element in minerals. Hydrothermal events can  
83 result in the formation of amorphous Fe oxides containing low amounts of Nb (Wu et al. 2021). In  
84 metasomatized mantle peridotites, rutile may host more than 95 % of the Nb budget (Kalfoun et al.  
85 2002). Niobium can also be enriched in Fe and Ti oxides that occur as veinlets or degradation  
86 products in laterites (Lottermoser and England 1988; Giovannini et al. 2017). These oxides  
87 highlight the capacity of Nb<sup>5+</sup> to substitute for cations such as Ti<sup>4+</sup>, Sn<sup>4+</sup>, W<sup>6+</sup>, Ce<sup>4+</sup> and Fe<sup>3+</sup> in  
88 various minerals (Černý and Ercit 1989; Giovannini et al. 2017), which also hinders the  
89 determination of Nb speciation in such geological contexts.

90 Here, we report the first analysis of Nb *L*<sub>2,3</sub>-edges XANES spectra using a selected set of Nb  
91 minerals (fluorcalciopyrochlore, hydroxyrochlore, niocalite, Nb perovskite, columbite) and  
92 synthetic oxides (hematite, goethite, rutile, anatase, cerianite, lueshite and Nb<sub>2</sub>O<sub>5</sub>). A few studies  
93 have been published on synthetic Nb oxides and fluorides (Sugiura et al. 1988; Kubouchi et al.  
94 2012; Wang et al. 2018). The objective of this work is twofold. (i) Relate spectral properties to the  
95 local structure around Nb in crystalline references. Crystal-field and ligand-field multiplet (CFM

96 and LFM) calculations provide the first data on crystal-field parameters and Nb–O bond covalence  
97 in minerals. This CFM and LFM approach has proven useful to model Fe bioavailability and  
98 mobility in terrestrial and subsurface environments (Bhattacharyya et al. 2019) and V speciation in  
99 fersite (Höche et al. 2013). (ii) Investigate the processes by which Nb substitutes for Fe, Ti and  
100 Ce in Nb-substituted oxides. These materials serve as models for model major Nb-bearing oxides  
101 found in geological contexts and used in industry. Overall, this first study on Nb speciation in  
102 mineralogical contexts demonstrates how the sensitivity of Nb  $L_{2,3}$ -edges XANES spectroscopy can  
103 be used to better characterize and understand Nb mineralogy. Deciphering Nb speciation will  
104 improve our understanding of Nb enrichment in primary and lateritic deposits and may help to  
105 diversify the range of primary sources and to upgrade the efficiency of ore processing (Černý and  
106 Ercit 1989).

107

## MATERIALS AND METHODS

### 108 Mineral synthesis procedures

109 **Niobium-substituted Fe oxides (1 wt% Nb).** The synthesis of Nb-bearing goethite ( $\alpha$ -  
110 FeOOH) has been adapted from the hydrothermal synthesis of Sc-bearing Fe oxides at 70 °C  
111 (Chassé et al. 2017). Nb-bearing goethite was converted into Nb-bearing hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) by  
112 dehydroxylation at 300 °C for 2 h. The solid was washed using H<sub>2</sub>SO<sub>4</sub> in order to remove potential  
113 adsorbed Nb species and poorly-crystallized material.

114 **Niobium-substituted Ti oxides (5 wt% Nb).** The synthesis of Nb-bearing anatase (TiO<sub>2</sub>)  
115 has been carried out using a sol-gel method at moderate temperature (Dufour et al. 2012). Niobium-  
116 bearing rutile (5 wt%) was obtained by heating Nb-bearing anatase (5 wt%) at 700 °C for 3 hours.  
117 Niobium-bearing anatase was also synthesized with 1 and 10 wt% Nb following this procedure.

118 **Niobium-substituted cerianite (1 wt% Nb).** Niobium-bearing cerianite was synthesized  
119 using a high temperature solid-state reaction at 1,300 °C by homogenizing CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and Nd<sub>2</sub>O<sub>3</sub>  
120 powders (Olegário et al. 2013).

121 **Lueshite.** This reference material was obtained by following a hydrothermal synthesis  
122 procedure at 200 °C over 24 h based on the experimental protocol of Gouget et al. (2019).

### 123 **Analytical methods**

124 **Powder X-ray diffraction (XRD) analyses.** The successful completion of the syntheses  
125 was verified by X-ray diffraction analysis. X-ray diffraction was performed using a  
126 PANALYTICAL X'pert Pro MPD diffractometer. Measurements were carried out in Bragg-  
127 Brentano geometry using a Co K $\alpha$  anode in order to minimize the X-ray absorption of Fe in  
128 hematite and goethite. Data were recorded with an X'Celerator detector between 3 °2 $\theta$  and 90 °2 $\theta$   
129 with 0.017 ° steps. The incident beam mask was fixed at 20 mm and the Soller slits at 0.04 rad.  
130 Total counting time of measurement was 3 hours per sample. The crystal structure of synthetic  
131 compounds was checked using the International Centre for Diffraction Data (ICDD) references  
132 (PDF-2 database). No secondary niobian phase was detected on the XRD patterns of Nb-bearing Fe,  
133 Ti and Ce oxides confirming that the Nb ions were incorporated into the crystal lattice and  
134 substituted for Fe, Ce and Ti (Supplemental Figs. S1 and S2).

135 **Single crystal XRD.** Single-crystal X-ray diffraction data were acquired on natural Nb  
136 reference materials on an Agilent Diffraction Xcalibur-S diffractometer equipped with a Sapphire  
137 CCD-detector with Mo K- $\alpha$ 1 radiation ( $\lambda = 0.71073 \text{ \AA}$ , graphite monochromator) at 293 K. Data  
138 reduction, cell refinement and space group determination were performed using the CrysAlisPro  
139 software.

140 **Electron microprobe (EMP) analyses.** Electron microprobe (EMP) analyses were used to  
141 determine the crystal chemistry of the Nb reference materials sourced from the mineralogical  
142 collections. Analyses were conducted on a CAMECA SX Five electron probe at the CAMPARIS  
143 facility (Sorbonne Université, Paris). After checking the homogeneity of the samples, two to seven  
144 spots were probed on each sample at 15 kV and 40 nA for the major elements and at 15 kV and  
145 299 nA for minor and trace elements. Wavelength-dispersive spectroscopy analyses were performed  
146 using the following standards: albite for Na, diopside for Mg, Si and Ca, orthoclase for Al and K,



147 MnTiO<sub>3</sub> for Mn and Ti, hematite for Fe, BaSO<sub>4</sub> for Ba, topaz for F, LiNbO<sub>3</sub> for Nb, metallic Ta for  
148 Ta, SrSi for Sr, zircon for Zr, galena for Pb, monazite for Th, uraninite for U, and allanite-(Y) for Y,  
149 La, Ce, Nd.

150 **X-ray absorption spectra acquisition.** Niobium *L*<sub>2,3</sub>-edges XANES spectra were recorded  
151 on the LUCIA beamline of the SOLEIL synchrotron radiation facility (Gif-sur-Yvette, France)  
152 operating with a storage ring current of 450 mA and energy of 2.75 GeV (Vantelon et al. 2016). A  
153 double crystal Si(111) monochromator crystal was used with an energy resolution of 0.25 eV at  
154 2400 eV (Schaefers et al. 2007). The monochromator was calibrated at the energy of the Nb *L*<sub>3</sub>-edge  
155 using Nb<sub>2</sub>O<sub>5</sub>. Due to the high Nb contents in Nb minerals, the spectra were recorded on cellulose-  
156 diluted pellets before being mounted on a holder. Pure pellets were used for synthetic Nb-  
157 substituted samples. Data were obtained between 2300 and 2550 eV at room temperature, under  
158 vacuum, in fluorescence mode. Energy steps were (2, 0.2, 1, 0.2, 1) eV for energy ranges of (2300–  
159 2350), (2350–2400), (2400–2455), (2455–2490) and (2490–2550) eV, respectively, with a 1 s  
160 integration time. Two measurements per sample were sufficient to get adequate signal-to-noise  
161 ratios and to check the reproducibility of the edge features.

## 162 **Data processing and simulations**

163 **X-ray absorption data processing.** Processing of the data was achieved using the Larch  
164 software (Newville 2013). The MBACK normalization algorithm was applied to prevent distortion  
165 in the XANES data and preserve the branching ratio (Weng et al. 2005). This method applies a  
166 single smooth background function over the entire *L*<sub>2,3</sub>-edges data range rather than normalizing  
167 each edge independently. The normalization function is a first order Legendre polynomial  
168 (Supplemental Fig. S3) and the edge energy chosen as the input parameter of the MBACK function  
169 implemented in Larch is 2371 eV. The spectra of Nb-substituted hematite, Nb-substituted goethite,  
170 lueshite, and niocalite were trimmed beyond 2475 eV because the S K-edge hides the high-energy  
171 features of the Nb *L*<sub>2</sub>-edge.

172 Niobium *L*<sub>2,3</sub>-edges XANES features were fitted using three pseudo-Voigt functions in

173 order to quantitatively compare and retrieve differences in the three features between the spectra.  
174 The continuum background was removed using an error function with fixed inflection points  
175 (2373.0 and 2467.0 eV) and large width (ca. 8 eV) to reproduce the slow onset of the electronic  
176 continuum (Brotton et al. 2007). No agreement or convention exists regarding the parameters of the  
177 background functions (Henderson et al. 2014) but similar procedures have been applied to Fe  $L_{2,3}$ -  
178 edges (Bourdelle et al. 2013) and Zr  $L_{2,3}$ -edges (Jollivet et al. 2013). An error function was  
179 preferred over the commonly-used arctangent because its width is related to the instrumental  
180 resolution rather than to the lifetime of the excited state, which is not known a priori. Because the  
181 best mathematic fits were obtained for a relative weight of Lorentzian to Gaussian components  
182 between 0.8 and 1.0 depending on the spectra, this parameter was fixed to 0.9 in all fits for  
183 comparative purposes.

184 **Crystal-field and ligand-field multiplet calculations.** Simulations of the Nb  $L_{2,3}$ -edges  
185 spectra were performed using the Crispy software as implemented in the Quancy library (Haverkort  
186 2016; Retegan 2019). Two approaches were tested to reproduce the spectral features. The first is a  
187 CFM calculation which takes into account the crystal-field effects acting on Nb. Ligand-field  
188 multiplet calculations offer a more comprehensive model by including the ligand-to-metal charge  
189 transfer, i.e. by mixing in the ground state the  $4d^0$ ,  $4d^1\bar{L}^1$ ,  $4d^2\bar{L}^2$ ,  $4d^3\bar{L}^3$  configurations through a  
190 hybridization Hamiltonian (more details on this notation are provided in the Supplemental  
191 Material).

192 Crystal- and ligand-field multiplet calculations both require the specific input parameters.  
193 To account for the lifetime broadening, Lorentzian functions with a full width at half-maximum of  
194 1.66 eV and 1.87 eV for the  $L_3$  and  $L_2$ -edges were used to simulate the features (Krause and Oliver  
195 1979). The experimental Gaussian broadening was set to ca. 1.5 eV to best reproduce the  
196 experimental spectra. The simulations of the experimental spectra were carried out by finding the  
197 best scaling factors for the Slater-Condon integrals that best account for direct and exchange  
198 interactions between the  $2p-4d$  orbitals ( $F^2_{pd} = 2.680$  eV,  $G^1_{pd} = 1.627$  eV and  $G^3_{pd} = 0.946$  eV for

199 the free ion). The reduction of these values modifies the relative intensity of the features. The values  
200 of the  $4d$  and  $2p$  spin-orbit coupling parameters were kept close to the atomic values of 0.124 eV  
201 and 63.97 eV. The crystal-field splitting parameter ( $10Dq$ ) was chosen to best reproduce the energy  
202 difference between the two features, which corresponds to the splitting of the final state of the  $d$   
203 orbitals. The extra parameters required for LFM calculations are the hybridization strength  $V_{mix}$   
204 ( $V_{t2g}$ ,  $V_{eg}$ ), the configuration-averaged energies of the charge transfer configuration ( $E(4d^1\bar{L}^1)$ –  
205  $E(4d^0)$ )  $\Delta$ , the core-hole potential  $U_{dc}$  and the average Coulomb interaction energies of a  
206 corresponding electron pair  $U_{dd}$ . Detailed explanations of these parameters and their influence on  
207 the spectral shapes are given in the Supplemental Material (Supplemental Fig. S7).

## 208 RESULTS

### 209 Characteristics of niobium $L_{2,3}$ -edges XANES spectra

210 The Nb  $L_{2,3}$ -edges XANES spectra (Fig. 1) are characterized by a split edge feature with two  
211 peaks (A and B features) followed by a peak of lower intensity, ca. 10 eV after the edge (C feature),  
212 as reported for other Nb-bearing materials (Sugiura et al. 1988; Wang et al. 2018). The energy of  
213 the  $L_3$ -edge features ( $A_3$ ,  $B_3$ ,  $C_3$ ) varies around ca. 2372, 2376 and 2387 eV, respectively (Fig. 1a).  
214 The energy of the  $L_2$ -edge features ( $A_2$ ,  $B_2$ ,  $C_2$ ) varies around ca. 2466, 270 and 2481 eV,  
215 respectively (Fig. 1b). At the  $L_3$ -edge, the energy position and width of the  $A_3$  feature are stable,  
216 whereas that of  $B_3$  varies among the reference materials. Niocalite, Nb-substituted hematite and Nb-  
217 substituted goethite spectra show narrower  $B_3$  features than the other reference materials. In  
218 contrast, the wide  $B_3$  feature of the Nb perovskite spectrum shows a shoulder at high energy ( $B'_3$  at  
219 2379–2380 eV, Fig 2b). The intensity ratio between the  $A_3$  and  $B_3$  features ( $A_3/B_3$ ) varies but  
220 remains larger than 1 except in the Nb-substituted cerianite  $L_3$ -edge spectrum. In all compounds,  $C_3$   
221 is of lower intensity than  $A_3$  and  $B_3$  with limited variation in position and width. Similar trends are  
222 observed at the  $L_2$ -edge.

## 223 Analysis of the niobium $L_{2,3}$ -edges XANES spectra

224           **Variation of the edge splitting.** The  $\Delta E$  parameter, corresponding to the energy splitting  
225 between the A and B features, ranges from ca. 2.6 to 4.0 eV at the  $L_3$ -edge and from ca. 2.3 to  
226 4.0 eV at the  $L_2$ -edge (Table 2). The Nb perovskite, lueshite, fluorcalciopyrochlore and  
227 hydroxyrochlore spectra have the largest  $\Delta E$  values (ranging from ca. 3.6 to 4.0 eV). Most spectra  
228 have  $\Delta E$  values between ca. 3.1 and 3.5 eV except for the Nb-substituted cerianite spectrum (ca.  
229 2.6 and 2.3 eV at  $L_3$ - and  $L_2$ -edges, respectively). Overall, the energy splitting at the  $L_3$ -edge follows  
230 the same trend ( $R^2 = 0.94$ ) as the energy splitting at the  $L_2$ -edge (Supplemental Fig. S6a).

231           **Variation of the intensity ratio.** The intensity ratio ( $I_A/I_B$ ) varies between ca. 0.8 and 2.1. It  
232 is higher at the  $L_2$ -edge (1.43) than at the  $L_3$ -edge (1.07). In most compounds, it ranges between ca.  
233 1.0–1.2 and 1.4–1.6 at the  $L_3$ - and  $L_2$ -edge, respectively (Table 2). Intensity ratios of Nb-substituted  
234 cerianite and  $Nb_2O_5$  spectra are below 1 at the  $L_3$ -edge. There is a strong positive correlation of this  
235 parameter between the two edges ( $R^2 = 0.95$ , Supplemental Fig. S6b).

236           **Variation of the bandwidth.** The ratio of the full width at half maximum of feature B with  
237 respect to feature A ( $FWHM_{B/A}$ ), ranges between ca. 1.0 and 2.2 for both edges. The spectra of Nb-  
238 substituted goethite and hematite (Fig. 2c) have the lowest  $FWHM_{B/A}$  values (ca. 1.1 and 1.4 at the  
239  $L_3$ - and  $L_2$ -edge, respectively). Most spectra exhibit intermediate  $FWHM_{B/A}$  values (ca. 1.4–1.7 and  
240 ca. 1.6–1.9 at the  $L_3$ - and  $L_2$ -edge, respectively). The Nb perovskite spectrum (Fig. 2b) stands out by  
241 its high  $FWHM_{B/A}$  value (ca. 2.1 and 2.4 at the  $L_3$ - and  $L_2$ -edges, respectively). Niobium-substituted  
242 anatase spectra (Fig. 2d) are also characterized by high  $FWHM_{B/A}$ , especially at the  $L_2$ -edge  
243 (ca. 1.8–1.9 eV). On average, the width ratios at the  $L_3$ -edge (1.54) are smaller than those at the  $L_2$ -  
244 edge (1.73). The  $FWHM_{B/A}$  parameter is correlated between the two edges ( $R^2 = 0.93$ ), after  
245 excluding the lueshite spectra, which deviate from the general trend (Supplemental Fig. S6c).

## 246 Multiplet calculations

247           **Crystal-field multiplet calculations.** The spectral features of Nb-substituted cerianite and



274 variability among octahedral reference materials is correlated with the average interatomic distances  
275 ( $R^2 = 0.84$ ), as expected from the relationship between  $10Dq$  and  $R^{-5}$  (Fig. 6) in a point-charge  
276 model (Burns 1993). Nonetheless, Nb-substituted Ti oxides deviate from this trend, showing  
277 distinct Nb–O and average Ti–O distances.

278 Among octahedral Nb reference materials, the spectra of Nb<sub>2</sub>O<sub>5</sub> show the lowest  $\Delta E$  values  
279 (3.06 and 3.28 eV at the  $L_2$ - and  $L_3$ -edge, respectively), slightly higher than previously reported (2.6  
280 and 2.8 eV; i.e Sugiura et al. 1988). Nb<sub>2</sub>O<sub>5</sub> powders may differ from each other in the nature and  
281 proportion of the polymorphs they contain (Pilarek et al. 2017). Unfortunately, the material  
282 investigated by Sugiura was not characterized by XRD. Our Nb<sub>2</sub>O<sub>5</sub> reference consists of several  
283 polymorphs in equivalent proportions, of which two crystallize in monoclinic (ca. 90 % of NbO<sub>6</sub>  
284 octahedra and 10 % NbO<sub>5</sub> polyhedra: Andersson 1967) and orthorhombic (NbO<sub>5</sub> and NbO<sub>7</sub>  
285 polyhedra; i.e. Waring et al. 1973) structures (Supplemental Fig. S2c). These structural differences  
286 may explain a lower splitting as compared to the other octahedrally-coordinated Nb reference  
287 materials.

288 The  $\Delta E$  value of the cerianite spectrum in which Nb is in a cubic site, is 6/9–7/9 times  
289 smaller compared to octahedral reference materials (Table 2). Crystal-field splitting values are  
290 lower than expected in cubic coordination ( $10Dq_c$  is 8/9 of  $10Dq_o$ ). Though not detected by XRD  
291 (Supplemental Fig. S2b), the occurrence of trace amounts of tetrahedrally-coordinated fergusonite-  
292 (Ce) could result from the low solubility of Nb in cerianite (Kolodiaznyi et al. 2016). In  
293 fergusonite, the crystal-field splitting parameter of tetrahedral Nb<sup>5+</sup> is even lower ( $10Dq_t$  is 4/9 of  
294  $10Dq_o$ ) explaining the small  $\Delta E$  value of cubic Nb-substituted cerianite spectra.

295 Comparison of the splitting of Nb<sup>5+</sup> XANES features with those of other  $4d^0$  elements  
296 indicates an increase of the splitting with increasing cation charge. The splitting of Zr<sup>4+</sup>, Nb<sup>5+</sup> and  
297 Mo<sup>6+</sup> coordinated to oxygen ligands in weakly distorted octahedra is 3.2 eV (Galoisy et al. 1999),  
298 3.5–3.9 eV (this study) and 4.5 eV (Bare et al. 1993), respectively. This trend highlights the  
299 decrease of the ionic radius with increasing cation charge ( $^{[6]}Zr^{4+} = 0.72 \text{ \AA}$ ,  $^{[6]}Nb^{5+} = 0.64 \text{ \AA}$ ,

300  $^{61}\text{Mo}^{6+} = 0.59 \text{ \AA}$ , i.e. Shannon 1976) demonstrating the high sensitivity of  $L_{2,3}$ -edges XANES  
301 spectroscopy to the speciation of  $4d^0$  elements.

302 **Spectral broadening, charge transfer and site distortion.** Consideration of the C features  
303 is required in the fitting procedure in order to avoid an overestimation of the broadening of the B  
304 features. Unlike their assignment to  $2p \rightarrow 5s$  transitions (Sugiura et al. 1988), our LFM calculations  
305 show that this feature results from hybridization between the  $4d$  orbitals of  $\text{Nb}^{5+}$  and the  $2p$  orbitals  
306 of  $\text{O}^{2-}$ , in agreement with the work of Okada and Kotani (1993) on Ti compounds.

307 Spectra of Nb-bearing minerals all display a high-energy shoulder of varying intensity at  
308 2378 eV. The high degree of distortion of  $\text{NbO}_6$  octahedra in columbite and niocalite (Table 1) is  
309 not evidenced from the fit of their XANES spectra, which are characterized by B' shoulders of  
310 limited intensity (Fig. 1). Furthermore, spectra of Nb perovskite and pyrochlore display the most  
311 intense B' shoulder but these reference materials are composed of regular octahedra. The intensity  
312 of the shoulder is therefore not related to the distortion of the  $\text{NbO}_6$  octahedra. Spectra of niobian  
313 perovskite, which exhibit the most intense C feature, is also the one with the largest B' shoulder.  
314 We therefore ascribe the B' shoulder to orbital hybridization. The failure of ligand-field multiplet  
315 calculations to reproduce both B' and C features (Fig. 5) may be due to the differences between the  
316  $\text{Ti}^{4+}$  charge-transfer parameters used here (Okada and Kotani 1993) and those of  $\text{Nb}^{5+}$ , which are  
317 unknown.

318 The broadening of the XANES features for  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  (De Groot et al. 1992; Ikeno et al.  
319 2013; Jollivet et al. 2013) indicates a distortion of the cation site. In contrast, the broadening of the  
320 Nb  $L_{2,3}$ -XANES features, probed by the  $\text{FWHM}_{\text{B/A}}$  parameter, is shaped by charge-transfer effects  
321 and there is no correlation with the degree of distortion of the  $\text{NbO}_6$  octahedra. The specifically  
322 high contribution of charge-transfer effects to Nb  $L_{2,3}$ -XANES spectra is related to the covalent  
323 character of the Nb–O bonds (Ikeno et al. 2011).

324 Spectra of Nb-substituted anatase and rutile display the poorest fit quality ( $\chi^2 = 0.2\text{--}0.5$ ) due  
325 to poor fitting of the wide B features. The absence of a B' shoulder, suggesting the limited effect of

326 charge transfer on the spectra, reflects the distortion of the Nb sites (Fig. 2d). On the contrary, only  
327 the spectra of Nb-substituted hematite and goethite exhibit A and B features of similar widths,  
328 suggesting a symmetrical Nb site rather than the expected low symmetry of Fe<sup>3+</sup> and the high  
329 distortion of FeO<sub>6</sub> octahedra. This hypothesis is supported by the good reproduction of the spectra  
330 of Nb-substituted hematite in *O<sub>h</sub>* symmetry using LFM calculations. The similarities between the  
331 spectra of Nb-substituted hematite and goethite suggest similar Nb environments despite the  
332 different geometry of the Fe-octahedra in these minerals.

333 **Spectral intensity variations and bond covalence.** The intensity ratios (*I<sub>A</sub>/I<sub>B</sub>*) exhibit low  
334 standard deviations in our dataset ( $\sigma = 0.13$  and  $0.20$  at the *L<sub>3</sub>* and *L<sub>2</sub>*-edges, respectively). The low  
335 intensity ratio in the *L<sub>3</sub>*-edge spectrum of Nb-substituted cerianite ( $0.75$ ) stands out from the other  
336 references ( $1.10$  on average for octahedral references). This can be explained by approximating the  
337 intensity ratio to the number of unoccupied states, i.e.,  $2/3$  or  $3/2$  in regular cubic and octahedral  
338 coordination, respectively (Ogasawara et al. 2001). The intensity ratio values retrieved from the  
339 fitting procedure are not equal to the statistical values due to ligand-field multiplet effects  
340 (Ogasawara et al. 2001). However, the intensity ratio at the *L<sub>2</sub>*-edge of the octahedral reference  
341 materials is close to the statistical value of  $3/2$  ( $1.46$  on average) because this edge is less affected  
342 by multiplet effects (De Groot, 1994).

343 The intensity of the multiplet effects can be retrieved from our simulations through the  
344 reduction factor of the Slater-Condon integrals. The values of the reduction factor range from  $0.35$   
345 to  $0.54$ , indicating a major contribution from the covalent nature of the Nb-O bonds. These values  
346 are remarkably low compared to those around  $0.7$ – $0.8$  observed in most oxides of *3d* elements (De  
347 Groot 2005). However, the modeling of other Nb compounds, such as CsNbF<sub>6</sub>, requires an even  
348 greater reduction of these parameters down to  $40\%$  (De Groot et al. 1994). Therefore, the reduction  
349 of the Slater-Condon parameters mirrors the covalent nature of the bonds formed by *4d* elements  
350 relative to *3d* elements (Singh et al. 2017).

351 **Why combine *L<sub>2</sub>* and *L<sub>3</sub>*-edge XANES spectroscopy?** As the spectral features are



352 correlated between the  $L_2$  and  $L_3$ -edge (Supplemental Fig. S5), the in-depth analysis of only one  
353 edge is sufficient to determine the coordination number of  $\text{Nb}^{5+}$  and characterize the the local Nb  
354 environment. However, the simulation of XANES spectra using CFM and LFM calculations cannot  
355 be carried out on a single edge. The lower sensitivity of the  $L_2$ -edge to atomic-multiplets effects  
356 involves several pairs of solutions of the  $10Dq$  value and the reduction of Slater integrals that  
357 satisfactorily reproduce the  $L_2$ -edge spectra. Only the joint modeling of both edges constrains the  
358 reduction of the Slater integrals, because of their higher sensitivity to atomic-multiplet effects. The  
359 choice for the acquisition and analysis of one or combined edges depends on the precision of the  
360 crystallographic information one wants to extract from the spectra.

### 361 **Mechanisms of Nb substitution in oxides**

362 **Niobium-substituted Ti oxides.** The discrepancy between the average Ti–O distance in the  
363 host structure and the observed Nb–O distances points out specific mechanisms of substitution in  
364 Nb-substituted  $\text{TiO}_2$  oxides (Fig. 6). Estimation of the Nb–O distances in Ti oxides by interpolation  
365 of the correlation between  $\Delta E$  and  $R^{-5}$  gives values of ca. 2.03 Å for Nb-substituted anatase and  
366 ca. 2.01 Å and for Nb-substituted rutile. Such an increase of the Nb–O distances is expected from  
367 the larger ionic radius of Nb with respect to Ti ( $^{[6]}\text{Nb}^{5+} = 0.64$  Å and  $^{[6]}\text{Ti}^{4+} = 0.605$  Å, i.e. Shannon  
368 1976). Moreover, the symmetry of the  $\text{Nb}^{5+}$  site in  $\text{TiO}_2$  is reduced to a lower symmetrical group as  
369 evidenced by the broadening of the  $B_3$  and  $B_2$  features (Fig. 2d and Table 2). Increasing Nb  
370 substitution leads to lower  $\Delta E$  and higher  $\text{FWHM}_{B/A}$  (Table 2), indicating an increased distortion of  
371 the Nb sites and increased Nb–O distances. Such distortion of Nb sites and an increase in Nb–O  
372 distances with increasing amounts of Nb were also evidenced using EXAFS (1.98 Å and 1.99 Å for  
373  $\text{Ti}_{0.97}\text{Nb}_{0.03}\text{O}_2$  and  $\text{Ti}_{0.92}\text{Nb}_{0.08}\text{O}_2$ , respectively, i.e. Gardecka et al. 2015). The mechanism allowing  
374 the incorporation of  $\text{Nb}^{5+}$  in rutile and anatase is the formation of one  $\text{Ti}^{4+}$  vacancy for every four  
375  $\text{Nb}^{5+}$  (Sheppard et al. 2006) following conditions of equilibrium and electroneutrality (Sheppard  
376 2007) as illustrated by the Kröger-Vink notation:

377 
$$2[Nb_2O_5] \Leftrightarrow 4[Nb_{Ti}^{\bullet}] + [V_{Ti}^{''''}] + 10[O_O^x](1)$$

378 
$$4[V_{Ti}^{''''}] = [Nb_{Ti}^{\bullet}](2)$$

379 In geological environments, the substitution of Nb<sup>5+</sup> for Ti<sup>4+</sup> in Ti oxides is also expected to be  
380 accommodated by interstitial Fe<sup>3+</sup> in oxidized environments following the substitution  
381  $2Ti^{4+} = Fe^{3+} + 2Nb^{5+}$  (Ruck et al. 1986) and by Fe<sup>2+</sup> in reducing environments, according to  
382  $3Ti^{4+} = Fe^{2+} + 2Nb^{5+}$  (Giovannini et al. 2020).

383 Recent EXAFS analyses have highlighted the splitting of the first shell into two Nb-O  
384 contributions at 1.88 and 2.01 Å in Nb-substituted anatase (Ribeiro et al. 2020). The increase of  
385 Nb-O distances up to ca. 2.01 Å in the latter study and this work could reflect the presence of  
386 Nb<sub>2</sub>O<sub>5</sub> clusters in Nb-substituted anatase and rutile (Atanacio et al. 2014), as the values of Nb-O  
387 distances in Nb<sub>2</sub>O<sub>5</sub> are also 2.01 Å (Table 1). Even if the formation of Nb<sub>2</sub>O<sub>5</sub> clusters cannot be  
388 excluded, the differences between the spectra of Nb<sub>2</sub>O<sub>5</sub> and Nb-substituted TiO<sub>2</sub> (Table 2) indicate  
389 that Nb clustering is not an important process.

390 **Niobium-substituted Fe oxides.** In hematite and goethite, Fe<sup>3+</sup> has a similar ionic radius  
391 (<sup>6</sup>Fe<sup>3+</sup> = 0.645 Å, i.e. Shannon 1976) to Nb<sup>5+</sup> (<sup>6</sup>Nb<sup>5+</sup> = 0.64 Å). The substitution of Nb<sup>5+</sup> for Fe<sup>3+</sup>  
392 in goethite has been shown to be isomorphic (Oliveira et al. 2008). Despite the difference between  
393 the Fe sites in hematite and goethite (Table 1), the similar Nb XANES spectra also argue for an  
394 isomorphic substitution in hematite. Charge balance may be maintained by substituting 5Fe<sup>3+</sup> for  
395 3Nb<sup>5+</sup>, which induces cation vacancies. Our study shows that Nb-substituted Fe oxides can be  
396 reproduced by CFM and LFM calculations in a regular O<sub>h</sub> site symmetry even though the initial Fe  
397 site has a C<sub>3</sub> symmetry (Figs. 3b and 4b). The regularity of the NbO<sub>6</sub> octahedra is also supported by  
398 the absence of broadening of features B<sub>3</sub> and B<sub>2</sub> (Fig. 2c). The alignment of their experimental ΔE  
399 values on the trend with respect to theoretical Fe-O distances (Fig. 6) indicates that the average  
400 Nb-O distances are not significantly modified with respect to the average Fe-O distances.

401 However, EXAFS data on Nb-substituted hematite indicate low values of Nb-O distances

402 (1.87 and 2.05 Å) compared to the Fe–O distances in hematite (1.92 and 2.11 Å, i.e. Silva et al.  
403 2009). The differences between our results and those of Silva et al. (2009) could reflect the high  
404 amounts of Nb incorporated in the Fe oxides (5 and 10 wt% Nb) or the synthesis protocol. The  
405 incorporation of Nb in Fe oxides may result in a symmetrization of the Nb site due to the relaxation  
406 of the crystal structure around Nb arising from the induced cation vacancies.

407 **Niobium-substituted cerianite.** Charge and size differences (0.97 and 0.64 Å, for Ce<sup>4+</sup> and  
408 Nb<sup>5+</sup> respectively, i.e. Shannon 1976) limit the substitution of Nb in cerianite. The substitution of  
409 Nb<sup>5+</sup> for Ce<sup>4+</sup> was explained by the displacement of Nb<sup>5+</sup> cations from ideal cubic symmetry that  
410 leads to oxygen vacancies (Hiley et al. 2018). It has also been suggested that half of the Ce ions  
411 become trivalent to account for charge balance. The other half of the charge compensation would be  
412 accommodated by interstitial oxygens (Kolodiazhnyi et al. 2016) according to:

$$413 \quad [Nb_{Ce}^{\bullet}] = [Ce'_{Ce}] + 2[O''_i] + [O'_i]$$

414 Our simulation of the Nb-substituted spectrum in  $O_h$  point symmetry (Fig. 3a) indicates that  
415 a Nb<sup>5+</sup>–Nd<sup>3+</sup> co-doping eases the charge balance equilibrium ( $2[Ce^{4+}] = [Nb^{5+}] + [Nd^{3+}]$ ) and  
416 prevents significant distortion of the Nb site by limiting the formation of interstitial oxygen and  
417 vacancies.

## 418 **IMPLICATIONS**

### 419 **Deciphering the origin of the properties of technological Nb-substituted oxides**

420 The synthetic Nb-bearing oxides selected in this study are considered important in meeting  
421 technological challenges associated with climate change mitigation or environmental  
422 decontamination (e.g., Ismael 2020; Ma et al. 2020). Among other applications, they are used for  
423 dye-sensitized solar cells (Lü et al. 2010), Na-ion battery anodes (Usui et al. 2015), direct solar fuel  
424 conversion (Fu et al. 2016) and catalysts for the removal of exhaust-gas nitrogen oxide (Lian et al.  
425 2015). These enhanced physico-chemical properties result from the substitution of Nb<sup>5+</sup> for a cation,  
426 leading to oxide mobility and transport properties due to charge unbalancing, oxygen vacancies or

427 interstitials. The properties of these Nb materials may be rationalized through a knowledge of the  
428 mechanisms of Nb insertion, which can be unveiled by Nb  $L_{2,3}$ -edges XANES spectroscopy.

#### 429 **Upgrading ore processing through quantitative analysis of Nb speciation**

430 The choice of Nb ore-processing strategies depends on the nature of the Nb minerals, their  
431 degree of alteration and their crystal-chemical variability. It is essential to correctly characterize the  
432 Nb ores to optimize ore processing (Černý and Ercit 1989). Niobium recovery from pyrochlore  
433 using amine collectors is currently being used in the three ore processing plants worldwide  
434 (Guimaraes and Weiss 2001). Nevertheless, this process induces a significant loss of columbite and  
435 Nb-rutile between feed and concentrate (Gibson et al. 2015). Moreover, high concentration of Fe in  
436 pyrochlore, which is a typical feature of hydropyrochlore, reduces its floatability and causes Nb loss  
437 during ore processing (Chehreh Chelgani et al. 2012). Niobian rutile has also been identified in the  
438 world-class deposit of Araxá but its significance in the overall Nb budget remains elusive  
439 (Neumann and Medeiros 2015). Niobium XANES spectroscopy is a useful tool to identify Nb  
440 speciation in ore minerals to optimize ore-processing strategies.

#### 441 **Unravelling Nb geochemical behavior in natural systems**

442 Recent findings in hydrothermal contexts (Andersson et al. 2018; Dietzel et al. 2019) and near-  
443 surface conditions (Wall et al. 1996; Chakrabarty et al. 2013; Giovannini et al. 2017) demonstrate  
444 the alteration of Nb minerals and question the presumed immobility of Nb (MacLean and Barrett  
445 1993). The demonstrated sensitivity of Nb  $L_{2,3}$ -edges XANES spectroscopy opens up the possibility  
446 to track Nb mineral speciation in weathered Nb-enriched samples. It can also be used to determine  
447 the mechanisms of alteration of primary Nb minerals and reveal the mechanisms of Nb  
448 incorporation in newly-formed phases. A combination of bulk and micro-XANES analyses can thus  
449 be used to enlighten the molecular-scale and geochemical factors that induce contrasted Nb  
450 dynamics in supergene environments as has been done for rare-earth elements (Janots et al. 2015;  
451 Chassé et al. 2019; Borst et al. 2020).

452

453

454

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464

465

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Minerals (group <i>i,ii,iii</i> )	Ideal formula	Structure	Coordination number	Nb site symmetry	Average cation–O distances (Å)	Distortion index (%)	Location
<i>Natural samples</i>							
(i) Fluorcalciopyrochlore	(Ca,Na) <sub>2</sub> (Nb,Ti) <sub>2</sub> O <sub>6</sub> F	Corner-sharing NbO <sub>6</sub> octahedra sharing edges with A site cation	6	<i>D</i> <sub>3d</sub>	1.944	0.0	Tatarka. Russia (SU)
(i) Hydropyrochlore	(H <sub>2</sub> O,□□)Nb <sub>2</sub> (O.OH) <sub>6</sub> (H <sub>2</sub> O)	Corner-sharing NbO <sub>6</sub> octahedra sharing edges with A site cation	6	<i>D</i> <sub>3d</sub>	1.972	0.0	Lueshe. Congo (SU)
(i) Columbite-(Mn)	(Mn,Fe)(Nb,Ta) <sub>2</sub> O <sub>6</sub>	Chains of edge-sharing NbO <sub>6</sub> octahedra	6	<i>C</i> <sub>1</sub>	2.017	6.0	Musha. Rwanda (ENSMP)
(ii) Niobian perovskite	CaTi <sub>1-2x</sub> Fe <sub>x</sub> Nb <sub>x</sub> O <sub>3</sub>	Perovskite structure (ABO <sub>3</sub> ) with interconnected NbO <sub>6</sub> octahedra with interstitial Ca	6	<i>C</i> <sub>1</sub>	1.966	0.6	Oka. Canada (ENSMP)
(ii) Niocalite	Ca <sub>7</sub> Nb(Si <sub>4</sub> O <sub>14</sub> )O <sub>3</sub> F	Isolated NbO <sub>6</sub> octahedra sharing edges and corners with CaO <sub>6</sub> octahedra	6	<i>C</i> <sub>1</sub>	2.049	6.1	Oka. Canada (ENSMP)
<i>Synthetic samples</i>							
(ii) Lueshire	NaNbO <sub>3</sub>	Perovskite structure (ABO <sub>3</sub> ) with interconnected NbO <sub>6</sub> octahedra with interstitial Na	6	<i>C</i> <sub>1</sub>	1.990	2.8	
(iii) Rutile (5 wt% Nb)	TiO <sub>2</sub>	Edge and corner-sharing TiO <sub>6</sub> octahedra (2 edges are shared with each other)	6	<i>D</i> <sub>2h</sub>	1.956	0.6	
(iii) Anatase (5 wt% Nb)	TiO <sub>2</sub>	Edge-sharing TiO <sub>6</sub> octahedra (4 edges are shared with each other)	6	<i>D</i> <sub>2d</sub>	1.949	1.0	
(iii) Hematite (1 wt% Nb)	α-Fe <sub>2</sub> O <sub>3</sub>	Face and edge-sharing FeO <sub>6</sub> octahedra	6	<i>C</i> <sub>3</sub>	2.031	4.2	
(iii) Goethite (1 wt% Nb)	α-FeOOH	Chains of edge-sharing FeO <sub>6</sub> octahedra joined by corner-sharing FeO <sub>6</sub>	6	<i>C</i> <sub>s</sub>	2.026	3.8	
(iii) Cerianite (1 wt% Nb)	CeO <sub>2</sub>	Edge-sharing CeO <sub>6</sub> cubes	8	<i>O</i> <sub>h</sub>	2.343	0.0	
Nb <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Edge and corner-sharing NbO <sub>6</sub> octahedra. 1 out of 28 Nb sites is a tetrahedron	6	<i>C</i> <sub>1</sub>	2.014	1.5	

Samples	L <sub>3</sub> -edge				L <sub>2</sub> -edge			
	$\Delta E$ (eV)	$I_A/I_B$	FWHM <sub>B/</sub> A	$\chi^2$	$\Delta E$ (eV)	$I_A/I_B$	FWHM <sub>B/</sub> A	$\chi^2$
Nb cerianite	2.55	0.75	1.47	0.0 6	2.29	0.9 6	1.73	0.0 6
Nb <sub>2</sub> O <sub>5</sub>	3.28	0.94	1.73	0.0 4	3.06	1.2 4	1.92	0.0 4
Fluorcalciopyrochlor e	3.90	1.18	1.48	0.0 9	3.83	1.5 5	1.69	0.0 6
Hydropyrochlore	3.76	1.07	1.62	0.0 5	3.64	1.4 1	1.67	0.0 4
Columbite	3.41	1.11	1.48	0.0 6	3.32	1.4 7	1.73	0.0 6
Niocalite	3.43	1.17	1.38	0.1 1	3.44	1.5 5	1.63	0.1 0
Lueshite	3.54	1.05	1.68	0.0 8	3.75	1.4 2	1.28	0.0 9
Nb perovskite	3.96	1.20	2.08	0.3 9	3.95	1.6 0	2.35	0.1 6
Nb hematite	3.44	1.08	1.12	0.2 8	3.47	1.4 5	1.39	0.1 0
Nb goethite	3.46	1.08	1.18	0.2 5	3.48	1.4 6	1.47	0.1 1
Nb anatase 1% Nb	3.38	1.10	1.58	0.5 1	3.30	1.4 8	1.84	0.1 9
Nb anatase 5% Nb	3.34	1.14	1.62	0.4 1	3.29	1.5 5	1.88	0.1 7
Nb anatase 10% Nb	3.33	1.14	1.61	0.3 9	3.28	1.5 5	1.92	0.1 5
Nb rutile 5% Nb	3.45	1.03	1.54	0.2 1	3.31	1.2 5	1.78	0.0 9

<b><u>CFM parameters</u></b>	Nb point group symmetry	Slater integrals reduction	$10Dq$	$Ds$	$Dt$
Nb-substituted cerianite	$O_h$	0.51	2.80	/	/
Nb-substituted hematite	$O_h$	0.51	3.70	/	/
Hydropyrochlore	$O_h$	0.54	3.90	/	/
Latrapite	$D_{4h}$	0.50	6.70	0.40	0.24

<b>Sample</b>	<b>Nb point group symmetry</b>	<b>Slater integrals reduction</b>	<b><math>10Dq</math> (eV)</b>	<b><math>U_{dd}</math> (eV)</b>	<b><math>U_{dc}</math> (eV)</b>	<b><math>\Delta</math> (eV)</b>	<b><math>V_{eg}</math> (eV)</b>	<b><math>V_{t2g}</math> (eV)</b>
Nb-substituted hematite	$O_h$	0.70	2.25	2.0	6.0	4.0	4.0	-2.0

Fig. 1

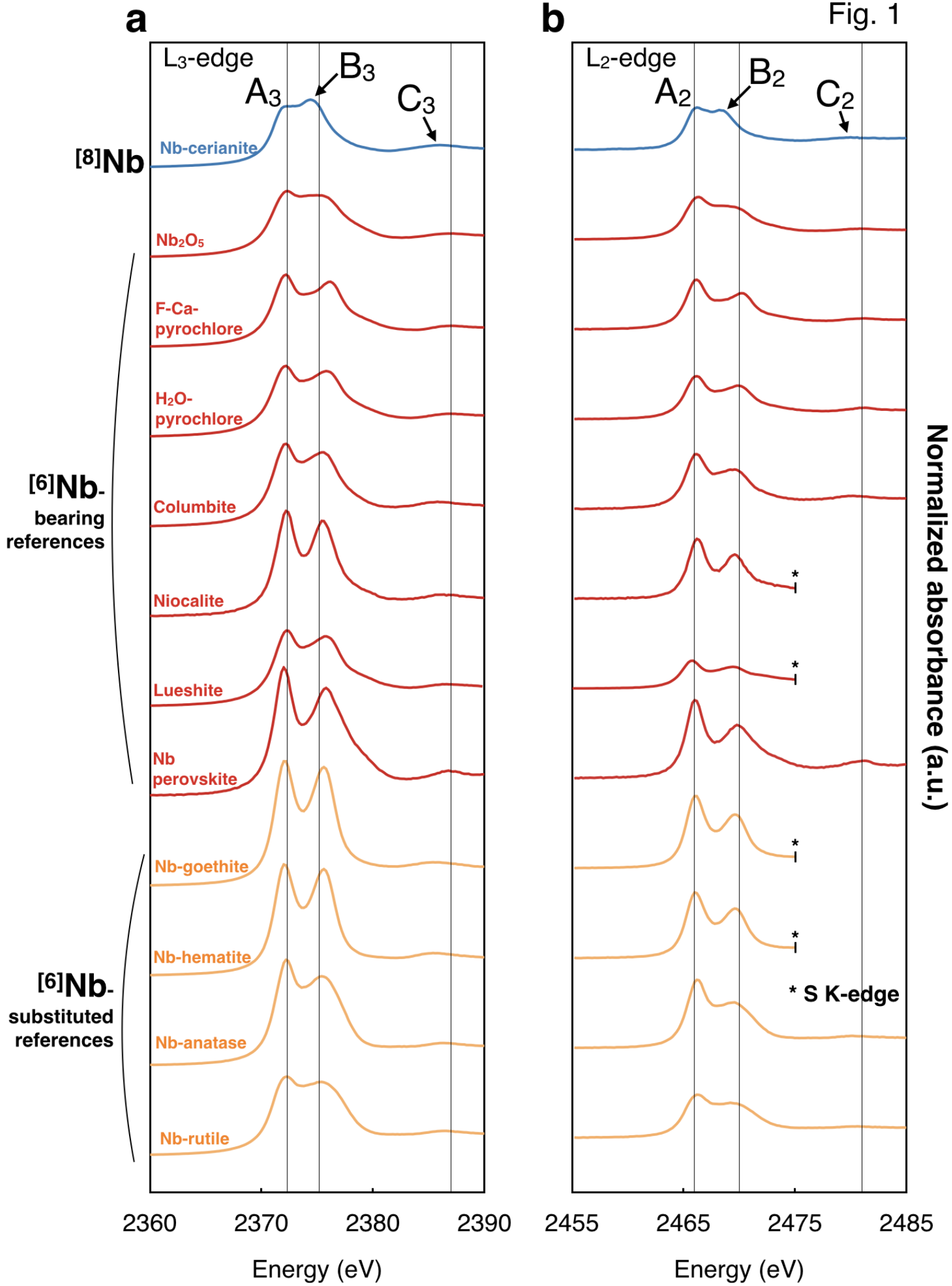


Fig. 2

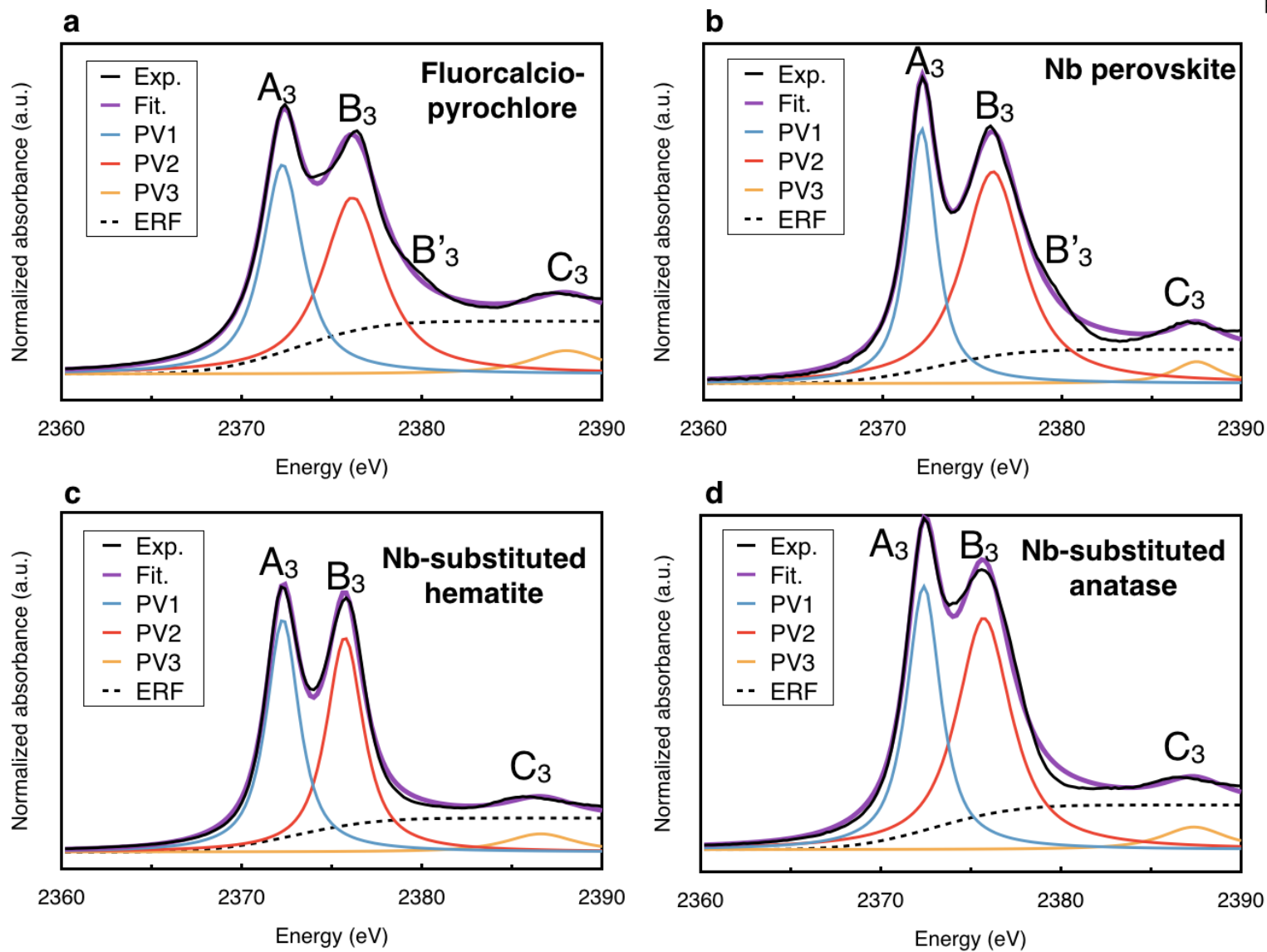


Fig. 3

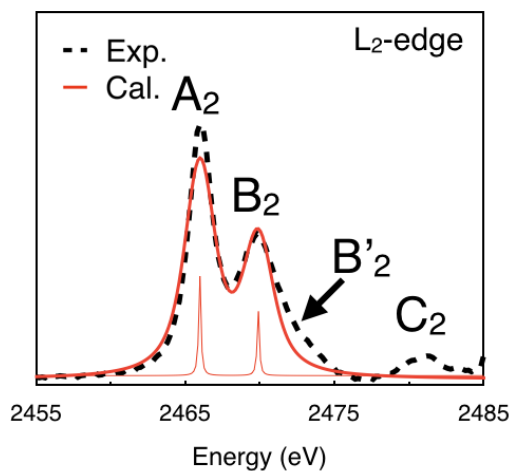
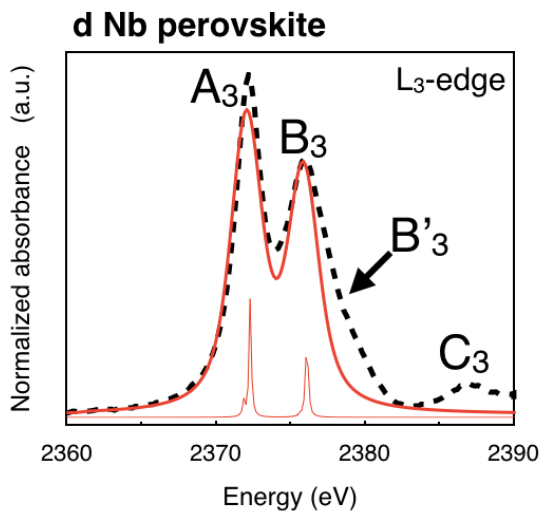
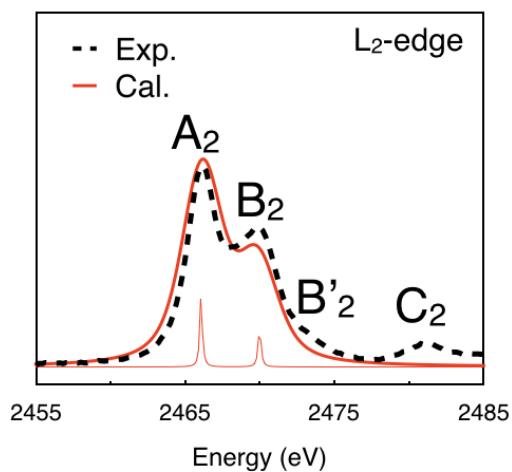
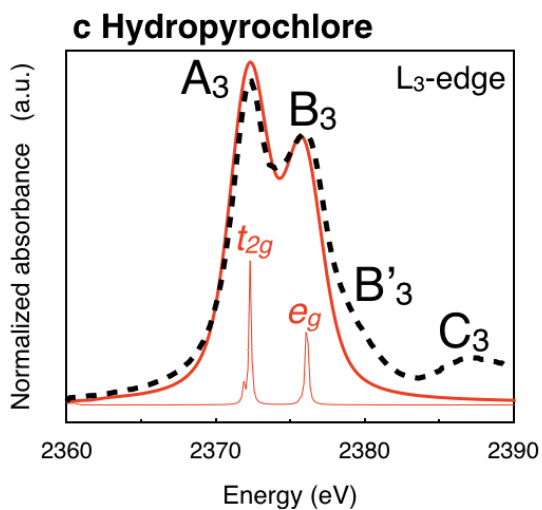
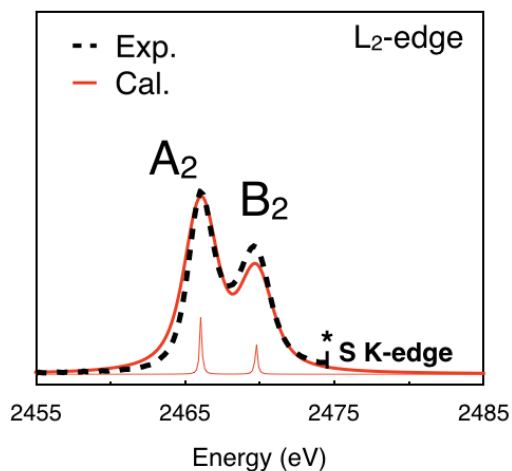
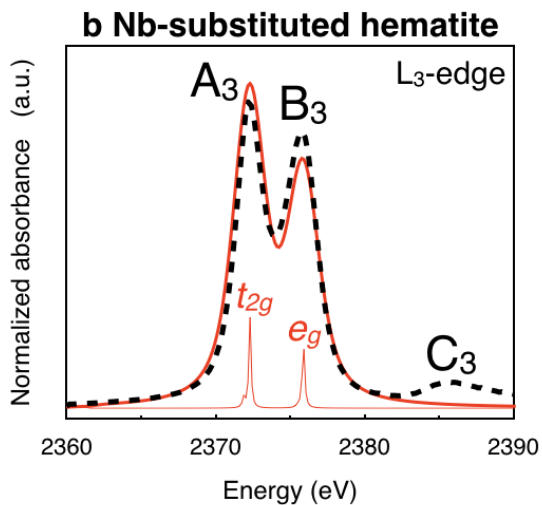
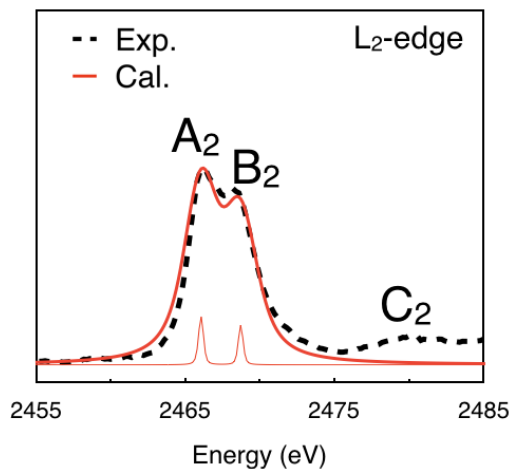
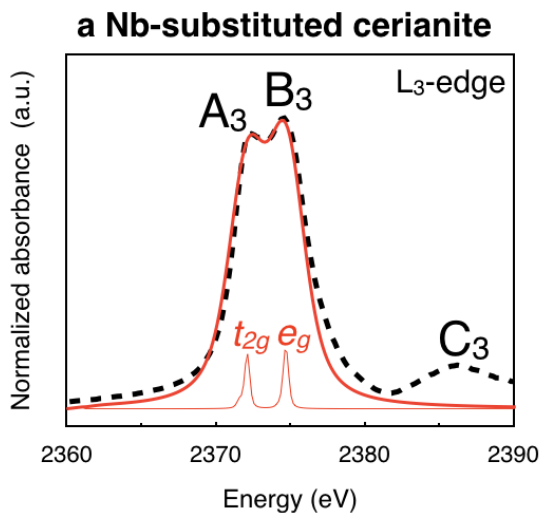


Fig. 4

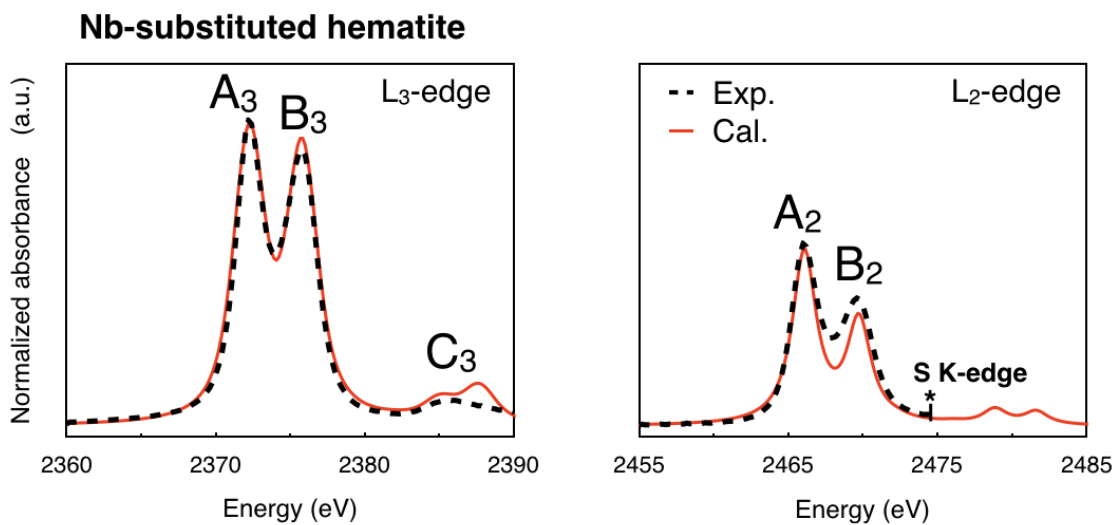




Fig. 5

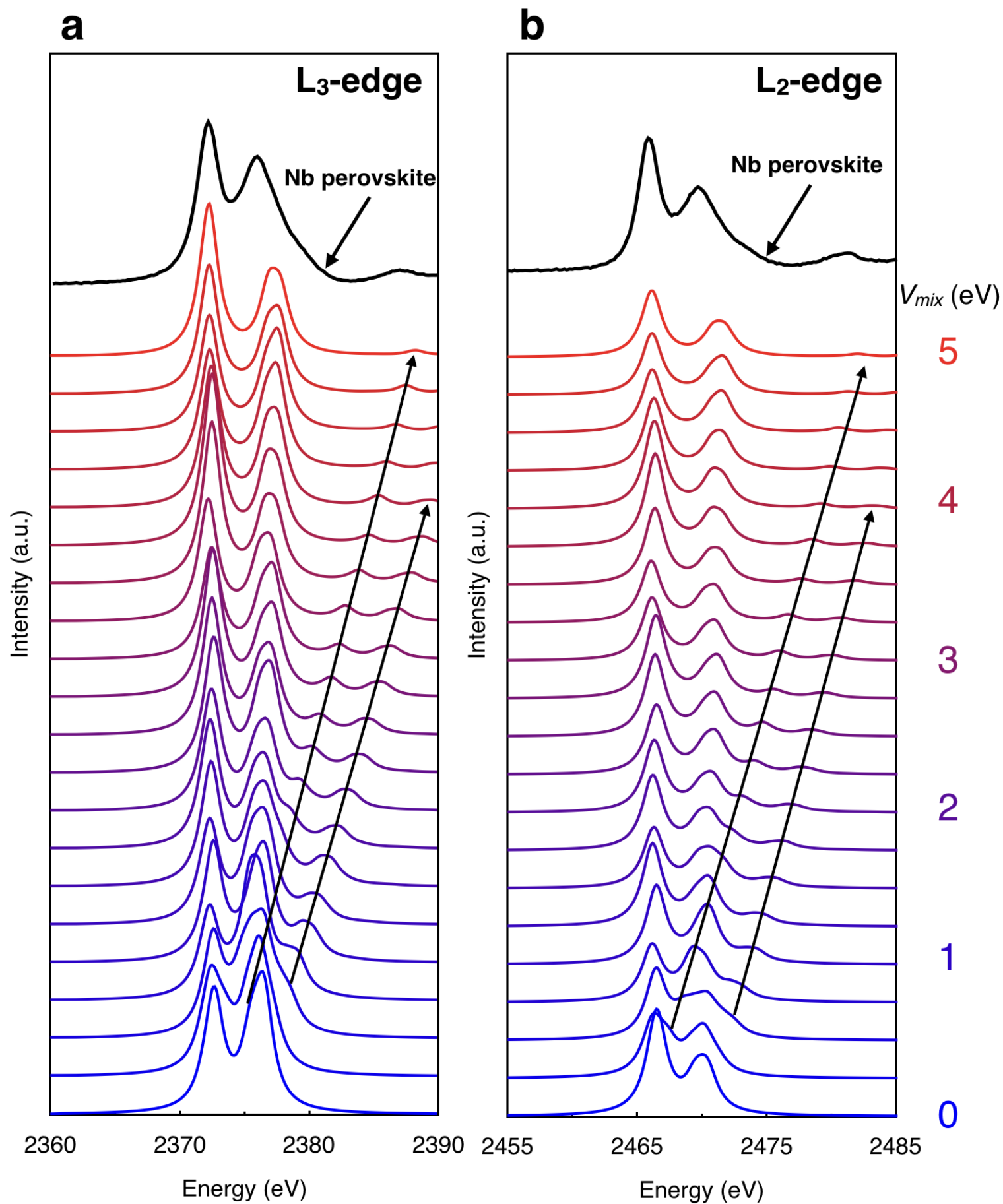


Fig. 6

