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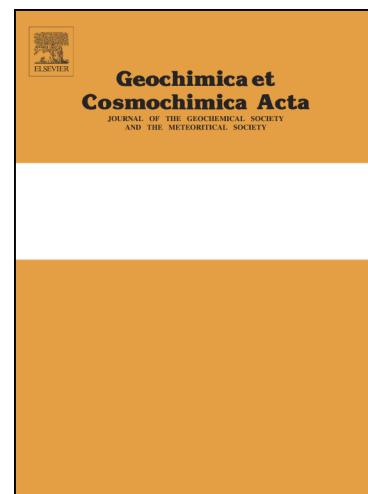
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1 **Multiscale processes controlling niobium mobility during supergene**  
2 **weathering**

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**ABSTRACT**

22 Niobium (Nb) is one of the most immobile elements during supergene weathering, widely used  
23 for mass-balance calculations, despite elusive information on the mechanisms controlling its  
24 dynamics in the critical zone. Here, a multiscale approach, from weathering profile to atomic-scale,  
25 is developed to monitor Nb speciation along a thick (about 50 m) lateritic regolith formed over the  
26 Pitinga pluton (Amazonas, Brazil). In the A-type parent granite, Nb is mainly hosted in ilmenite  
27 (1.5–2 wt% Nb<sub>2</sub>O<sub>5</sub>) and, to a lesser extent, in rutile (2–3 wt% Nb<sub>2</sub>O<sub>5</sub>). A quantitative assessment of  
28 the average Nb speciation from the parent rock to the upper horizons has been carried out by  
29 combining spectroscopic and spatially-resolved chemical techniques. The contribution of Nb-  
30 bearing Ti oxides (2–6 wt% Nb<sub>2</sub>O<sub>5</sub>) and Fe oxides (0.1–0.3 wt% Nb<sub>2</sub>O<sub>5</sub>) in the average Nb  
31 speciation increases with the degree of weathering and reaches 80 % in the most altered horizon.  
32 This unusual Nb speciation results from the nature of the primary Nb carriers, less resistant to  
33 weathering than common Nb ore minerals such as pyrochlore. X-ray absorption spectroscopy  
34 demonstrates that Nb released from the weathering of ilmenite substitutes for Fe and Ti in goethite  
35 and Ti oxides, respectively, providing atomic-scale evidence of the high affinity of Nb for these  
36 phases. Elemental mobility of Nb, Ta and Sn followed by geochemical mass-transfer calculations  
37 evidences lateral transport from Nb-Sn-enriched laterites developed over the surrounding Nb-  
38 enriched facies of the Pitinga granite to the studied profile. Elements such as Ti, Zr and Hf, often  
39 considered immobile, are leached or redistributed in the studied profile. Our results demonstrate Nb  
40 remobilization during intense weathering. Although Nb scavenging by secondary Fe and Ti oxides  
41 limits Nb mobility at the mineral scale, this work questions the unrestricted use of Nb as a chemical  
42 invariant during surficial alteration processes.

43 **Keywords** : Niobium, supergene weathering, laterite, speciation, XANES spectroscopy, mass-  
44 balance calculations, elemental mobility

45

## 1. INTRODUCTION

46 Niobium (Nb) is among the most immobile elements during weathering processes (MacLean  
47 and Barrett, 1993) due to corrosion resistance of Nb-bearing minerals (McMaster et al., 2018) and  
48 low solubility in fluids (Peiffert et al., 2010). Such conservative behavior is essential to document  
49 geological processes (Hickmott and Spear, 1992; Ballouard et al., 2016) including mass-balance  
50 calculations of weathering budget (Nahon and Merino, 1996; Kurtz et al., 2000). Niobium  
51 immobility is at the origin of world-class deposits such as those found in Brazilian laterites, i.e.  
52 Araxá and Catalão Nb deposits, which represent about 90 % of the world production of this critical  
53 metal (U.S.G.S, 2022). Unparalleled Nb enrichment in laterites results from the tropical alteration of  
54 Nb-enriched carbonatite hosting weathering-resistant Nb phases from the pyrochlore supergroup  
55 minerals  $[A_{2-x}B_2(O,OH)_6(OH,F,H_2O)_{1-y}]$  (Mitchell, 2015). However, these Nb-enriched carbonatites  
56 are formed during complex multi-stage processes and, consequently, they are neither representative  
57 of typical carbonatite nor of the continental crust (Chakhmouradian, 2006).

58 In magmatic rocks, multicomponent Nb oxides are not the only Nb-bearing minerals.  
59 Widespread Ti oxides such as rutile, brookite and ilmenite are also typical hosts of Nb (Černý and  
60 Ercit, 1989). Niobium substitution for titanium (Ti) can reach high levels (30 wt% Nb<sub>2</sub>O<sub>5</sub> in brookite  
61 and rutile and 15 wt% Nb<sub>2</sub>O<sub>5</sub> in ilmenite) due to the vicinity of Nb and Ti ionic radii  
62 (Chakhmouradian and Mitchell, 1999; Ballouard et al., 2020). As titanium oxides are expected to be  
63 resistant to weathering (Milnes and Fitzpatrick, 1989; Meinhold, 2010), Nb should be preserved in  
64 these primary carriers and will remain immobile. However, the alteration of Ti oxides and ilmenite  
65 during intense chemical weathering in tropical regions has long been evidenced (Anand and Gilkes,  
66 1984; Nahon and Merino, 1996; Du et al., 2012), questioning the fate of Nb after the dissolution of  
67 such minerals. Our understanding of Nb dynamics in supergene context is limited by the lack of data  
68 on Nb solubility and mobility in fluids (Lukyanova et al., 2017; Filella and May, 2020) and by the  
69 scarcity of studies identifying the evolution of Nb carriers during alteration of lithotypes distinct

70 from pyrochlore-bearing carbonatite. The study of Nb speciation in regoliths that formed at the  
71 expense of rocks containing Nb-bearing Ti oxides- and ilmenite allows to discuss Nb mobility in the  
72 critical zone.

73 In this study, we investigate Nb speciation in regolith samples from the region of the world-  
74 class tin (Sn)-Nb-tantalum (Ta) Pitinga deposit (Bastos Neto et al., 2009). Lateritic profiles formed  
75 from the weathering of the albite-enriched granite (Horbe and da Costa, 1999; Alves et al., 2018)  
76 exhibit exceptional Nb concentration (*ca* 1500 ppm Nb) due to the combination of singular  
77 magmatic and hydrothermal processes (Bastos Neto et al., 2009). Pyrochlore and columbite  
78 [(Mn,Fe)Nb<sub>2</sub>O<sub>6</sub>] from the parent rock have been preserved in the altered horizons despite the  
79 fragmentation of columbite into thin particles and the minor release of Nb from pyrochlore and  
80 columbite which was later incorporated into Fe oxides (Alves et al. 2018). Here, we complement the  
81 knowledge of the Pitinga province by studying Nb speciation in a laterite developed over the barren  
82 biotite alkali-feldspar granite (Lenharo et al., 2003). The investigation of this profile will uncover  
83 the processes of Nb concentration during supergene weathering that apply to widespread continental  
84 rocks and help discuss the role of the parent rock mineralogy.

## 85 2. MATERIALS AND METHODS

### 86 2.1 Geological context and sampling

87 The Pitinga province is located within an A-type granitoid belt typical of extensional settings  
88 in the southern part of the Guiana shield, dated at 1.82 Ga (Bastos Neto et al., 2009; Bettencourt et  
89 al., 2016). As the Pitinga alluvial ore deposit is now exhausted, the Sn-Nb-Ta-enriched Pitinga  
90 granite is now mined for Sn, Nb and Ta. The studied lateritic profile (S0°44'52",W60°6'28") was  
91 sampled over the biotite–alkali feldspar Pitinga granite (1.822 ± 0.002 Ga) (Costi et al., 2000)  
92 exhibiting a moderate Nb enrichment (Fig. 1), more representative of granitic rocks than

93 surrounding highly-enriched facies characterized by a unique association of cryolite ( $\text{Na}_3\text{AlF}_6$ ), Sn,  
94 Nb and several other rare metals (Bastos Neto et al., 2009).

95 The Pitinga region in the Amazon rainforest is characterized by a tropical-humid climate  
96 with intense rainfall ( $2000 \text{ mm} \cdot \text{yr}^{-1}$ ) year-round, warm temperatures (*ca*  $26 \text{ }^\circ\text{C}$  on average) and a  
97 long wet season (5–6 months). The lateritic cover is located on the summit of regional plateaus at *ca*  
98 250 m elevation. In the region, they attain 50 m thick (Horbe and Da Costa, 1990; Alves et al.,  
99 2018). The minimum age assessed for such thickness is 1 Ma, considering an estimate of the  
100 progression of the weathering front at a rate of  $0.05 \text{ mm} \cdot \text{yr}^{-1}$  in this region (Mathieu et al., 1995).  
101 Such long-term development of lateritic regolith is made possible by the elevation of the alteration  
102 profile providing protection from marine transgression events and by the stability of the latitude of  
103 the Amazon craton since 160 Ma, thus maintaining a tropical climate over the Cenozoic and part of  
104 the Mesozoic (Monteiro et al., 2018).

105 From the bottom to the top horizons, the studied regolith is composed of five units  
106 distinguished from their macroscopic properties: the granitic parent rock, the clayey mottled zone,  
107 the lateritic horizon, the bauxitic horizon and the ferruginous duricrust. Ten regolith samples,  
108 representative of these different horizons were collected from 3 to 50 m depth. The saprock and  
109 saprolite were not accessible at the outcrop and could not be sampled.

## 110 2.2 Bulk mineralogical characterization

111 X-ray diffraction was performed on powdered samples with a PANALYTICAL X'pert Pro  
112 MPD diffractometer. Measurements were carried out in Bragg-Brentano geometry using a  $\text{Co K}\alpha$   
113 anode in order to minimize the X-ray absorption of Fe, enriched in the uppermost lateritic horizons.  
114 Data were recorded with an X'Celerator detector between  $3^\circ 2\theta$  and  $90^\circ 2\theta$  with  $0.017^\circ$  steps.  
115 Incident beam mask was fixed at 20 mm and Soller slits at 0.04 rad. Total counting time of  
116 measurement was 6 hours per sample. Identification and semi-quantification of the major mineral

117 phases were performed with X'Pert HighScore software. The accuracy of the mineralogical  
118 quantification is discussed in Supplementary Material (Table S1).

### 119 2.3 Bulk geochemical characterization

120 Two grams of powdered samples, representative of each horizon, were sent to the SARM  
121 (Service d'Analyses des Roches et des Minéraux, CRPG, Nancy) for chemical analysis (Table S2).  
122 Bulk concentrations of major and trace elements were analyzed by ICP–OES (iCap6500  
123 ThermoFisher) and quadrupole ICP–MS (iVapQ ThermoFisher), respectively, after a lithium  
124 tetraborate alkali fusion (Carignan et al., 2001). Loss on ignition (L.O.I.) was obtained by  
125 gravimetric analysis at 1020 °C.

### 126 2.4 Mass-balance calculations

127 Quantification of the net chemical gains and losses was carried out using the following mass  
128 conservation equation (Brimhall et al., 1991).

$$129 \frac{V_p \rho_p C_{j,p}}{100} + m_{j,flux} = \frac{V_w \rho_w C_{j,w}}{100} (1)$$

130 where  $V$  is the volume in  $\text{cm}^3$ ,  $\rho$  is the dry bulk density ( $\text{g}/\text{cm}^3$ ) and  $C$  is the concentration (wt%) of  
131 an element  $j$  in the parent material  $C_{j,p}$  and in the weathered product  $C_{j,w}$ . The mass of an element  $j$  is  
132 denoted by the  $m_{j,flux}$  term which is positive when an element  $j$  accumulates in the sample and  
133 negative when it is leached from the sample. In this work, we use the biotite granite from Pitinga as  
134 the parent rock in order to capture the chemical transfers due to lateritization processes. The use of  
135 thorium (Th) as the conservative element is further discussed.

136 Volumetric strain index ( $\epsilon_{i,w}$ ) corresponding to the volume change between the weathered  
137 material and the parent rock is estimated by :



$$\varepsilon_{i,w} = \left( \frac{\rho_p C_{i,p}}{\rho_w C_{i,w}} \right) - 1 \quad (2)$$

where  $\rho$  is the bulk density ( $\text{g/cm}^3$ ) obtained by the paraffin method (Blake, 1965),  $C_{i,p}$  and  $C_{i,w}$  are the concentration of a reference element (considered as immobile during weathering) in the parent rock and weathered material, respectively. Volumetric strain around zero indicates isovolumetric weathering. Positive values indicate expansion and negative ones indicate collapse (Table S3).

Quantification of chemical mass gain or loss through a profile uses the open-system mass-transport function  $\tau_{j,w}$  (Table S4), defined by :

$$\tau_{j,w} = \left( \frac{\rho_w C_{j,w}}{\rho_p C_{j,p}} \right) (\varepsilon_{i,w} + 1) - 1 \quad (3)$$

If  $\tau_{j,w}$  is equal to 0, the element is immobile during weathering. A positive value reflects an absolute mass gain in element  $j$  of the weathered rock compared to the mass present in the parent rock whereas negative value indicates a mass loss. For instance, a positive value of 0.5 indicates that the mass of the element  $j$  results from an addition of 50 % relative to the mass of  $j$  present in the fresh parent rock.

## 2.5 Spatially-resolved chemical analyses

Polished sections of selected samples were made by impregnating chips in epoxy resin and polishing on cloth with diamond pastes.

Scanning electron microscopes (SEM) equipped with focused electron gun (FEG) (Zeiss Ultra55, Sorbonne Université and Zeiss Sigma, École Normale Supérieure, Paris) were used to map the polished sections with an AsB detector collecting backscattered electrons. The optimal working distance was chosen according to the geometry of the sample chamber and the beam energy fixed to 15.0 kV. Energy dispersive X-ray spectroscopy (EDS) chemical mapping was performed with a Bruker Quantax EDS system using an Oxford 50  $\text{mm}^2$  silicon drift detector (SDD).

160 Electron probe microanalysis (EPMA) was performed on a CAMECA SXFive EPMA  
161 equipped with five wavelength-dispersive spectrometers (WDS) at the Centre d'Analyse des  
162 Minéraux de Paris (CAMPARIS). An accelerating potential of 15 keV and a sample current of  
163 40 nA have been used except for Fe oxides. Due to their small size and to protect them from beam  
164 radiation damage, the current was decreased to 15 nA. As a consequence, counting time was  
165 increased to analyze minor and trace elements such as Nb. Wavelength dispersive spectrometer  
166 analyses were performed using the following standards: Fe<sub>2</sub>O<sub>3</sub> for iron (Fe), almandine for  
167 aluminum (Al) and silicon (Si), MnTiO<sub>3</sub> for manganese (Mn) and Ti, NaNbO<sub>3</sub> for Nb, metallic Ta  
168 for Ta, monazite for Th.

## 169 2.6 Reference compounds for X-ray absorption analyses

170 A large set of natural and synthetic Nb-bearing reference materials were considered as  
171 potential compounds for X-ray absorption near-edge structure (XANES) analyses (Bollaert et al.,  
172 2023). Apart from columbite-(Mn) and Nb-bearing ilmenite which were provided by École  
173 Nationale Supérieure des Mines de Paris (MINES ParisTech), Nb reference materials were  
174 synthesized in order to incorporate Nb concentrations representative of natural enrichment.

175 Niobium-substituted goethite was prepared by adapting a hydrothermal method used for Sc-  
176 bearing Fe oxides (Chassé et al., 2017). Niobium-substituted goethite was converted into Nb-  
177 substituted hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) by dehydroxylation. The synthesis of Nb-substituted anatase and  
178 rutile has been carried out using a sol-gel method at moderate temperature. Detailed mineral  
179 synthesis procedures are described in Bollaert et al. (2023). The synthesis of Nb-sorbed phases at  
180 concentrations representative of natural lateritic media could not be carried out because Nb oxides  
181 reprecipitation instantly before adsorption.

## 182 2.7 Procedures for synchrotron-based analyses

183 XANES data at Nb L<sub>3</sub>- and K-edges have been collected at SOLEIL synchrotron facility  
184 (Saint-Aubin, France) operating with a storage ring current of 450 mA and energy of 2.75 GeV on  
185 the LUCIA (Vantelon et al., 2016) and SAMBA (Fonda et al., 2012) beamlines. The acquisition of  
186 spectra at the K and L<sub>3</sub>-edges is complementary, since two similar spectra at the L<sub>3</sub>-edge may be  
187 different at the K-edge, or inversely, since the information about the atomic-scale environment of  
188 Nb is different (Fig. S1).

189 A Si(111) double-crystal monochromator crystal was used on the LUCIA beamline with an  
190 energy resolution of 0.25 eV at 2400 eV (Schaeffers et al., 2007). The monochromator was calibrated  
191 at the energy of the Nb L<sub>3</sub>-edge using a Nb<sub>2</sub>O<sub>5</sub> powder pellet. Due to high Nb contents in Nb  
192 mineralogical references, the spectra were recorded on cellulose-diluted pellets before being  
193 mounted on a sample-holder. The low penetration depth of X-rays at this energy or the low Nb  
194 contents required a data acquisition in the fluorescence mode. Energy steps were (2, 0.2, 1) eV for  
195 energy ranges of (2300–2350), (2350–2400) and (2400–2455) eV, respectively, with a 1 s  
196 integration time. Two measurements per sample at room temperature and under vacuum were  
197 sufficient to get adequate signal-to-noise ratio and check for reproducibility of the edge features.

198 Spatially resolved  $\mu$ -XRF and  $\mu$ -XANES analyses were conducted by focusing the beam with  
199 four total reflection mirrors in Kirkpatrick-Baez geometry. Micro-XRF element maps were carried  
200 out on polished sections using an energy dispersive–silicon drift diode (SDD). For each map, from 5  
201 to 10  $\mu$ -XANES spectra of pre-identified minerals were recorded with an excitation energy of  
202 2450 eV and a micro-beam focus of 2.8 x 3.8  $\mu$ m.

203 Bulk Nb K-edge scans were collected from 18,700 to 20,000 eV using a continuous scan  
204 acquisition mode on the SAMBA beamline. The XANES region corresponds to the first 50 eV  
205 above the energy of the edge (*ca* 18,990–19,040 eV). The energy range for the EXAFS region is  
206 between the end of the XANES region up to 20,000 eV. The beamline was equipped with a Si(220)

207 monochromator providing a 2 x 0.5 mm (H x V) monochromatic beam. The samples were analyzed  
208 at 20 K using a He cryostat. Scans were obtained in 170 s and featured 1625 data points with a *ca*  
209 0.8 eV step. Multiple scans were collected for each sample until no significant improvement in the  
210 signal-to-noise ratio of their merged spectra was observed. Up to 30 scans were collected for the  
211 bulk rock samples.

212 Normalization and least-squares linear combination fitting of X-ray absorption spectra were  
213 performed using Larch software (Newville, 2013).

### 214 3. RESULTS

#### 215 3.1 Mineralogy and geochemistry

216 The biotite-alkali feldspar granite is a medium- to fine-grained leucocratic granite with a  
217 texture ranging from equigranular to porphyritic. It is composed of mesoperthitic alkali feldspar  
218 (Fig. 2a,b) (*ca* 53 %), albite (*ca* 33 %), quartz (*ca* 11 %) and biotite (*ca* 4 %) with chlorite, fluorite,  
219 zircon, monazite, ilmenite, rutile, apatite, xenotime, thorite, columbite, galena, cassiterite and barite,  
220 in order of abundance as characterized using SEM. Zircon, monazite, ilmenite and rutile are 10-  
221 20  $\mu\text{m}$  large and found embedded in large biotite flakes (Fig. 2c), partially replaced by chlorite (Fig.  
222 2d). Rutile also occurs as submicrometric grains within biotite. Thorite, apatite, monazite and  
223 cassiterite are found as isolated submicrometric crystal within feldspar. The alkali concentration of  
224 the granite in comparison to alumina concentration classifies it as a peraluminous granite. The  
225 concentration in high-field-strength elements (HFSE: i.e., zirconium (Zr), hafnium (Hf), Th, Nb, Ta,  
226 uranium (U) and rare-earth elements - REE) is *ca* 1200 ppm including *ca* 700 ppm of REE (Table  
227 S2). Niobium concentration is 46 ppm.

228 Above the parent granite, the lateritic profile consists of four distinct horizons (Fig. 3a). The  
229 clayey mottled zone exhibits pinkish (10R 8/4, from Munsell color chart, Soil Survey Staff, 2017)

230 and light red (2.5YR 7/6) colors with white clayey areas. The friable lateritic horizon is  
231 characterized by the predominance of reddish yellow matrix (5YR 7/8) composed of clays. A dark  
232 indurated bauxitic horizon (2.5YR 6/8) with white mottles is identified. The ferruginous duricrust  
233 (5YR 6/8) corresponds to a Fe-enriched crust containing consolidated nodules of Fe oxides (Fig. 3b,  
234 c).

235 The dominant mineral throughout the profile is kaolinite in variable proportions depending on  
236 the horizon (Fig. 3b). Gibbsite is found from the lateritic horizon up to the duricrust forming the top  
237 horizon and reaches a maximum in the bauxitic horizon (*ca* 45 wt%). Other minerals include quartz  
238 (5–13 wt%), Fe oxides (i.e., hematite and goethite, 2–11 wt%), anatase (2–3 wt%). Small amounts  
239 of rutile (< 1 wt%) are detected by XRD in the bauxitic horizon and the ferruginous duricrust. The  
240 proportion of Fe oxides increases from the bottom to the top of the profile (Fig. 3b). In the bauxitic  
241 horizon with the highest Zr content, zircon was also identified as a trace mineral on the XRD pattern  
242 (Fig. 3d).

243 The clayey mottled horizon is texturally similar to the lateritic horizon (Fig. 4a, b).  
244 Submillimetric grains of quartz are found along the profile (Fig. 4c). In the bauxitic horizon,  
245 kaolinite can be found as microcrystalline, forming stacks of lamellae discordant to the surrounding  
246 matrix (Fig. 4d). Iron oxides occur both as agglomerates of submicron size crystals (Fig. 4d) and as  
247 crystals of hundreds of microns isolated in the matrix in the lateritic horizon (Fig. 4b). Accessory  
248 minerals identified are zircon, Ti oxides, monazite, xenotime, thorite, columbite and cassiterite.

249 The bulk concentrations of major and minor elements reflect the mineralogical evolution. The  
250 Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents increase toward the surface with a maximum in the bauxitic horizon (41.5  
251 and 1.0 wt%, respectively) and then slightly decrease in the ferruginous duricrust (Fig. 3c). The  
252 concentration of Fe<sub>2</sub>O<sub>3</sub> increases up to 25 wt% in the duricrust while SiO<sub>2</sub> is depleted. The  
253 concentrations of Zr, Sn, Nb and Th increase from the bottom to the top of the laterite (Fig. 3d). The

254 concentration of REE in the laterite is below that of the granite and displays a complex evolution  
255 throughout the profile (Fig. 3d). The index of lateritization ( $IOL = 100 \times [(Al_2O_3 + Fe_2O_{3(T)}) / (SiO_2 + Al_2O_3 + Fe_2O_{3(T)})]$ ) used to quantify the stage of chemical weathering of a sample (Babechuk  
256 et al., 2014) varies between 47 and 71 % from the bottom to the top of the profile. Using this index,  
257 the investigated profile is considered as kaolinitized to weakly laterititized (Fig. 5a). The  
258 concentrations of HFSE such as Nb, Th, Zr are positively correlated ( $r = 0.81-0.99$ ) with the IOL  
259 index (Fig. 5b).

261 The mobility of some HFSE and immobile elements were investigated in the profile  
262 considering Th as immobile (Fig. 6). Globally, the REE are lost throughout the profile (Fig. 6). The  
263 mass loss of most light REE (LREE) is strong in the entire profile ( $\tau$  from -0.8 to -1.0) whereas the  
264 mass loss of heavy REE (HREE) and Y is weak to moderate in the bottom profile ( $\tau$  from -0.3 to -  
265 0.6) and then reaches 0.8–0.9 of mass loss in the uppermost part of the profile (Table S4). The  
266 evolution of the mass fraction transport function  $\tau$  for Zr and Ti is similar with a mass gain in the  
267 lower laterite followed by a continuous loss from -0.2 up to -0.7. Although the evolution of Hf and  
268 Zr is similar along the profile, the loss of Hf is lesser compared to Zr. (Fig. 6). On the scale of the  
269 profile, we note a moderate mass gain of Nb and Ta through the profile ( $\tau = 0.1-0.7$ ). Finally, we  
270 note a net gain of Sn of 1.0–2.0 relative to the parent rock with a maximum occurring in the  
271 ferruginous duricrust ( $\tau = 2.8$ ).

### 272 3.2 Identification and characterization of the niobium carriers

273 In the granitic parent rock, ilmenite is the main Nb-bearing phase. Ilmenite forms euhedral  
274 crystals of tens of micron isolated in millimetric biotite crystals (Fig. 7a, b). It is chemically  
275 characterized by high Mn and Nb concentrations (up to 10 wt % MnO and 2 wt % Nb<sub>2</sub>O<sub>5</sub>, Table 1).  
276 Niobium-bearing ilmenite (Fig. 7c) is replaced by another Nb-bearing Ti-Fe oxide (Fig. 7d). This  
277 mineral is presumably pseudorutile (Table 1) according to its Ti/(Fe+Ti) ratio, between 0.6 and 0.7,

278 and low totals obtained by microprobe analysis expected from its hydration (Grey et al., 1994).  
279 Alternatively, this phase could be a mixture between ilmenite and rutile. Micron-size crystals of Nb-  
280 bearing rutile also occur within the biotite matrix. Two types of Nb-bearing oxides occurring as  
281 trace minerals are also found. Micrometric Nb-bearing inclusions in ilmenite exhibiting preferential  
282 orientation (Fig. 7a) may be ascribed to fergusonite-(Y) or to Y-enriched columbite. Ferrocolumbite  
283 with slight enrichment in Sc is also identified (Fig. 7b).

284 In the altered horizons, based on chemical and textural differences, two types of Nb-bearing  
285 ilmenite (i.e. (i) preserved and (ii) altered ilmenite) and of Nb-bearing Ti oxides (i.e. (i) type-1 and  
286 (ii) type-2) are identifiable (Fig. 8). We found preserved Nb-bearing ilmenite in all the horizons. In  
287 the bauxitic horizon, Nb-bearing ilmenite are found within lamellae of kaolinite (Fig. 8a). Compared  
288 to the parent rock, Nb-bearing ilmenite is also manganoan but with a little less Mn (typically *ca*  
289 5.0 wt% MnO) and with lower Nb concentrations (*ca* 1.0 wt % Nb<sub>2</sub>O<sub>5</sub>, Table 2). The replacement of  
290 Nb-bearing ilmenite by pseudorutile as observed in the granite (Fig. 7d) is not found in the laterite.  
291 Instead, some crystals can be described as pseudorutile surrounding an ilmenite core (Fig. 8b). Other  
292 ilmenite crystals display signs of alteration such as corrosion features and cracks (Fig. 8c,d).  
293 Although altered in all the horizons, the most evident signs of alteration of Nb-bearing ilmenite are  
294 observed in the bauxitic horizon.

295 Type-1 Nb-bearing Ti oxide with low amounts of Fe (*ca* 5 wt% Fe<sub>2</sub>O<sub>3</sub>) and without Mn is  
296 only observed in the bauxitic horizon. Significant amounts of Th observed on the EDS spectra of  
297 type-1 Ti oxide (*ca* 0.5 wt% ThO<sub>2</sub>) may result from a substitution of Th for Ti (Gamaletsos et al.,  
298 2011). The presence of nanoscale Th-bearing inclusions in Ti oxide is also expected, as this Th for  
299 Ti substitution is limited by the large difference in ionic radii (1.0 and 0.61 Å). Thorium adsorption  
300 is excluded considering the low solubility of Th. The composition of these oxides could not be  
301 analyzed using EPMA due to their sub-micrometric size. Type-1 Ti oxide occurs as elongated

302 lamellae crystallizing between kaolinite sheets (Fig. 8e) and as poorly crystalline minerals  
303 surrounding kaolinite (Fig. 8f). Pure Nb-bearing Ti oxide is also observed (type-2 Ti oxide, Fig. 8 g,  
304 h). The crystals are larger than for type-1 Ti oxide ( $> 20 \mu\text{m}$ ) and they contain more Nb than  
305 ilmenite (Table 2).

306 Micrometric size Fe oxides with low Nb contents (0.1–0.3 Nb<sub>2</sub>O<sub>5</sub> wt%, Table 3) are also  
307 evidenced (Fig. 9a, b). The last Nb-bearing phase identified is columbite-(Mn) and -(Fe) (Table 4),  
308 found as fragmented grains (10–20  $\mu\text{m}$ ) within the kaolinite matrix (Fig. 9c). Columbite-(Fe) with  
309 low amounts of Sc is also found as inclusion in Nb-bearing ilmenite (Fig. 9d). The detection of Ti on  
310 the EDS spectrum may result from the interaction volume of the electron beam, larger than the  
311 columbite size (Fig. 9d). As for type-1 Ti oxide, the size of the inclusions of columbite prohibits an  
312 accurate determination of their composition, an EDS spectrum is shown instead (Fig. 9d). The  
313 qualitative evolution of Nb speciation along the regolith obtained by SEM observations is  
314 summarized in Table 5.

### 315 3.3 Characteristics of the X-ray absorption spectra of niobium carriers

316 The atomic environment of Nb in type-1 and type-2 Ti oxides, Fe oxides, ilmenite and  
317 columbite has been characterized using Nb L<sub>3</sub>-edge micro-XANES spectroscopy and compared with  
318 spectra of mineral references (Bollaert et al., 2023).

319 The Nb XANES spectra of columbite (Fig. 10a) and Fe oxide (Fig. 10b) from Pitinga match  
320 those of the mineral references. We find two distinct spectra between type-1 and type-2 Ti oxides.  
321 The position and intensity of the features of type-1 Ti oxide match the reference spectrum of Nb-  
322 bearing anatase considering the resolution of the spectra (Fig. 10c). The relative intensity of the  
323 features of type-2 Ti oxide spectrum better matches that of Nb-bearing rutile (Fig. 10d). As the  
324 spectra of mineral references match those of the Nb carriers from Pitinga, the reference spectra can



325 be used as components in the linear combination fitting procedure (Fig. 11,12). In absence of a  
326 reference for Nb-bearing ilmenite spectrum, we compare the spectrum of Pitinga ilmenite with Nb-  
327 bearing hematite and anatase in order to highlight the specificities of this spectrum (Fig. 10e). The  
328 micro-XANES spectrum of ilmenite being distinct from the other spectra, it will be further used as a  
329 fitting component.

### 330 3.4 Quantitative evolution of the average niobium speciation

331 A least-squares linear combination fitting procedure of Nb L<sub>3</sub>- and K-edges XANES spectra  
332 on bulk samples was performed using spectra of relevant mineral references (Fig. 10, S1) to  
333 quantitatively follow the average Nb speciation along the profile (Fig. 11, 12).

334 The Nb L<sub>3</sub>-edge spectrum of the clayey mottled horizon can be reproduced with the spectra  
335 of Nb-bearing ilmenite (60 %) and anatase (40 %), identified by SEM as the major Nb-bearing  
336 phases (Fig. 11). For the lateritic horizon, the combination of Nb-bearing ilmenite and Nb-bearing  
337 anatase spectra does not reproduce the L<sub>3</sub>-edge spectrum (Fig. S2) and the addition of a 50%  
338 contribution of the spectrum of Nb-bearing Fe is required (Fig. 11). The result of the fit does not  
339 change depending on whether Nb-bearing hematite or goethite spectra is used due to their  
340 resemblance (Fig. 10b). In the bauxitic horizon, the contribution of Nb-bearing Fe oxides reaches  
341 60 % (Fig. 11). Average Nb speciation derived from Nb L<sub>3</sub>-edge XANES is summarized in Table 5.

342 The Nb XANES spectrum of the granite is only collected at the Nb K-edge due to low Nb  
343 concentration (45 ppm) preventing the acquisition of a spectrum with a good signal-to-noise ratio at  
344 the L-edge. The fit is not satisfactory with ilmenite and rutile reference spectra, which are the main  
345 Nb carriers in the granite according to SEM-EDS observations (Fig. S3). This discrepancy stems  
346 from major differences between the spectra of reference ilmenite and Pitinga ilmenite which was  
347 characterized by microanalysis (Fig. S4). The Nb K-edge XANES spectrum of Pitinga ilmenite has  
348 matching features in energy and relative intensity with the granite spectrum thus suggesting it is the

349 main Nb carrier (Fig. S4). The low signal-to-noise ratio of the  $\mu$ -XANES spectrum of Pitinga  
350 ilmenite prevents the quantitative analysis of the Nb speciation of the granite (Fig. 12). In the  
351 following fits, the spectra of Nb-bearing rutile and anatase will be used to account for the  
352 proportions of Nb-bearing Ti oxides and ilmenite in absence of relevant Nb-bearing ilmenite  
353 spectrum. As a complement to the  $L_3$ -edge which allows determining the nature of the Ti oxides, the  
354 fit at the K-edge (Fig. 12) is thus used to distinguish the nature of the Nb-bearing Fe oxides, which  
355 have distinct spectra at the K-edge (Fig. S1). We obtain a satisfactory fit of the clayey mottled  
356 horizon spectrum only with Nb-bearing Ti oxides (60 % anatase and 40 % rutile). Like at the  $L_3$ -  
357 edge, the combination of Nb-bearing ilmenite and Ti oxides spectra does not reproduce the K-edge  
358 spectra of the lateritic and bauxitic horizons (Fig. S5). The best fit for the lateritic horizon spectrum  
359 is found when Nb-bearing goethite spectrum (50 %) is added to Nb-bearing Ti oxides (Fig. 12). In  
360 the bauxitic horizon, the fit with only Nb-bearing goethite and Ti oxides components fails to  
361 reproduce the features of the edge (Fig. S6). As ilmenite contributes less to the average Nb  
362 speciation in this horizon, this difference is more likely due to a missing component. The addition of  
363 15 % of columbite, for which SEM-EDS analyses indicate increasing abundance in the top horizons  
364 (Fig. 9c), to 60 % goethite and 25 % anatase significantly improves the quality of the fit (Fig. 12).  
365 We also collected the Nb K-edge spectrum of the duricrust horizon which stands out by an intense  
366 pre-edge at ca. 18, 980 eV and a low intensity feature between the two main features (Fig. 12). This  
367 spectrum can only be fitted with a high proportion of columbite (50 %) and with Nb-bearing  
368 goethite (50 %). On average, Nb speciation obtained at the K-edge is consistent with that provided at  
369 the  $L_3$ -edge (Table 5).

370

## 4. DISCUSSION

### 371 4.1 Origin of the parent niobium mineralization

372 The Nb mineralization of the biotite granite from Pitinga is dominated by ilmenite and rutile  
373 with minor columbite (Fig. 7). The equilibrium temperature and pressure of formation of the granite  
374 were estimated to be 800–860 °C and 7.5 kbar (Lenharo et al., 2003). The Nb/Y value of the parent  
375 rock is typical of a A2-type granite indicating emplacement in post-collisional environment (Ferron  
376 et al., 2010). The low Nb/Ta ratio of the granite (*ca* 7) arises from the early crystallization of micas  
377 ( $D_{\text{Nb}}/D_{\text{Ta}} = 2.00$ ) (Stepanov et al., 2014; Ballouard et al., 2016). The presence of ilmenite rather than  
378 magnetite indicates that the melt first evolved in reducing conditions ( $< \text{Ni-NiO}$  buffer, Ishihara,  
379 1977). The formation of pseudorutile (Fig. 7d) is controlled by an increase of the oxygen fugacity of  
380 the magma body during its ascent, which increases the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio (Anand, 1984). This supports  
381 the hypothesis of Lenharo et al., (2003) suggesting that the biotite granite underwent partial  
382 crystallization followed by emplacement at shallow levels. Reduced Fe and Mn from the ilmenite  
383 structure are oxidized and released explaining the lower amount of Mn in pseudorutile (Schroeder et  
384 al., 2002).

385 At the late magmatic stage, the exsolution of a Y-rich Nb oxide from ilmenite, either  
386 fergusonite-(Y) or yttrrocolumbite (Fig. 7d), is controlled by substitution of heterovalent cations  
387 other than  $\text{Fe}^{2+}$ , namely  $\text{Mn}^{2+}$ ,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  and by the oxidation state of Fe. The manganoan nature  
388 of ilmenite may have prevented greater incorporation of Nb due to the limited solubility of Nb in  
389 manganoan ilmenite at low temperature (Capitani, 2017). Despite its rarity, the presence of  
390 yttrrocolumbite is likely as columbite has been reported in the studied biotite granite (Lenharo et al.,  
391 2003) and as inclusions in ilmenite (Beurlen and Thomas, 2006; Capitani, 2017). Similar orientation  
392 of exsolved phases may result from the crystallization process of columbite during exsolution which  
393 follows the crystallographic orientation of the octahedral chains of ilmenite (Capitani, 2017). The  
394 exsolution process may have concentrated Y and HREE explaining the formation of a Y-rich  
395 columbite.

**396 4.2 Crystal-chemical and geochemical controls on niobium mobility in the critical zone**

397 The combination of SEM (Fig. 8e, f) and XANES data (Fig. 11,12) demonstrates the  
398 alteration of ilmenite due to chemical weathering. Ilmenite can be resistant to supergene alteration  
399 (Berger et al., 2014; Janots et al., 2015) or prone to weathering (Mordberg et al., 2001; Du et al.,  
400 2012) depending on the geochemical conditions or on its crystal-chemistry. In oxidic weathering  
401 environment, Mn-rich ilmenite would be destabilized due to the possible formation of soluble  $Mn^{3+}$   
402 and  $Mn^{4+}$  easing its weathering. In the studied profile, Nb speciation is therefore controlled by the  
403 capacity of alteration of primary ilmenite, releasing Nb in supergene fluids and leading to  
404 scavenging by secondary Fe and Ti oxides (Fig. 11,12).

405 Goethite is the main Nb-bearing Fe oxide as shown by the fit of K-edge XANES spectra of  
406 lateritic samples (Fig. 12, Fig. S7) and by crystal-chemistry of the Fe oxides (Table 3). The  
407 scavenging of Nb by Fe oxides is favored by the formation of goethite at the expense of hematite  
408 under cool and humid tropical climate with near-neutral pH fluids (Schwertmann, 1983; Kämpf and  
409 Schwertmann, 1983), in agreement with the expected conditions of alteration in the studied profile.

410 According to XRD results, anatase is the main Ti oxide in the profile but rutile is also  
411 detected in the bauxitic horizon and in the duricrust. The fingerprint analysis of type-1 and type-2 Ti  
412 oxides XANES spectra indicates they may be anatase and rutile, respectively (Fig. 10c, d). Type-2  
413 Ti oxide is probably primary, inherited from the biotite granite. As Nb-bearing rutile component is  
414 not required in the fitting procedure (Fig. 11), the proportion of Nb hosted in rutile is likely minor at  
415 the scale of the profile.

**416 4.3 Atomic-scale processes controlling niobium mobility during supergene weathering**

417 Atomic-scale mechanisms of Nb incorporation into supergene phases will control the affinity  
418 of Nb for Ti and Fe oxides and Nb mobility after its release from ilmenite. They can be deduced

419 from the XANES signature of supergene Nb carriers (Fig. 10).

420 Goethite is a major host of Nb in the weathering profile (Table 5). Due to similar ionic radius  
421 ( $[^6\text{Fe}^{3+}] = 0.645 \text{ \AA}$  and  $[^6\text{Nb}^{5+}] = 0.64 \text{ \AA}$ , - Shannon, 1976) substitution between  $\text{Nb}^{5+}$  and  $\text{Fe}^{3+}$  is made  
422 possible by the formation of Fe vacancies ( $5\text{Fe}^{3+}$  for  $3\text{Nb}^{5+}$ ) which maintain charge balance (Bollaert  
423 et al., 2023). In goethite, the  $\text{Nb}^{5+}-\text{Fe}^{3+}$  substitution process could be accompanied by the loss of two  
424  $\text{H}^+$  occupying the tunnels between the double chains which would lead to the formation of  
425  $\text{NbO}_5(\text{OH})$  octahedra. Although goethite from Pitinga incorporates only 0.1–0.3 %  $\text{Nb}_2\text{O}_5$ , goethite  
426 incorporating more than 1 %  $\text{Nb}_2\text{O}_5$  has been reported in supergene environments (Wall et al.,  
427 1996 ; Melgarejo et al., 2012). Experimental studies have shown that goethite can accommodate up  
428 to 0.3 apfu (atom per formula unit) of Nb (Oliveira et al., 2008, 2009) but increasing Nb content  
429 leads to a decrease of the crystallinity due to the transformation of double octahedral chains into  
430 single ones as a result of the withdrawal of H atoms (Bolanz et al., 2013). The absence of Nb in  
431 hematite could be due to the limited affinity of Nb for this phase. Niobium ions would occupy face-  
432 sharing octahedra of the hematite structure leading to a strong electrostatic repulsion between  
433 cations (Bolanz et al., 2013).

434 The occurrence of Nb-adsorbed Fe oxides is unlikely at the concentrations found in goethite  
435 (*ca* 0.20 wt %  $\text{Nb}_2\text{O}_5$ ) considering the low solubility of Nb ( $< 1.10^{-7} \text{ mol.kg}^{-1}$ , Peiffert et al. 2010).  
436 The similarity of Nb-substituted goethite reference XANES spectrum with that of the Pitinga  
437 goethite also excludes the possibility of Nb adsorption onto Fe oxides. Such chemisorption process  
438 occurring onto hematite and goethite is nonetheless possible in near-neutral pH with 80–90 % of Nb  
439 being adsorbed (Ghosh et al., 2017) but only at extremely low Nb concentrations (*ca*  $2.10^{-9} \text{ mol.L}^{-1}$ ).

440 The comparison between type-1 and type-2 Ti oxide XANES spectra with their respective  
441 reference counterparts (Fig. 10) gives access to the mechanisms of incorporation of Nb in Ti oxides.  
442 The significant shift of 0.5 eV of the second feature on type-1 Ti oxide XANES spectrum relative to

443 Nb-bearing anatase of reference mirrors distinct Nb environments (Fig. 10c). The presence of Fe in  
444 type-1 Ti oxide may ease Nb incorporation by a co-substitution of  $\text{Nb}^{5+}$  and  $\text{Fe}^{3+}$  for  $2\text{Ti}^{4+}$  ( $2\text{Ti}^{4+} =$   
445  $\text{Fe}^{3+} + \text{Nb}^{5+}$ ) and may prevent significant distortion of the local environment of Nb in type-1 Ti  
446 oxide. Such substitution, expected to occur in Nb-bearing Ti oxide from other laterites (Giovannini  
447 et al., 2020) is common in presence of high amounts of Fe such as it is the case in the studied  
448 profile. By contrast, the similarity between the spectra of type-2 Ti oxide and Nb-bearing rutile  
449 reference indicates similar Nb environment and therefore similar mechanisms of substitution. In  
450 absence of Fe, the incorporation of Nb results in the increased distortion of the Nb site and Nb–O  
451 distances (Bollaert et al., 2023). In this case, the incorporation of Nb is made possible by the  
452 formation of one  $\text{Ti}^{4+}$  vacancy for four  $\text{Nb}^{5+}$  which leads to the increase of Nb–O distances (Bollaert  
453 et al., 2023).

#### 454 4.4 Selection of an immobile element for mass-balance calculations in the profile

455 The choice of the immobile element is a challenging task in mass-balance calculations as it is  
456 critical in determining element leaching or redistribution within the regolith and constraining  
457 biogeochemical cycles (Oh and Richter, 2005). In addition to Nb, typical elements chosen as  
458 immobile include Al, Ti, Zr, Hf, Ta (Grant, 2005; Szilas et al., 2016). However, the mineral carriers  
459 of these elements display signs of alteration in the studied profile. Ilmenite (Fig. 8c) and zircon (Fig.  
460 S6) are altered in the lateritic units making Ti, Zr and Hf unsuitable for such purpose. Tantalum,  
461 being carried by ilmenite, it cannot be used either. Given the textural characteristics of weathering-  
462 resistant cassiterite ( $\text{SnO}_2$ ) found in the lateritic units (Fig. S6), Sn may be the least mobile element  
463 of the alteration profile. However, the use of Sn as a conservative element in mass-balance  
464 calculations leads to extreme mass loss of other relatively immobile elements (up to 90 % for Ti, Nb  
465 and Zr) which seems inconsistent with the relative abundance of Ti oxides and zircon. Such low  
466 values could be explained by an addition of Sn in the profile. The Sn concentration is 250 times

467 higher in the albite-enriched granite facies nearby than in the studied parent granite (Table S5). Even  
468 limited lateral transport of material from the laterite developed over the Sn-enriched granite would  
469 lead to a significant Sn mass gain in the studied laterite through a nugget effect. The use of Sn thus  
470 skews the results of mass-balance calculations leading to overestimation of elemental mass loss.  
471 Such lateral transport is evidenced mineralogically by the rare presence of Zr-enriched thorite (Fig.  
472 9b) and columbite-(Mn) (Fig. 9c), absent in the parent rock but present in the surrounding enriched  
473 albite-enriched granite facies (Alves et al., 2018). As the profile is located on a slope downstream of  
474 the mineralized laterite (Fig. 1c), these minerals may have been brought in the form of solid particles  
475 to the studied profile by circulation of sub-surficial fluids or by mechanical sliding. Their occurrence  
476 is unlikely related to heterogeneities between the two granitic facies given the continuity of the  
477 geochemical data along the profile (Fig. 3c, d) and the absence of minerals typical of the albite-  
478 enriched granite (such as pyrochlore, columbite, cryolite) in the biotite granite.

479 Despite signs of monazite weathering mirrored by the mass loss of LREE (Table S4), the  
480 weak signs of alteration of thorite (Fig. S8) and the smaller difference in Th concentration between  
481 the studied parent rock and the neighboring albite-enriched granite (6-fold enrichment, Table S5),  
482 Th was chosen as the best conservative element for mass-balance calculations.

#### 483 4.5 Assessment of Nb mobility at the scale of the profile

484 As evidenced by the weathering of ilmenite and further incorporation of Nb into Ti oxides  
485 and goethite, the remobilization of Nb at the micrometric scale implies potential mass loss of Nb at  
486 the scale of the profile which would result in  $\tau_{\text{Nb}}$  close to 0 or slightly negative. Mass-balance  
487 calculations nonetheless indicate a moderate mass gain of Nb relative to the parent rock all along the  
488 profile (Fig. 6). Together with the contribution of columbite to Nb speciation in the bauxitic horizon  
489 and duricrust (Fig. 12), this supports the hypothesis of lateral transport. The importance of such  
490 lateral transport has been shown in laterites, where it affects directly the vertical evolution of trace



491 elements such as Ni and Sc along alteration profiles (Quesnel et al., 2017; Chassé et al., 2019). The  
492 very high contribution of columbite in the fit of the duricrust XANES spectrum could be due to a  
493 higher proportion of columbite in the analyzed powdered sample than in the rest of the sample. This  
494 nugget effect is corroborated by the  $\tau_{\text{Nb}}$  value in the duricrust (0.24), lower than that of the bauxitic  
495 horizon (0.58).

496 Due to the *ca* 30-fold difference in the concentrations of Nb between the albite-enriched and  
497 biotite granite facies (Table S5), lateral transport masks potential losses of Nb due to supergene  
498 weathering and prevents to conclude on the mobilization of Nb at the profile scale. This may explain  
499 the absence of correlation between the index of lateritization (IOL) and the mass fraction transport  
500 function  $\tau$  (Fig. 13a). Given the poor solubility of oxide species that Nb could form under the  
501 slightly acidic to near-neutral pH prevailing in laterites (Peiffert et al., 2010) and the affinity of Nb  
502 for supergene Fe and Ti oxides demonstrated by this study, Nb mobility is likely low and  
503 constrained to the scale of mineralogical assemblages. Along with this significant influence of pH  
504 on Nb speciation and therefore on Nb mobility, the effect of the presence of inorganic (sulphate,  
505 chloride, phosphate) and organic ligands remains to be explored (Friis and Casey, 2018)

#### 506 4.6 Comparison with other 'immobile' elements

507 The behavior of other elements considered as immobile during supergene weathering was  
508 also studied. The study of Ta and Sn dynamics is hindered by mass gain resulting from lateral  
509 transport. The weak correlation obtained between the IOL index and  $\tau$  for Ta (Fig. 13b) can be  
510 explained in the same way as for Nb because Ta, which is 30 times more enriched in the albite  
511 granite, substitutes for Nb in columbite which is transported to the studied profile. For Sn, the  
512 magnitude of  $\tau$  is explained by lateral transport due the extreme differences in Sn concentration  
513 between the two source granites (by a factor of 250). The positive correlation showing that  $\tau$   
514 increases with the IOL index (Fig. 13c) and thus with depth (Fig. 5a), suggests that lateral transport



515 occurs in the entire profile and is more important in the top horizons. The negative correlations  
516 between the mass loss experienced by Ti (Fig. 13d), Zr (Fig. 13e) and Hf (Fig. 13f) and the IOL  
517 index evidence the increasing mobility of these elements with increasing degree of weathering. For  
518 these elements, lateral transport does not compensate the net mass loss induced by supergene  
519 weathering because the difference of concentrations between the biotite and albite facies is less  
520 significant (Table S5).

521 Several 'immobile' elements proved to be mobile in specific conditions of alteration (Braun  
522 et al., 2005). Titanium is mobile at the macroscopic scale due to intense weathering and  
523 complexation with organic matter (Cornu et al., 1999). Zirconium was found to be mobile in  
524 weathering profiles formed over rocks with alterable Zr-bearing silicates (Duvallet et al., 1999) but  
525 also with zircon which experienced metamictization (Balan et al., 2001). Intense and long-term  
526 alteration processes are responsible for a series of precipitation-dissolution reactions which induce  
527 Sc remobilization at least at the local scale (Chassé et al. 2019). Along with this study, possible  
528 mobility of 'immobile' elements shows that the choice of the best chemical invariant for mass-  
529 balance calculations must be a thought-out choice according to the conditions of formation of the  
530 studied profile and to the mineralogy of the source rock to accurately quantify element fluxes in the  
531 critical zone.

#### 532 **4.7 Influence of primary mineralization on Nb mobility**

533 The role of the parent rock on the fate of Nb in the inherited lateritic profile is illustrated by  
534 the mineralogy of lateritic profiles resulting from the weathering of different granitic facies from  
535 Pitinga. These profiles formed within the same geodynamic context and under similar climatic  
536 conditions but over different granitic facies and distinct primary Nb-bearing phases. In the laterites  
537 formed from the albite-enriched facies, pyrochlore and columbite have been preserved despite the  
538 fragmentation of columbite into thin particles and the Nb released from pyrochlore and columbite

539 later incorporated secondary Fe oxides (Horbe and da Costa, 1999; Alves et al., 2018). The  
540 differences of Nb speciation in laterites from the Pitinga region are related to the diversity of  
541 primary Nb minerals in the parent rock. Lateritization processes will be more amenable to mobilize  
542 Nb from rocks containing Nb-bearing ilmenite and rutile than from rarer lithotypes bearing  
543 pyrochlore or columbite phases which are more resistant to supergene alteration.

## 544 CONCLUSION

545 The speciation of Nb along an entire lateritic regolith has been determined and quantitatively  
546 monitored with a multiscale approach combining SEM and EPMA microanalyses and XANESS  
547 data. The Nb mineralogy of the parent biotite granite, characterized by Ti-bearing oxides, i.e.  
548 ilmenite and rutile, is distinct from that encountered in the surrounding Nb-enriched Pitinga granites  
549 with complex multicomponent Nb oxides. Lateritization processes result in the formation of Nb-  
550 bearing Ti oxides (2–6 wt% Nb<sub>2</sub>O<sub>5</sub>) and goethite (0.1–0.3 wt% Nb<sub>2</sub>O<sub>5</sub>) at the expense of primary  
551 carriers in the altered horizons.

552 The mobility of Nb in the studied profile results from the alteration of primary Nb-bearing  
553 minerals which releases Nb in supergene fluids. However, the high affinity of Nb for Ti oxides and  
554 goethite, evidenced at the atomic-scale using XANES spectroscopy, limits the mobility of Nb to the  
555 scale of the mineralogical assemblage. Mass-balance calculations evidence a mass gain of Nb in the  
556 upper laterite which is explained by lateral transport of surrounding Sn-Nb-enriched laterite formed  
557 from the albite-enriched granite. XANES data show that this mass gain of Nb comes from a lateral  
558 transfer of columbite towards the studied profile, in particular in the upper horizons. An enrichment  
559 through lateral transport is also observed for Sn and Ta. By contrast, Zr, Hf and Ti, usually  
560 immobile, are leached in the studied profile.

561 The difference of Nb speciation in laterites from the Pitinga region is related to the diversity of  
562 primary Nb minerals with different degrees of resistance to weathering. The use of Nb as a chemical

563 invariant must be carefully considered as the mobility of Nb is dependent on the processes  
564 controlling primary Nb mineralization.

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## 574 RESEARCH DATA

575 Research Data associated with this article can be accessed at  
576 <https://doi.org/10.5281/zenodo.7376789>.

## 577 APPENDIX A. SUPPLEMENTARY MATERIAL

578 Supplementary material includes additional information on semi-quantitative analysis (Table  
579 S1), geochemical data (Table S2), mass-transfer calculations (Tables S3 and S4) and a comparison  
580 between the concentration of the biotite granite and the mineralized albite-enriched facies (Table  
581 S5). Supplementary figures show the Nb K-edge spectra of references (Fig. S1), comparison of  
582 spectra and tests of fits (Figs. S2, S3, S4, S5, S6, S7) and backscattered images of trace minerals  
583 more or less resistant to weathering (Fig. S8).

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585 **Figure 1.** Geological context of the sampled profile: (a) location and geological map of the Pitinga  
586 region (modified after Costi et al. 2000); (b) close-up of the sampling region indicating Nb  
587 concentration in the different facies of the Madeira pluton. (c) Geological cross-section close to the  
588 studied profile (modified after Bastos Neto et al. 2009).

589 **Figure 2.** Backscattered electron images of representative mineral assemblages in the parent granite:  
590 (a) perthitic feldspars (Kfs) and local alteration of biotite (Bt); (b) EDS map of perthitic feldspars;  
591 (c) zircon (Zrn), monazite (Mzn), ilmenite (Ilm) and xenotime (Xtm) around biotite; (d) ilmenite,  
592 monazite and zircon within biotite.

593 **Figure 3.** Mineralogical and geochemical evolution of the studied profile: (a) log diagram of the  
594 profile; (b) bulk mineralogy obtained by semi-quantitative analyses of X-ray diffraction patterns  
595 (Ab: albite, Kfs: alkaline feldspar, Qz: quartz, Bt: biotite, Hem: hematite, Gt: goethite, Kln:  
596 kaolinite, Ant: anatase, Gbs: gibbsite); (c) evolution of the concentration of major and (d) some  
597 selected trace elements including HFSE with depth.

598 **Figure 4.** Backscattered electron images representative of the different horizons: (a) clayey mottled  
599 horizon with quartz (Qz) and zircon (Zrn) grains dispersed in the kaolinite (Kln) matrix; (b) lateritic  
600 horizon with scattered ilmenite (Ilm), zircon and Fe oxides in a gibbsite matrix; (c) bauxitic horizon  
601 exhibiting large crystals of quartz distributed in a clay and gibbsite matrix on the scale of the thin  
602 section; (d) stacking of kaolinite lamellae are associated to partially altered ilmenite. Numerous  
603 micrometric crystals of Fe oxides are embedded in gibbsite (Gbs).

604 **Figure 5.** Evolution of the degree of weathering of the profile: (a) mass  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_{3(\text{T})}$  (SAF)  
605 ternary plot showing the degree of weathering experienced and the sampling depth; (b) correlations  
606 between the index of lateritization (IOL) and Nb, Sn, Th, Zr. Pearson correlation coefficient  $r$  is  
607 calculated for each element.

608 **Figure 6.** Mass fraction transport function  $\tau$  obtained by mass-balance calculations as a function of  
609 depth for Nb, Ta, Zr, Hf, Sn, Y and Ti using Th as the immobile element of reference. Uncertainties  
610 on  $\tau$  are between  $\pm 1$  and 20%.

611 **Figure 7.** Backscattered electron images of the Nb carriers of the parent granite: (a) inclusion of Nb-  
612 Y-bearing oxide (Nb-Y ox.) in Nb-bearing ilmenite (Nb ilm) that crystallized within biotite (Bt); (b)  
613 partial replacement of Nb-bearing ilmenite by Sc-rich ferrocolumbite (Sc-Clb); (c) mineralogical  
614 relationship between Nb-bearing ilmenite, monazite (Mnz), biotite and zircon (Zrn); (d) close-up on  
615 (c) showing the exsolution of Nb-Y-bearing oxide in Nb-bearing ilmenite. Niobium-bearing ilmenite  
616 is replaced by Nb-bearing pseudorutile (Nb pdrt).

617 **Figure 8.** Backscattered electron images of the different types of Nb-bearing ilmenite and Ti oxides  
618 found in the laterite: (a) EDS-SEM map of a heterogeneous crystal of Nb-bearing ilmenite (Nb ilm)  
619 within kaolinite (Kln) in the bauxitic horizon; (b) Nb-bearing pseudorutile (Nb pdrt) crystal in the  
620 clayey mottled horizon displaying relics of Nb-bearing ilmenite and inclusions of columbite (Clb);  
621 (c) and (d) typical alteration features of Nb-bearing ilmenite in a kaolinitic matrix (Kln) in the  
622 bauxitic horizon; (e) type-1 Nb-bearing Ti oxide crystallized at the margins and between the  
623 kaolinite layers (Kln); (f) porous and fibrous type-1 Ti oxide crystallizing at the margins of  
624 kaolinite; (g) large crystal of pure Nb-bearing Ti oxide associated with monazite (Mnz) in the  
625 lateritic horizon; (h) euhedral type-2 Ti oxide intergrown with kaolinite.

626 **Figure 9.** Backscattered electron SEM images of Nb-bearing Fe oxides and columbite: (a) micron-  
627 size Nb-bearing Fe oxides in the clay matrix; (b) Zr-rich thorite probably mixed to Fe oxides  
628 overgrown by Nb-bearing Fe oxides; (c) euhedral crystal of columbite-(Mn) (Clb-Mn) in a kaolinite  
629 matrix (sample Col.1 in Table 4); (d) inclusion of ferrocolumbite (Clb-Fe) in ilmenite. The region of  
630 analysis of associated SEM-EDS spectra is indicated by the star symbols.

631 **Figure 10.** Fingerprint analysis of Nb L<sub>3</sub>-edge XANES spectra with reference spectra: (a)  
632 columbite; (b) Nb-bearing Fe oxides (c) type-1 Nb-bearing Ti oxide; (d) type-2 Nb-bearing Ti oxide;  
633 (e) Nb-bearing ilmenite.

634 **Figure 11.** Evolution of the average Nb L<sub>3</sub>-edge XANES spectra along the profile. Least-squares  
635 linear combination fitting of the altered horizons performed at the L<sub>3</sub>-edge using Nb-bearing Fe  
636 oxides (Nb-Fe), Nb-bearing anatase (Nb-ant) and Nb-bearing ilmenite (Nb-ilm).

637 **Figure 12.** Evolution of the average Nb K-edge XANES spectra along the profile. Least-squares  
638 linear combination fitting of the lateritic horizons performed at the K-edge using Nb-bearing  
639 goethite (Nb-gt), Nb-bearing anatase (Nb-ant), Nb-bearing rutile (Nb-rt) and columbite (Clb). The  
640 spectrum of the granite cannot be reproduced in absence of relevant ilmenite spectrum, this phase  
641 being the main Nb host (Fig. S3).

642 **Figure 13.** Binary plots of the index of lateritization (IOL) versus mass fraction transport function  $\tau$ .  
643 The increase of IOL is correlated with the decrease of  $\tau$  for Ti, Zr and Hf (Pearson correlation  
644 coefficient:  $r > 0.8$ ). Uncertainties on  $\tau$  are between  $\pm 1$  and 20%.

645 **Table 1.** Representative compositions of Nb carriers from the parent granite (ILM: ilmenite, PDRT:  
646 pseudorutile, RT : rutile). Ti/(Ti+Fe) at% ratios between 0.6 and 0.7 are indicative of pseudorutile.

647 The sum of cations above 1 in rutile may arise from the interaction volume of the electron beam,  
 648 larger than the rutile size, which may also analyze biotite and ilmenite.  
 649

| wt%                            | ILM.1  | ILM.2  | ILM.3 | ILM.4 | PDRT.1 | PDRT.2 | PDRT.3 | RT.1   | RT.2  | RT.3  |
|--------------------------------|--------|--------|-------|-------|--------|--------|--------|--------|-------|-------|
| TiO <sub>2</sub>               | 52.66  | 50.17  | 48.76 | 50.69 | 61.93  | 67.06  | 65.62  | 78.84  | 73.19 | 70.00 |
| MnO                            | 10.09  | 7.60   | 7.49  | 9.55  | 0.78   | 0.47   | 0.68   | 0.38   | 0.42  | 0.42  |
| FeO                            | 35.76  | 39.20  | 40.29 | 37.38 | 28.76  | 25.73  | 27.12  | 18.04  | 20.15 | 20.15 |
| Nb <sub>2</sub> O <sub>5</sub> | 1.60   | 1.74   | 2.11  | 1.87  | 1.17   | 2.25   | 2.32   | 2.74   | 2.57  | 2.57  |
| Ta <sub>2</sub> O <sub>5</sub> | 0.11   | 0.38   | 0.22  | 0.31  | 0.08   | 0.08   | 0.18   | 0.22   | 0.34  | 0.34  |
| Al <sub>2</sub> O <sub>3</sub> | /      | 0.22   | /     | /     | /      | /      | /      | /      | /     | /     |
| SiO <sub>2</sub>               | 0.08   | 1.30   | 0.03  | 0.11  | 0.70   | 0.91   | 1.36   | 1.25   | 1.75  | 1.75  |
| Total                          | 100.30 | 100.60 | 98.90 | 99.91 | 93.42  | 96.50  | 97.28  | 101.47 | 98.42 | 98.42 |
| Ti/(Ti+Fe)<br>at%              | 0.53   | 0.50   | 0.48  | 0.51  | 0.66   | 0.70   | 0.68   | 0.77   | 0.74  | 0.74  |
| <i>Structural formulae</i>     |        |        |       |       |        |        |        |        |       |       |
| Ti                             | 0.99   | 0.95   | 0.95  | 0.97  | 3.48   | 3.570  | 3.731  | 0.85   | 0.823 | 0.823 |
| Mn                             | 0.21   | 0.16   | 0.16  | 0.206 | 0.049  | 0.028  | 0.042  | 0.005  | 0.005 | 0.005 |
| Fe                             | 0.75   | 0.82   | 0.87  | 0.795 | 1.795  | 1.523  | 1.603  | 0.216  | 0.252 | 0.252 |
| Nb                             | 0.018  | 0.02   | 0.025 | 0.022 | 0.039  | 0.072  | 0.074  | 0.018  | 0.017 | 0.017 |
| Ta                             | 0.001  | 0.003  | 0.002 | 0.002 | 0.002  | 0.002  | 0.002  | 0.001  | 0.001 | 0.001 |
| Al                             | /      | 0.007  | /     | /     | /      | /      | /      | /      | /     | /     |
| Si                             | 0.002  | 0.033  | 0.001 | 0.001 | 0.052  | 0.064  | 0.097  | 0.018  | 0.026 | 0.026 |
| ∑ Cations                      | 1.971  | 1.993  | 2.008 | 1.996 | 5.417  | 5.259  | 5.549  | 1.108  | 1.124 | 1.124 |

650

651 **Table 2.** Representative compositions of Nb-bearing ilmenite (Ilm) and type-2 Ti oxide from

652 lateritic horizons. Some analyses are far from 100 % due to contamination with neighboring phases.

653 Type-1 Ti oxide could not be analyzed using EPMA.

| wt%                            | ILM.1 | ILM.2  | ILM.3 | ILM.4 | Type-2<br>Ti ox.1 | Type-2<br>Ti ox.2 | Type-2<br>Ti ox.3 |
|--------------------------------|-------|--------|-------|-------|-------------------|-------------------|-------------------|
| TiO <sub>2</sub>               | 52.92 | 53.08  | 53.93 | 55.47 | 98.60             | 92.39             | 96.45             |
| MnO                            | 4.86  | 6.33   | 4.89  | 4.05  | /                 | /                 | 0.04              |
| Fe <sub>2</sub> O <sub>3</sub> | 42.36 | 42.71  | 35.00 | 36.08 | 0.15              | 0.53              | 0.43              |
| Nb <sub>2</sub> O <sub>5</sub> | 0.79  | 0.91   | 1.27  | 1.01  | 1.42              | 3.69              | 2.13              |
| Ta <sub>2</sub> O <sub>5</sub> | 0.57  | 0.17   | 0.20  | 0.16  | 0.23              | 0.15              | 0.40              |
| Al <sub>2</sub> O <sub>3</sub> | /     | /      | /     | /     | /                 | 0.33              | /                 |
| SiO <sub>2</sub>               | /     | /      | 0.01  | /     | 0.03              | 0.60              | /                 |
| Total                          | 101.5 | 103.20 | 95.30 | 96.78 | 100.43            | 97.69             | 99.45             |

*Structural  
formulae*

|    |       |       |       |       |       |       |       |
|----|-------|-------|-------|-------|-------|-------|-------|
| Ti | 0.995 | 0.982 | 1.049 | 1.059 | 0.988 | 0.956 | 0.981 |
| Mn | 0.103 | 0.132 | 0.107 | 0.087 | /     | /     | 0.000 |
| Fe | 0.885 | 0.879 | 0.757 | 0.766 | 0.002 | 0.006 | 0.005 |
| Nb | 0.009 | 0.010 | 0.015 | 0.012 | 0.009 | 0.023 | 0.013 |

| wt%              | ILM.1 | ILM.2 | ILM.3 | ILM.4 | Type-2<br>Ti ox.1 | Type-2<br>Ti ox.2 | Type-2<br>Ti ox.3 |
|------------------|-------|-------|-------|-------|-------------------|-------------------|-------------------|
| Ta               | 0.004 | 0.001 | 0.001 | 0.001 | 0.001             | 0.001             | 0.001             |
| Al               | /     | /     | /     | /     | /                 | 0.005             | /                 |
| Si               | /     | /     | 0.001 | /     | 0.000             | 0.008             | /                 |
| $\Sigma$ Cations | 1.996 | 2.004 | 1.930 | 1.925 | 1.000             | 0.999             | 1.000             |

654

655 **Table 3.** Representative compositions of Nb-rich goethite (Gt) from the lateritic horizons. The  
656 presence of Si may result from the simultaneous analysis of kaolinite due to the interaction volume  
657 of the electron, similar to the size of the analyzed Fe oxides crystals.

| wt%                            | Gt.1  | Gt.2  | Gt.3  | Gt.4  | Gt.5  | Gt.6  | Gt.7  |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Fe <sub>2</sub> O <sub>3</sub> | 78.03 | 73.72 | 78.34 | 85.60 | 86.92 | 75.43 | 81.10 |
| TiO <sub>2</sub>               | 1.75  | 1.31  | 0.16  | 2.01  | 0.76  | 0.99  | 1.10  |
| Nb <sub>2</sub> O <sub>5</sub> | 0.12  | 0.20  | 0.01  | 0.04  | 0.18  | 0.21  | 0.20  |
| Al <sub>2</sub> O <sub>3</sub> | 5.92  | 7.08  | 8.55  | 4.74  | 3.53  | 10.93 | 8.28  |
| SiO <sub>2</sub>               | 1.74  | 5.59  | 2.09  | 1.05  | 2.27  | 8.98  | 6.07  |
| Total                          | 87.56 | 87.89 | 89.15 | 93.45 | 93.67 | 96.53 | 96.76 |

658

659 **Table 4.** Representative compositions of columbite-(Mn) (Col) from the Pitinga weathering profile.  
660 The composition of Sc-rich columbite could not be determined by EPMA due to their sub-  
661 micrometric size (Fig. 9d).

| wt%                            | Col.1 | Col.2 | Col.3 |
|--------------------------------|-------|-------|-------|
| FeO                            | 5.76  | 9.10  | 17.92 |
| MnO                            | 13.68 | 10.40 | 1.97  |
| Al <sub>2</sub> O <sub>3</sub> | 0.12  | 0.05  | /     |
| Nb <sub>2</sub> O <sub>5</sub> | 70.82 | 71.27 | 73.27 |
| TiO <sub>2</sub>               | 0.22  | 0.87  | 4.39  |
| Ta <sub>2</sub> O <sub>5</sub> | 7.50  | 6.95  | 2.88  |

| wt%                        | Col.1 | Col.2 | Col.3  |
|----------------------------|-------|-------|--------|
| Total                      | 98.12 | 98.63 | 100.42 |
| <i>Structural formulae</i> |       |       |        |
| Fe                         | 0.298 | 0.464 | 0.848  |
| Mn                         | 0.717 | 0.537 | 0.094  |
| Al                         | 0.009 | 0.003 | 0.000  |
| Nb                         | 1.980 | 1.965 | 1.874  |
| Ti                         | 0.010 | 0.040 | 0.187  |
| Ta                         | 0.126 | 0.115 | 0.044  |
| A site                     | 2.117 | 2.121 | 2.105  |
| B site                     | 1.024 | 1.005 | 0.942  |

662

663 **Table 5.** Comparison of the average Nb speciation between the L<sub>3</sub>- and K-edges obtained by linear  
664 combination fitting procedures. Qualitative Nb speciation as observed using SEM is also indicated.  
665 Relative abundances range from trace (o) to dominant (+++) phases.

| Technique               | Sample                 | Nb speciation |        |         |          |           |
|-------------------------|------------------------|---------------|--------|---------|----------|-----------|
|                         |                        | Ilmenite      | Rutile | Anatase | Goethite | Columbite |
| SEM                     | Bauxitic horizon       | +             | /      | ++      | +        | +         |
|                         | Lateritic horizon      | +             | /      | ++      | +        | o         |
|                         | Clayey mottled horizon | ++            | /      | ++      | o        | o         |
|                         | Biotite granite        | +++           | +      | /       | /        | o         |
|                         |                        |               |        |         |          |           |
| Nb L <sub>3</sub> -edge |                        | Ilmenite      | Rutile | Anatase | Fe oxide | Columbite |
|                         | Bauxitic horizon       | 20 %          | /      | 20 %    | 60 %     | /         |

|                  |                        |                          |   |                 |                  |   |
|------------------|------------------------|--------------------------|---|-----------------|------------------|---|
|                  | Lateritic horizon      | 20 %                     | / | 30 %            | 50 %             | / |
|                  | Clayey mottled horizon | 60 %                     | / | 40 %            | /                | / |
| <b>Nb K-edge</b> |                        | <b>Ilmenite/Ti oxide</b> |   | <b>Goethite</b> | <b>Columbite</b> |   |
|                  | Duricrust horizon      | /                        |   | 50 %            | 50 %             |   |
|                  | Bauxitic horizon       | 25 %                     |   | 60 %            | 15 %             |   |
|                  | Lateritic horizon      | 50 %                     |   | 50 %            | /                |   |
|                  | Clayey mottled horizon | 100 %                    |   | /               | /                |   |

666

667

668 **Declaration of interests**

669

670 x The authors declare that they have no known competing financial interests or personal  
671 relationships that could have appeared to influence the work reported in this paper.

672

673  The authors declare the following financial interests/personal relationships which may be considered as  
674 potential competing interests:

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676

677