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1 Evaluation of Sc concentrations in Ni-Co laterites using Al as a geochemical proxy

2

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9

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11

12

13 **Keywords**

14 Scandium; laterite; Ni-laterite; sequential extraction; New Caledonia

15

16 **Abstract**

17 Scandium (Sc) is used in several modern industrial applications, including aluminium-based alloys and
18 solid oxide fuel cells. So far, Sc production remains marginal as the lack of reliable and cost-effective
19 production limits its widespread adoption by the industry. Recently, significant Sc concentrations (~100
20 ppm) were reported in some nickel-cobalt lateritic ores, where Sc may be valuably co-produced along
21 with Ni and Co. However, Sc is typically not included in routine analyses of Ni-Co ores, precluding the
22 assessment of Sc concentration and distribution in existing Ni-Co deposits. This contribution examines
23 the relevance of using routinely analysed elements as geochemical proxies for providing first-order
24 estimates of Sc concentration and distribution in already assayed Ni-Co deposits. Three Ni-Co lateritic
25 deposits from New Caledonia, developed after harzburgite (Ma-Oui deposit, Koniambo mine),
26 harzburgite-dunite (Coquette Red tenement, Cap Bocage mine) and lherzolite (East Alpha deposit,
27 Tiébaghi mine), were investigated. In each deposit, we demonstrate that Sc is globally well correlated
28 with Al₂O₃, providing that the parent lithology is homogeneous and relatively depleted in Al. Deposit-

29 scale Sc-Al₂O₃ regression lines are remarkably controlled by the composition of enstatite from the
30 parent rock. In all deposits, zones of maximum Sc enrichment are situated in the yellow limonite, above
31 the zones of highest Ni and Co enrichments. Sequential extractions highlight that Sc- and Al-bearing
32 crystalline goethite is predominant, though Sc shows a higher affinity for amorphous iron oxides than
33 Al. We propose that, in already assayed Ni-Co lateritic ores, the concentration and distribution of Sc
34 can be estimated from that of Al, assuming that the Sc-Al₂O₃ correlation is valid at the deposit scale.
35 Such deposit-scale correlations may be determined after analysing a limited number of spatially and
36 chemically representative samples. Therefore, mining operators may get a first-order evaluation of the
37 Sc potential resource in Ni-Co lateritic deposits at low additional costs.

38

39 **1 Introduction**

40 Scandium (Sc) is mainly used as a hardening additive to aluminium to form Al-Sc alloys for aerospace
41 industries and manufacture of high-quality sports equipment (Royset and Ryum, 2005; Toropova et al.,
42 1998). In addition, Sc is notably used in high-temperature lights, lasers and ceramics manufacturing
43 and finds promising application in the development of Solid Oxide Fuel Cells (SOFCs). The global Sc
44 supply and consumption remain marginal (~15 to 25t/yr Sc₂O₃, US Geological Survey, 2022). Sc is solely
45 recovered as a by-product through titanium, zirconium, uranium, cobalt and nickel process streams.
46 Nevertheless, the development of energy-saving technologies and Sc extraction techniques have
47 raised interest in this metal. In the last decade, Sc-rich occurrences with economically attractive grades
48 and tonnages have been identified in some oxide-rich laterites developed after mafic and ultramafic
49 rocks (Aiglsperger et al., 2016; Audet, 2008; Bailly et al., 2014; Chassé et al., 2017, 2019; Hoatson et
50 al., 2011; Maulana et al., 2016; Qin et al., 2020; Sun et al., 2021; Teitler et al., 2019; Ulrich et al., 2019).
51 There, Sc enrichment is largely residual and results from the intense leaching of mobile cations during
52 the lateritisation of the parent rock. Scandium is thus trapped and concentrated in neo-formed
53 goethite, and moderate remobilisation can occur during repeated stages of goethite dissolution-
54 recrystallisation and transformation into hematite. The chemical speciation of Sc in laterites from

55 Australia and the Philippines has been investigated using a combination of X-ray absorption near-edge
56 structure (XANES) spectroscopy and sequential extractions (Chassé et al., 2017, 2019; Qin et al., 2020).
57 These studies further support the preferential affinity of Sc for goethite compared to hematite or
58 smectite. However, the relative importance of adsorption and incorporation processes and the impact
59 of goethite crystallinity in the formation of Sc-rich goethite zones remain debated. They may vary from
60 one deposit to another. In New Caledonia, significant Sc concentrations were reported in several Ni-
61 Co lateritic oxide ores (Teitler et al., 2019; Ulrich et al., 2019). There, maximum Sc grades reach ~100
62 ppm in the yellow limonite horizon. Although such concentrations are too low to be economically
63 attractive as primary resources, Sc could be a valuable by-product of Ni and Co processing, provided
64 that Sc-rich zones sufficiently overlap Ni- and Co-rich zones (Teitler et al., 2019). However, Sc is typically
65 not routinely analysed during exploration and resource estimation of Ni-Co laterites. Consequently,
66 mining operators do not evaluate the potential Sc resources hosted in Ni-Co lateritic ores.

67 In contrast, Fe, Al and Cr are routinely analysed and could serve as geochemical proxies for inferring
68 the distribution of Sc concentrations in lateritic Ni-Co ores as suggested by previous investigations
69 (Teitler et al., 2019). Although Fe is the predominant constituent of lateritic oxide ores with up to 80
70 wt% Fe₂O₃, Teitler et al. (2019) suggested that Fe may be correlated to Sc only in the lower to
71 intermediate sections of the lateritic profiles and that the Sc-Fe₂O₃ correlation is usually not valid in
72 the Sc-rich, yellow limonite horizon. In contrast, Sc is better correlated with Al in all the facies of the
73 lateritic profiles, except for the uppermost ferruginous duricrust.

74 Nevertheless, the Sc-Al₂O₃ correlation proposed by Teitler et al. (2019), based on the combined
75 analysis of individual vertical profiles from several deposits, shows significant dispersion and does not
76 allow to assess how reliable the Sc-Al₂O₃ proxy is at the deposit scale. In this contribution, we discuss
77 the relevance of the Sc-Al₂O₃, Sc-Fe₂O₃ and Sc-Cr₂O₃ correlations at the deposit scale in three Ni-Co
78 deposits from the Koniambo, Cap Bocage and Tiébaghi mines, New Caledonia, based on the
79 geochemical analysis of spatially and lithologically representative samples from each deposit. Using
80 laser ablation inductively coupled mass spectroscopy (LA-ICP-MS), we then examine the dependency

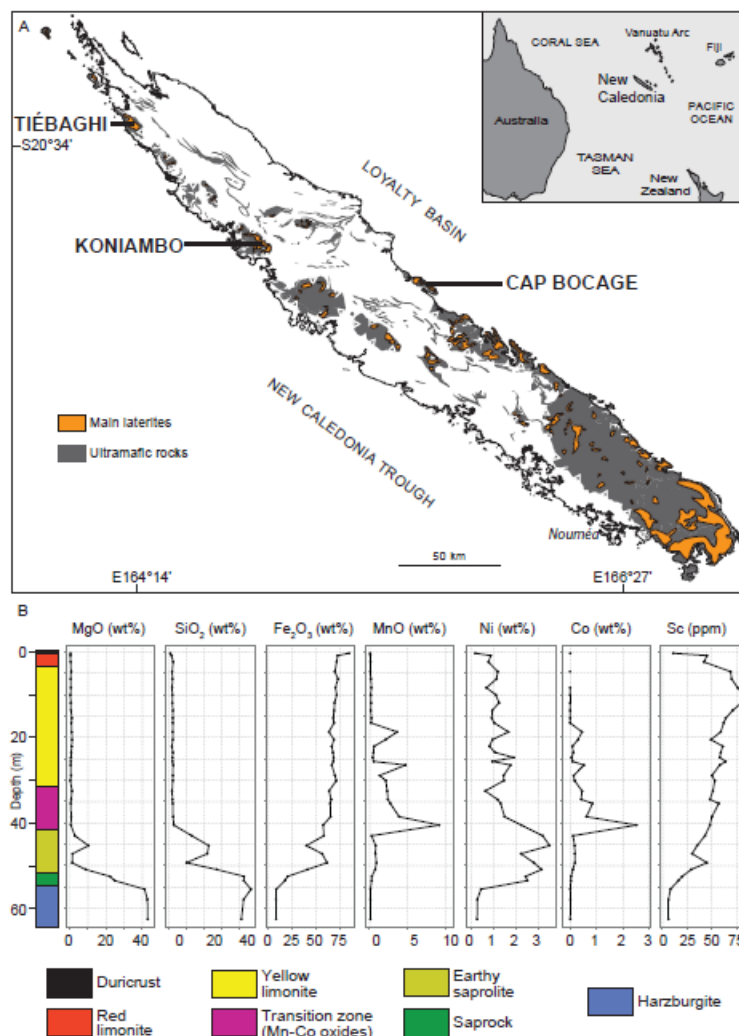
81 of bedrock mineral compositions on the Sc-Al₂O₃ regression coefficients and the variability of Al and Sc
82 contents in secondary-formed minerals. Third, we conduct selective chemical leaching on some Sc-
83 bearing samples to provide further insights on the speciation of Sc in the investigated deposits. These
84 results are used to discuss the potential of the Al proxy for the evaluation of Sc concentrations and
85 distribution in peridotite-hosted laterites in the perspective of Ni-Co-Sc co-valorisation.

86

87 **2 Regional geology**

88 The “Grande Terre” island of New Caledonia (Fig. 1A) consists of a 300 km long allochthonous
89 peridotite ophiolite referred to as the “Peridotite Nappe”. The peridotite Nappe, formed at ca. 35 Ma
90 (Cluzel et al., 2001, 2012; Paquette and Cluzel, 2007), represents about 30% of the surface of Grande
91 Terre and is exposed in the “Massif du Sud” and several isolated tectonic klippe, mainly aligned in the
92 N140° direction along the west coast of the island (Koniambo, Tiebaghi, Poum massifs). The Peridotite
93 Nappe is primarily composed of harzburgite locally interlayered with dunite, except in the
94 northernmost klippe where lherzolite dominates (Ulrich et al., 2010). Notably, the extensive
95 lateritisation of the peridotite ophiolite during or soon after obduction led to the development of a
96 thick regolith cover and the formation of world-class Ni-Co(-Sc) lateritic resources representing about
97 10% of the world's nickel reserves (Maurizot et al., 2020). The development of Ni-Co(-Sc) laterites in
98 New Caledonia results from (i) the leaching of most cations including Mg and Si after hydrolysis of
99 olivine and pyroxene, (ii) the redistribution and concentration of Ni within the saprock as secondary
100 hydrous silicates, (iii) the development of Ni-bearing saprolite, containing both silicates and oxides, at
101 the expense of the saprock, and (iv) the development of oxide-rich, Ni-bearing limonite and duricrust
102 at the expense of the saprolite (Butt and Cluzel, 2013; Cathelineau et al., 2016, 2017; Freyssinet et al.,
103 2005; Golightly, 2010; Manceau et al., 2000; Trescases, 1975; Wells et al., 2009). The Ni-rich (> 2.0 wt%
104 Ni) Ni-silicates ore reserves are rapidly being depleted as they have been actively mined since the late
105 19th century. Lower-grade (1.0–2.0% Ni) oxide ore (“limonite”) reserves will therefore represent the
106 bulk of Ni reserves of New Caledonia in the future. Also, Ni oxide ores often yield elevated Co (>2000

107 ppm) and Sc (60-100 ppm) concentrations adding significant value to the ore (Fig. 1B). Maximum Co
 108 concentrations (> 2000 ppm) typically occur at the interface between saprolite and limonite (referred
 109 to as transition zone), where Co is mainly associated with Mn-oxides (e.g. asbolane, lithiophorite).
 110 Upwards in the limonitic horizons, Co concentrations decrease being partially scavenged and trapped
 111 in ochreous goethite (Dublet et al., 2017). Maximum Sc grades are reached in the yellow limonite
 112 horizon (Fig. 1B). Therefore, Ni-, Co- and Sc-rich zones in limonite may partly overlap each other, and
 113 the degree of such overlap is critical in the perspective of co-valorising Ni, Co and Sc from lateritic Ni
 114 ores.
 115



117 Fig. 1: (A) Geological map of New Caledonia and location of the investigated mine sites. Modified from
 118 Maurizot and Vendé-Leclerc (2009). (B) Geochemical evolution along a typical Ni-lateritic profile in
 119 New Caledonia (modified from Bailly et al., 2014).

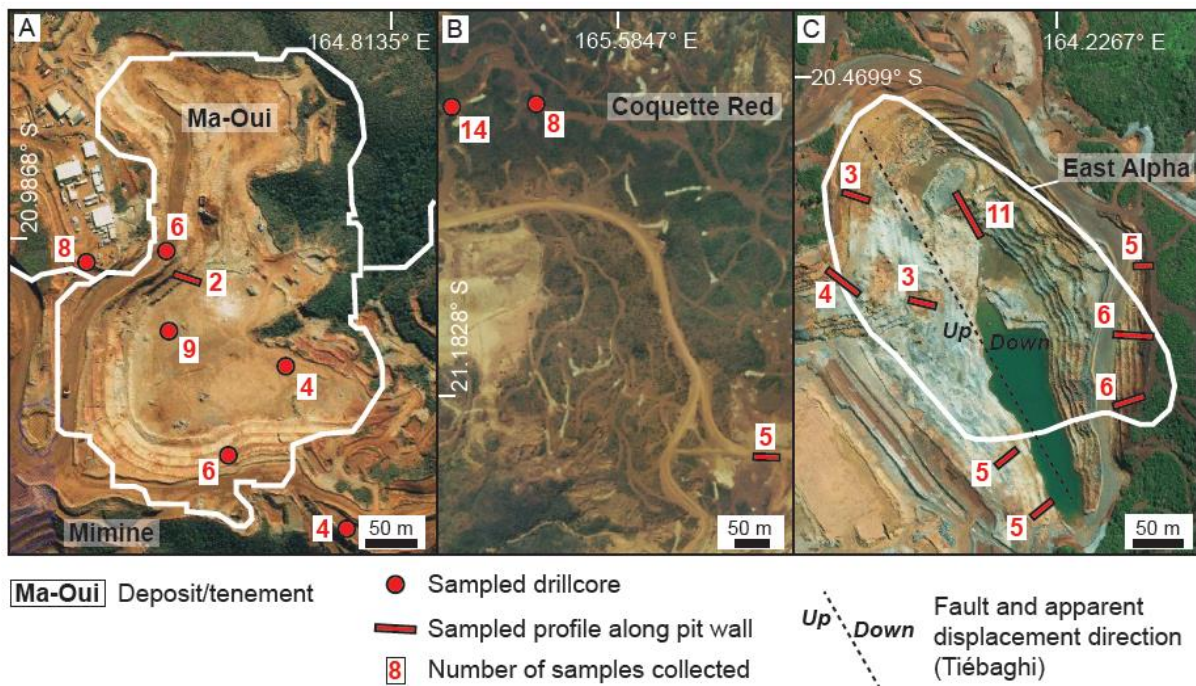
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121 3 Methodology

122 3.1 Sampling strategy

123 Sampling was conducted in multiple locations within the investigated deposits, along several drillcores
 124 and pit walls, encompassing the diversity of representative lithofacies. The objective was to check
 125 whether Sc-Al₂O₃ correlations may be generalised at the deposit scale. At the Ma-Oui deposit
 126 (Koniambo), 39 samples were collected along 6 drillcores and one pit wall profile (Fig. 2A). At the
 127 Coquette Red tenement (Cap Bocage), 27 samples were collected along 2 drillcores and one outcrop
 128 profile (Fig. 2B). At the East Alpha deposit (Tiébaghi), 48 samples were collected along 9 pit wall
 129 profiles, including one located in saprolite formed after gabbro (Fig. 2C).

130



132 Fig. 2: Outline of the investigated deposits and location of collected samples. (A) Ma-Oui deposit
 133 (Koniambo). (B) Coquette Red tenement (Cap Bocage). (C) East Alpha deposit (Tiébaghi).

134

135 **3.2 Analytical strategy**

136 Among the 114 samples collected for whole-rock geochemical analysis, 49 samples (batch 1) were
137 analysed at the SARM analytical service of the CRPG (France), and 65 samples (batch 2) were analysed
138 at the NILAB laboratory (New Caledonia). Sixteen thin polished sections were prepared and examined
139 using reflected/transmitted light and scanning electron microscopy with a JEOL JSM7600F at
140 Georessources Laboratory and SCMEM. *In situ* mineral chemistry analysis for major/minor elements
141 (Mg, Al, Si, Ca, Cr, Mn, Fe, Co, Ni) was conducted using a CAMECA SX100 electron microprobe (EPMA,
142 WDS analysis) at the SCMEM with typical beam conditions of 15 kV and 10 nA. *In situ* analysis for Sc
143 and minor/trace elements was conducted using LA-ICP-MS (193 nm MicroLas ArF Excimer coupled with
144 Agilent 7500c quadrupole ICP-MS). Sequential extractions were performed at the CEREGE laboratory
145 on seven Sc-bearing samples from Cap Bocage and Tiébaghi. Four reagents were successively used to
146 extract major and trace elements selectively: (i) ultrapure water for easily soluble elements, (ii) 0.1
147 mol.L⁻¹ hydroxylamine hydrochloride NH₂OH-HCl at pH = 3.5, which is particularly efficient and
148 selective for mangiferous phases, (iii) 0.2 mol.L⁻¹ ammonium oxalate (NH₄)₂C₂O₄ at pH = 3 for
149 amorphous and poorly crystallised iron oxides and (iv) citrate-bicarbonate-dithionite Na₂S₂O₄ (22% Na-
150 citrate and 1 g Na-dithionite) for well-crystallised iron oxides (Bailly et al., 2014). Additional
151 information on analytical procedures and PCA are given in Appendix A.

152

153 **4 Lithofacies and mineral assemblages**

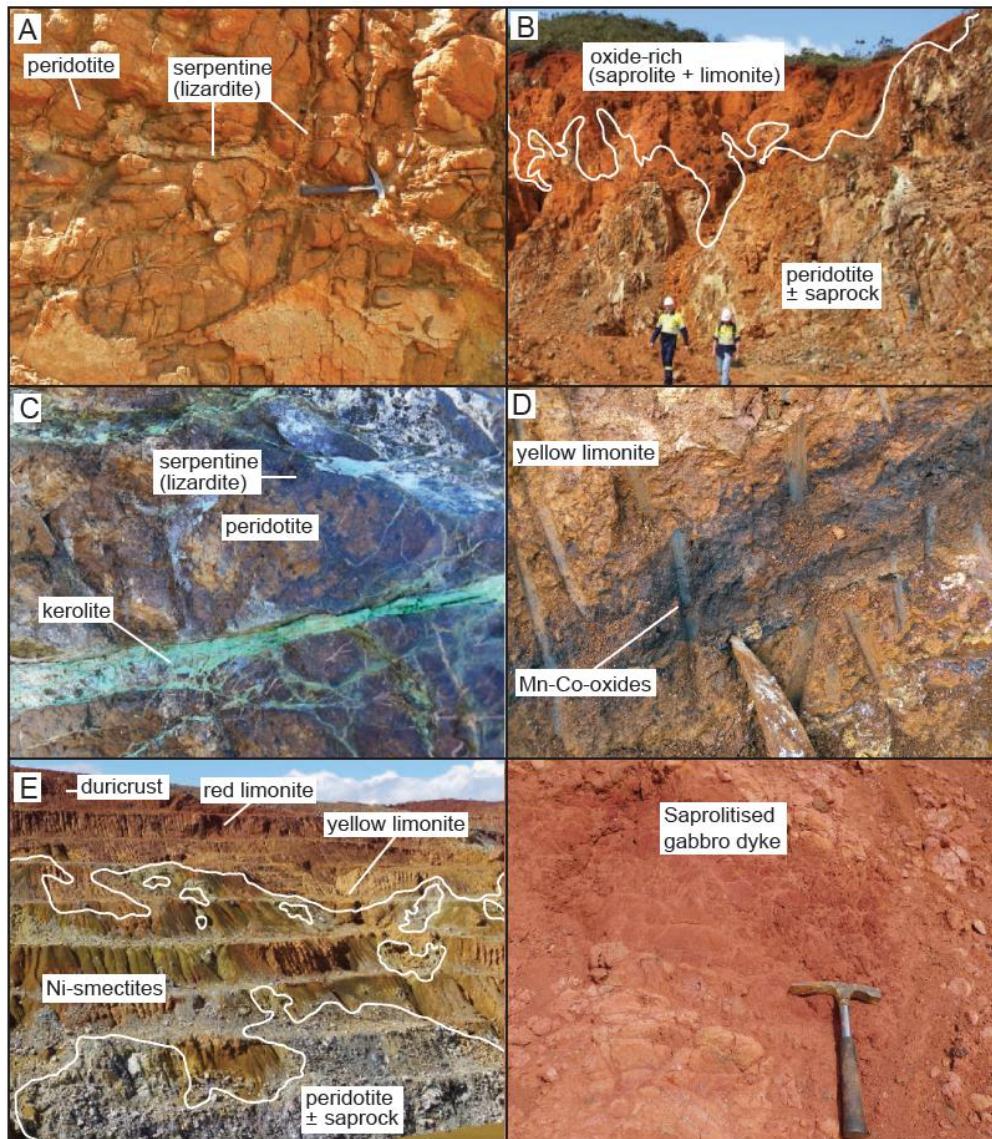
154 Progressive weathering of peridotite involves hydration and hydrolysis of primary silicates and the
155 formation of secondary silicates and oxides-oxyhydroxides. Therefore, the investigated Ni-Co deposits
156 exhibit a continuum of alteration facies with specific mineral assemblages and textures. At Koniambo
157 and Cap Bocage, moderately serpentinised harzburgite represents the predominant parent rock of Ni-
158 Co laterites (Fig. 3A, 4). It is worth noting that the Coquette Red tenement investigated at Cap Bocage
159 hosts significant volumes of dunite lenses so that the lateritic profiles are developed both on

160 harzburgite and dunite. Serpentinisation occurs within the peridotite as mm to dm-large veins of
161 serpentine (mostly lizardite) distributed as fracture networks and progressively replacing mantle
162 silicates resulting in a typical mesh texture (Fig. 3A, 3C, 5A, 6A). At Tiébaghi, lherzolite dominates over
163 harzburgite, although the intensive serpentinisation of the peridotite complicates its univocal
164 recognition in the field. In the saprock, weathering initiates through the progression of the mantle
165 silicate alteration front, marked by the onset of forsterite and enstatite hydrolysis (Fig. 5A, 6A) and the
166 development of Ni-rich (up to 15–20 wt% Ni), greenish talc-like (kerolite) veins that root into the
167 unweathered peridotite (Fig. 3C, 5A, 6A). Congruent hydrolysis of mantle silicate leads to the formation
168 of 100-micron large pores with the development of skeletal goethite along silicate grain boundaries
169 and crystallographic planes. Serpentine veins and mesh are preserved from dissolution in the saprock,
170 although partly transformed into secondary, nickeliferous serpentine/talc-like (Fig. 5A, 5B). At
171 Koniambo and Cap Bocage, local evidence for incongruent hydrolysis and epigenetic replacement of
172 mantle silicate by smectite is also observed but is spatially restricted to the bedrock-saprock interface
173 (Fig. 6A, 6C). There, epigenetic smectite is, in turn, readily replaced (e.g. by Mn-Co-Ni-rich lithiophorite,
174 Fig. 6C) or dissolved and does not occur upwards in the profile. The evolution from the saprock to the
175 saprolite, wherein weathering is more pronounced but remains isovolumetric, is characterised by the
176 complete disappearance of mantle silicate and the partial replacement of serpentines by goethite (Fig.
177 3B, 5B, 6D). In contrast, at Tiébaghi, smectite extensively develops at the expense of both mantle
178 silicates and serpentine (Fig. 3E, 4, 5C, 6B) and remains preserved throughout most of the saprolite
179 until it is eventually replaced by ochreous goethite (Fig. 5D). The interface between the saprolite and
180 the overlying limonite, referred to as the transition zone, is marked by the progressive disappearance
181 of macroscopic primary structures and the accumulation of Mn-Co-Ni oxides (lithiophorite, asbolane)
182 either as mm- to cm-thick veins or as diffuse accumulations in the iron-rich matrix (Fig. 3D). Upwards,
183 the transition zone evolves into the yellow limonite wherein ochreous goethite predominates,
184 characterised by the disappearance of all primary minerals except chromiferous spinel that remains
185 mostly resistant to weathering throughout the entire profile. This horizon is marked by significant

186 compaction. However, primary textures such as fragmented relics of serpentine veins or skeletons of
187 mantle silicates, both replaced by goethite, may still be recognised at the microscopic scale (Fig. 5E,
188 6E). The yellow limonite then grades into the red limonite, wherein hematite forms at the expense of
189 ochreous goethite resulting in a mineral assemblage dominated by goethite but containing significant
190 amounts (> 5 vol%) of hematite (Fig. 5F). Lateritic profiles are capped by a ferruginous duricrust that is
191 either directly developed after the underlying limonite or derived from the ferrugination of
192 transported material (Fig. 5G, 5H). Following the terminology of Anand et al. (2002), the term duricrust
193 describes regolith materials cemented by Fe, irrespective of the substrate origin. When it is residual,
194 the iron-cemented material is called a lateritic residuum, and when it is formed and indurated in a
195 transported cover, ferricrete. Lateritic residuum exhibits, at the microscopic scale, some locally
196 preserved textural relics (Fig. 6F). There, both goethite and hematite are largely recrystallised into
197 coarser crystallites. In contrast, ferricrete shows angular goethite and hematite nodules with goethite
198 pisolitic envelopes. They are cemented by vitreous goethite (Fig. 6G). Subvertical dykes of amphibolitic
199 gabbros locally exposed in the East Alpha deposit, Tiébaghi, alter to form a mineral assemblage
200 composed of kaolinite-gibbsite-hematite (Fig. 3F, 6H, 6I).

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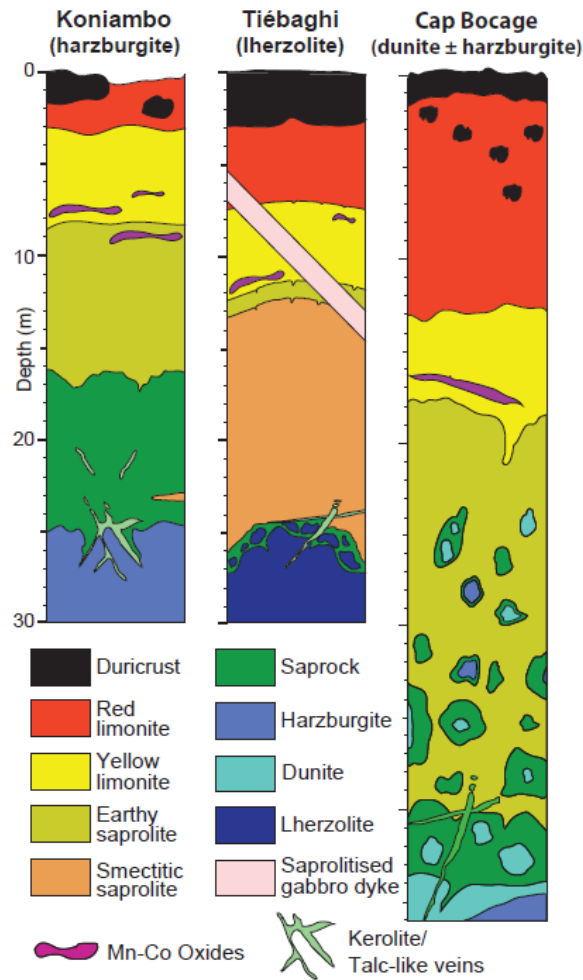
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204 Fig. 3: Field photographs of representative lithofaciès as observed in the Koniambo, Cap Bocage and
 205 Tiébaghi Ni-Co laterites. (A) Unweathered harzburgite with networks of serpentine (lizardite) veins
 206 (Koniambo). (B) Typical sharp transition from silicate-dominated bedrock and saprock to oxide-
 207 dominated saprolite and limonite (Koniambo). (C) Ni-rich talc-like (kerolite) vein developed at the
 208 bedrock – saprock interface (Koniambo). (D) Mn-Co oxide-rich transition zone developed at the
 209 saprolite – yellow limonite interface (Cap Bocage). (E) Well-developed Ni smectite-rich zone (up to >15
 210 m in vertical thickness) above lherzolitic serpentinite at Tiébaghi. (F) gabbro saprolite with hematite
 211 and kaolinite, cross-cutting limonitised lherzolite (Tiébaghi).

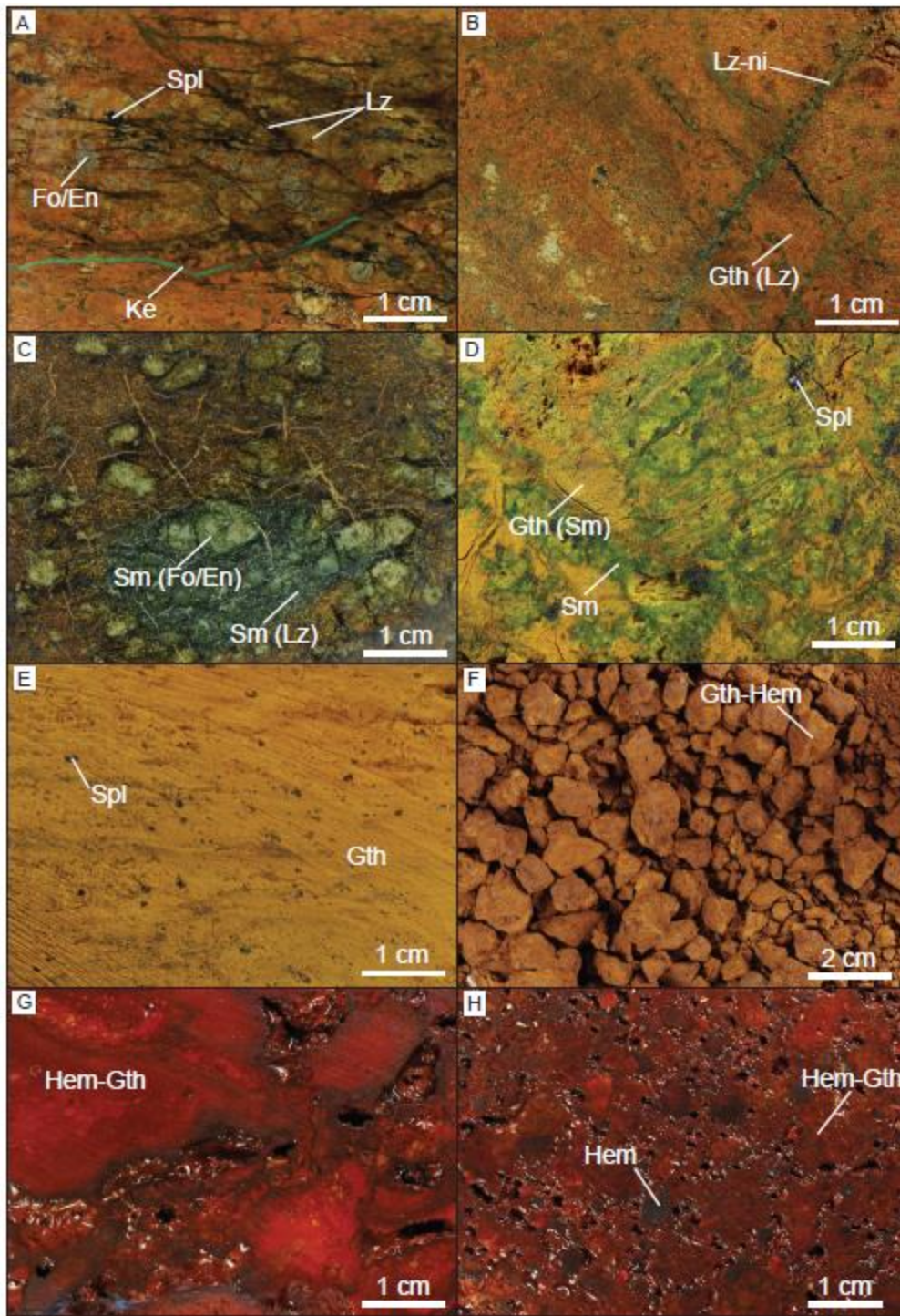
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214 Fig. 4: Stratigraphic logs of representative Ni-Co laterites from the Koniambo, Cap Bocage and
 215 Tiébaghi mines.

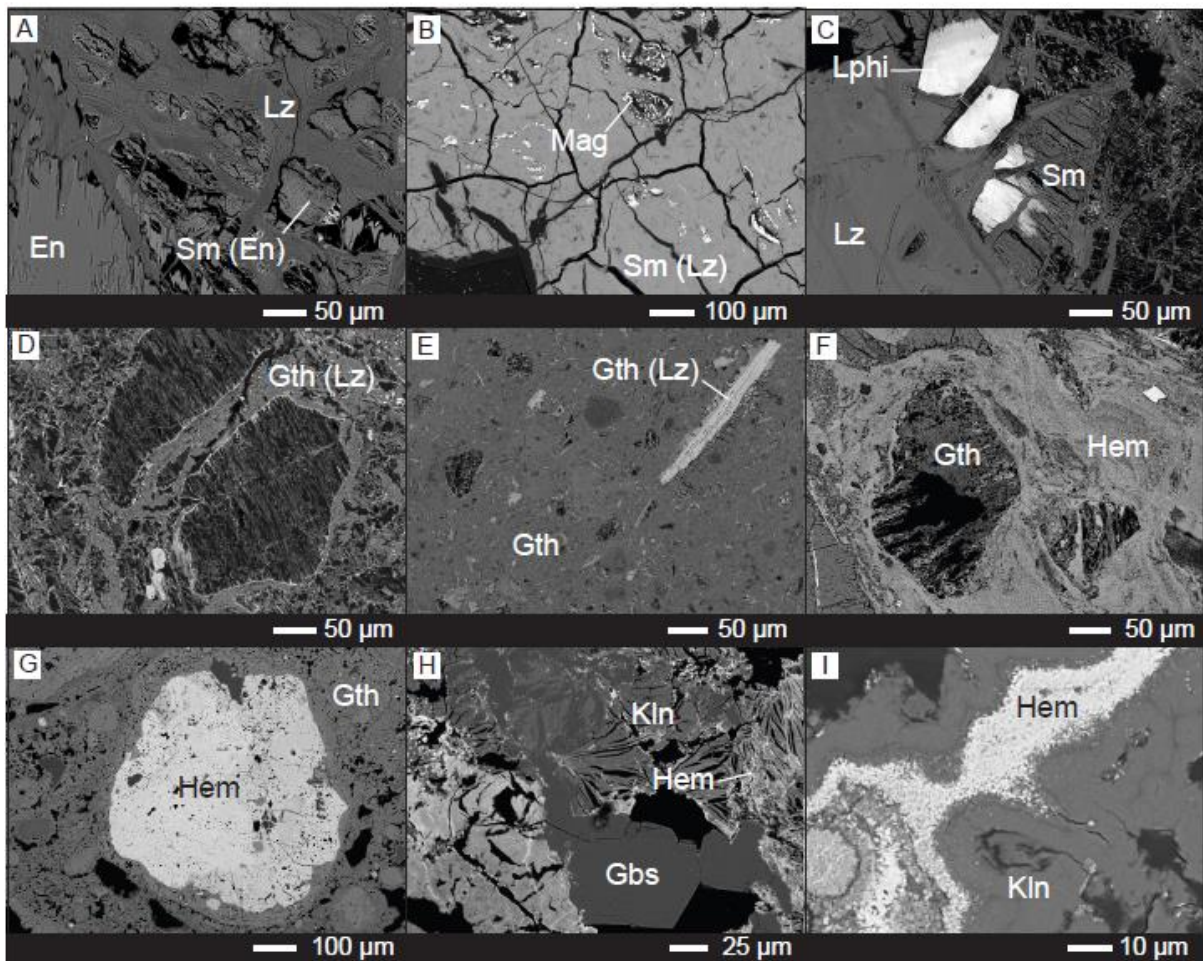
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217

218 Fig. 5: Representative alteration facies observed in the investigated deposits. (A) Kerolite vein and
 219 slight goethitisation in the saprock developed after moderately serpentinised harzburgite (Koniambo).
 220 (B) Transition from saprock to earthy saprolite, marked by the disappearance of mantle silicate, Ni
 221 enrichment in the serpentine veins and the partial replacement of serpentine by goethite (Cap
 222 Bocage). (C) Complete replacement of lizardite by smectite in the saprolite horizon (Tiébaghi), (D)

223 Transition from the smectitic saprolite to the yellow limonite (Tiébaghi). (E) Ochreous goethite-rich
 224 yellow limonite with residual enrichment in chromiferous spinel (Tiébaghi). (F) Pulverulent goethite-
 225 hematite-bearing red limonite (Cap Bocage). (G) Vesicular hematite-goethite-bearing lateritic
 226 residuum (Tiébaghi). (H) Nodular/pisolitic ferricrete (Tiébaghi). Mineral abbreviations: En = enstatite,
 227 Fo = forsterite, Gth = goethite, Hem = hematite, Ke = kerolite, Lz = lizardite, Lz-ni = nickel-enriched
 228 lizardite, Spl = chromiferous spinel. Precursor minerals are indicated in brackets.
 229



230
 231 Fig. 6: Backscattered Electron (BSE) microphotographs. (A) Onset of mantle silicate dissolution (here
 232 enstatite) and partial epigenetic replacement by smectite at the bedrock-saprock interface
 233 (Koniambo). (B) Extensive replacement of lherzolite-derived serpentinite by smectite in the saprolite
 234 (Tiébaghi). (C) Partial replacement of smectite by lithiophorite in the saprock/saprolite (Koniambo). (D)
 235 Epigenetic replacement of the serpentine vein mesh by ochreous goethite while preserving primary

236 textures in the earthy saprolite (Koniambo). (E) Advanced texture obliteration and fragmentation of
237 pre-existing structures in the yellow limonite (Koniambo). (F) Recrystallisation of goethite and
238 hematite with local preservation of inherited textures at the microscopic scale in the lateritic residuum,
239 Tiébaghi. (G) Goethitic pisolitic cortexes overgrowing onto nodular hematite in a goethite-bearing
240 cement, ferricrete horizon, Tiébaghi. Mineral abbreviations: Gbs = gibbsite, Kln = kaolinite, Lphi =
241 lithiophorite, Mag = magnetite, Sm = smectite. See caption of Fig. 5 for additional abbreviations.
242 Precursor minerals are indicated in brackets.

243

244 **5. Whole-rock geochemical correlations at the deposit scale**

245 Whole-rock geochemical analysis of the investigated lateritic profiles shows that the lateritisation of
246 unweathered peridotites is associated with the progressive enrichment of poorly mobile elements. In
247 particular, Fe, Al, Cr, and Sc concentrations co-increase during weathering, exhibiting positive
248 correlation trends (Fig. 7, Supplementary Table 1). In the Ma-Oui deposit, Al₂O₃, Fe₂O₃, Cr₂O₃ and Sc
249 concentrations progressively increase from the bedrock to the oxide-rich horizons up to about 6 wt%,
250 80 wt%, 4.5 wt% and 80 ppm, respectively. The Sc-Al₂O₃, Sc-Fe₂O₃ and Sc-Cr₂O₃ linear regression
251 models encompassing variable lithofacies (unweathered harzburgite, saprock, saprolite, Mn-Co-rich
252 transition zone, yellow and red limonite) provide a particularly relevant fit of the data (Fig. 7A).
253 Scandium concentrations may be approximatively estimated from the Al₂O₃, Fe₂O₃ and Cr₂O₃
254 concentrations from the bedrock to the red limonite as follows:

255

256 (1) $Sc \text{ (ppm)} = 12.03 * Al_2O_3 \text{ (wt\%)} + 2.42 ; R^2 = 0.93$

257 (2) $Sc \text{ (ppm)} = 0.92 * Fe_2O_3 \text{ (wt\%)} + 0.07 ; R^2 = 0.86$

258 (3) $Sc \text{ (ppm)} = 16.27 * Cr_2O_3 \text{ (wt\%)} + 0.31 ; R^2 = 0.91$

259

260 The Sc-Fe₂O₃ correlation trend shows low dispersion in the low-Sc concentration range (0-50 ppm) but
261 significant dispersion in the higher-Sc concentration range (50-80 ppm). In addition, two samples

262 collected in the transition and yellow limonite zone, respectively, fall well out of the Sc-Fe₂O₃
263 regression line. The Sc-Cr₂O₃ correlation trend is better defined, yet it presents moderate data
264 dispersion. Comparatively, the best fit is obtained for the Sc-Al₂O₃ regression line, which exhibits the
265 lowest dispersion of the data. Notably, the decrease in Al and Sc concentrations from the yellow to red
266 limonite, as commonly identified by Teitler et al. (2019) in New Caledonian lateritic profiles, is not
267 observed in the Ma-Oui geochemical dataset. In the Coquette Red tenement (Cap Bocage), Al₂O₃,
268 Fe₂O₃, Cr₂O₃ and Sc concentrations increase to about 5 wt%, 80 wt%, 5.5 wt% and 65 ppm in the
269 limonite, respectively. Like the Ma-Oui deposit, the Sc-Al₂O₃ regression line efficiently fits the data from
270 the bedrock to the red limonite, although the laterite is developed on dunite and harzburgite (Fig. 7B).
271 Analysed duricrust samples exhibit a large offset from the trend, with a substantial depletion in Sc
272 relative to Al₂O₃. It is worth noting that the Sc-Al₂O₃ regression lines obtained at Ma-Oui and Coquette
273 Red have similar regression coefficients (respectively 12.03 and 12.84; equations 1 and 4).
274 In contrast, Fe₂O₃, Cr₂O₃ and Sc concentrations do not correlate when considering the limonitic
275 horizons. Therefore, Al₂O₃ here constitutes the only relevant explanatory variable for Sc concentrations
276 among major elements. More specifically, Sc and Al₂O₃ are significantly enriched compared to Fe₂O₃ in
277 the yellow limonite and, at the opposite, depleted in the red limonite. Regression lines obtained from
278 Coquette Red samples, accounting for all lithologies apart from the duricrust, may be expressed as
279 follows:

280

281 (4) $Sc \text{ (ppm)} = 12.84 * Al_2O_3 \text{ (wt\%)} + 1.52 ; R^2 = 0.93$

282 (5) $Sc \text{ (ppm)} = 0.68 * Fe_2O_3 \text{ (wt\%)} + 3.91 ; R^2 = 0.82$

283 (6) $Sc \text{ (ppm)} = 9.20 * Cr_2O_3 \text{ (wt\%)} + 12.05 ; R^2 = 0.62$

284

285 The East Alpha deposit (Fig. 7C), developed after strongly serpentinised Iherzolite, exhibits Sc
286 concentrations up to 115 ppm in the limonite, i.e. significantly higher than those observed at Ma-Oui
287 and Coquette Red. Also, Al₂O₃ concentrations reach about 15 wt% in the Iherzolite-derived limonite,

288 i.e. about three times more elevated than in the harzburgite±dunite-derived limonite at Koniambo and
289 Cap Bocage. In comparison, gabbro-derived saprolite yields Al₂O₃ concentrations up to about 30 wt%.
290 Maximum Fe₂O₃ and Cr₂O₃ concentrations at East Alpha are similar to those observed in the other
291 investigated sites, at 80 and 4 wt%, respectively. The Sc-Al₂O₃ regression line modelled for East Alpha
292 samples fits relatively well the data, except duricrust and gabbro samples that fall well out of the
293 correlation trend. The regression coefficient of the Sc-Al₂O₃ line is about twice lower at East Alpha than
294 at Ma-Oui and Coquette Red (equation 7). It is worth noting that smectitic saprolite samples from East
295 Alpha exhibit Al, Sc, Fe and Cr co-variations along a quite extensive concentration range (Fig. 7C).
296 Nevertheless, significant dispersion from the regression line is also observed in the yellow and red
297 limonite horizons compared to the Ma-Oui deposit and the Coquette Red tenement (Fig. 7C). Similar
298 to Coquette Red, Sc and Al₂O₃ are significantly enriched in the yellow limonite and depleted in the red
299 limonite compared to Fe₂O₃. The Sc-Fe₂O₃ and Sc-Cr₂O₃ correlations in the East Alpha deposit are
300 poorly defined, especially in the yellow and red limonite wherein Fe₂O₃, Cr₂O₃ and Sc concentrations
301 do not exhibit any correlation. Regression lines obtained for East Alpha, modelled after exclusion of
302 duricrust and gabbro-derived samples, may be expressed as follows:

303

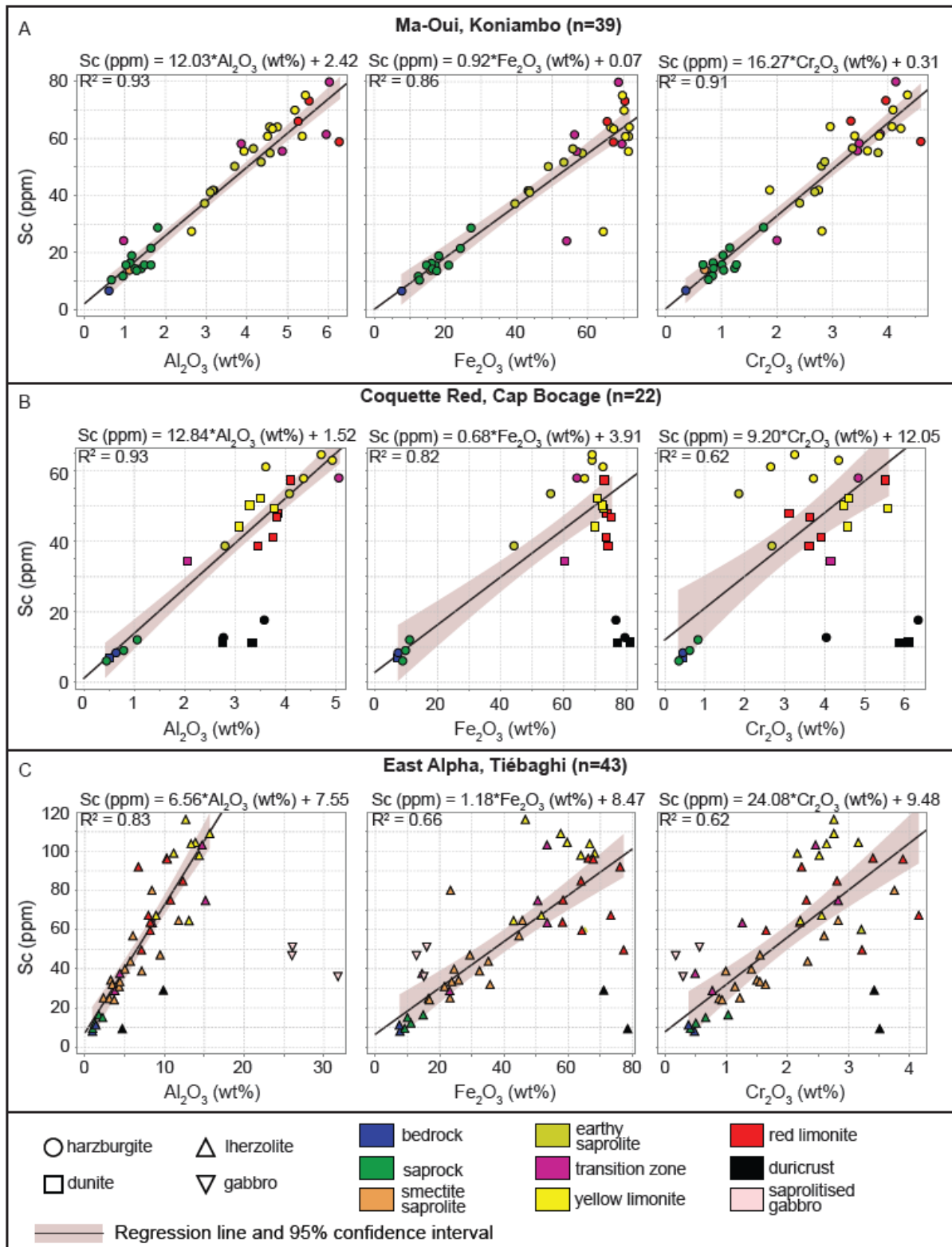
304 (7) Sc (ppm) = 6.56* Al₂O₃ (wt%) + 7.55 ; R² = 0.83

305 (8) Sc (ppm) = 1.18* Fe₂O₃ (wt%) + 8.47 ; R² = 0.66

306 (9) Sc (ppm) = 24.08* Cr₂O₃ (wt%) + 9.48 ; R² = 0.62

307

308



309

310 Fig. 7: Sc-Al₂O₃, Sc-Fe₂O₃ and Sc-Cr₂O₃ scatter plots and regression lines obtained for samples collected

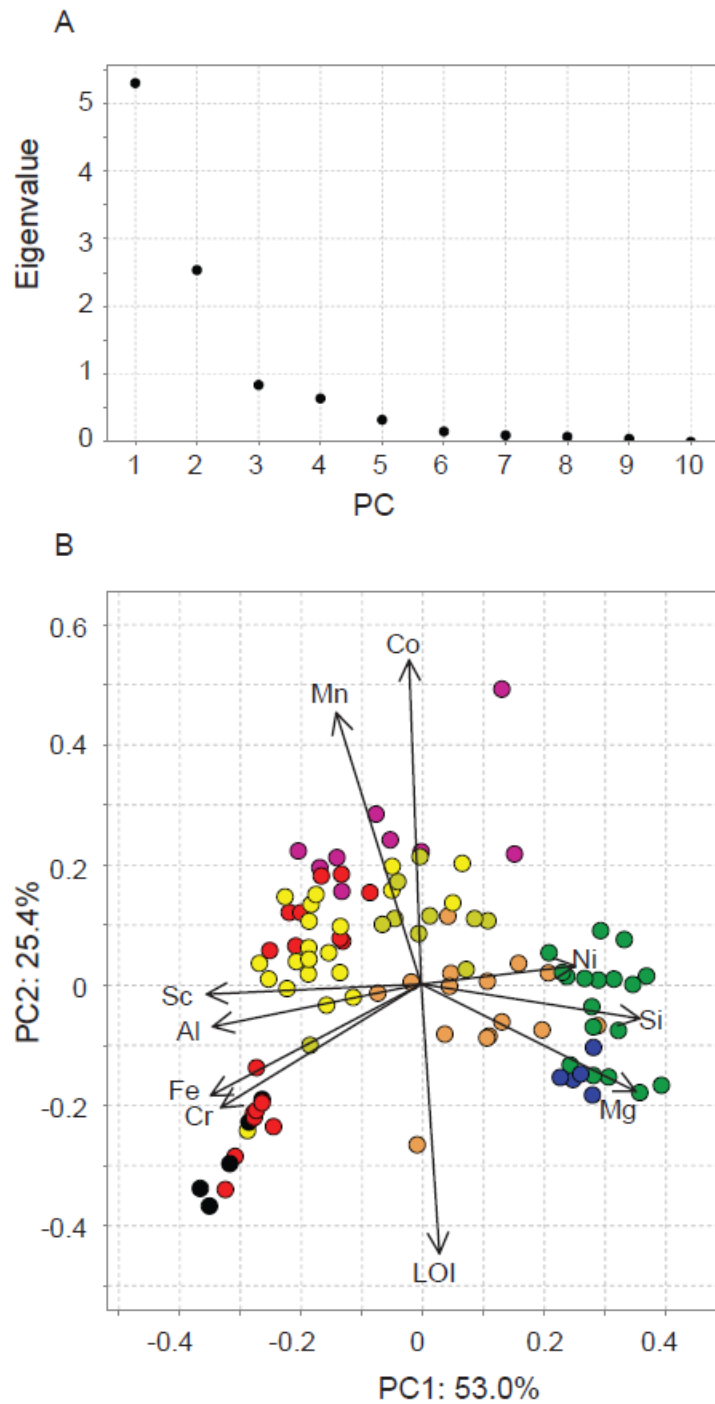
311 at (A) the Ma-Oui deposit (Koniambo), (B) the Coquette Red tenement (Cap Bodge) and (C) the East

312 Alpha deposit (tiébaghi) (B). Peridotite-derived duricrust and gabbro-derived saprolite samples lie out
313 of the correlation trends and are therefore excluded from the regression line modelling.

314 Principal Component Analysis (PCA) allows us to explore further the overall compositional variability
315 of the samples and the strength of the colinearity between Sc and poorly mobile elements. The PCA,
316 performed after centred log-ratio transformation of the data, shows that the cumulated explained
317 variance in the PC1-PC2 plane reaches 78.4% of the overall variability of the initial dataset (respectively
318 53.0 and 25.4 % for PC1 and PC2, Fig. 8A, 8B). All of the elements constitutive of the samples except
319 Mn and Co predominantly contribute to PC1, with Mg, Si and Ni having a positive contribution to PC1.
320 At the same time, Fe, Al, Cr and Sc display a negative contribution to PC1 (Fig. 8B). PC1 therefore
321 underlines a contrast between Mg-Si-Ni and Al-Sc-Fe-Cr, and PC2 describes the Mn and Co positive
322 correlation. LOI exhibits a strong negative contribution to PC2. It is worth noting that the angles
323 between Mg, Si and Ni rays are low, yet these rays are not coincident. Similarly, Sc and Al, on the one
324 hand, and Fe and Cr, on the other hand, form two pairs of strongly coincident rays. These two pairs of
325 coincident rays are at a relatively low angle, yet they are not colinear with one another. Sc is, therefore,
326 better correlated with Al than with Fe or Cr. Regarding sample scores, bedrock samples fall close to
327 the Mg ray. Saprock samples, in contrast, appear globally shifted towards the Si and Ni rays. Most
328 smectitic saprolite samples still display a positive PC1 score, but lower than that of bedrock and saprock
329 samples, with a low PC2 score. Earthy saprolite samples exhibit small positive and negative PC1 scores
330 and significant shift towards positive PC2 scores. Earthy saprolite samples represent, therefore,
331 intermediate compositions between the Mg-Si-Ni and the Al-Sc-Fe-Cr groups along PC1, together with
332 the onset of an Mn-Co compositional signature along PC2. Comparatively, transition zone samples are
333 slightly shifted towards negative PC1 scores, indicative of an increasing contribution of the Al-Sc-Fe-Cr
334 group.

335 Moreover, transition zone samples exhibit the highest PC2 scores, consistent with their enrichment in
336 Mn and Co. Yellow limonite samples are further shifted towards negative PC1 scores, while still
337 displaying positive PC2 scores indicating the subsistence of an Mn-Co signature. Red limonite samples

338 also show negative PC1 scores but appear to be forming two subgroups, one with positive PC2 scores
339 similar to the yellow limonite and one with negative PC2 scores, identical to duricrust samples.
340



341
342 Fig. 8: Results of PCA performed after centred log-ratio transformation of Mg, Al, Si, Sc, Cr, Mn, Fe, Co,
343 Ni concentrations and LOI from the global whole-rock geochemical dataset of peridotite-derived
344 laterites (Ma-Oui, Coquette Red and East Alpha). Saprolitised gabbro samples from East Alpha were

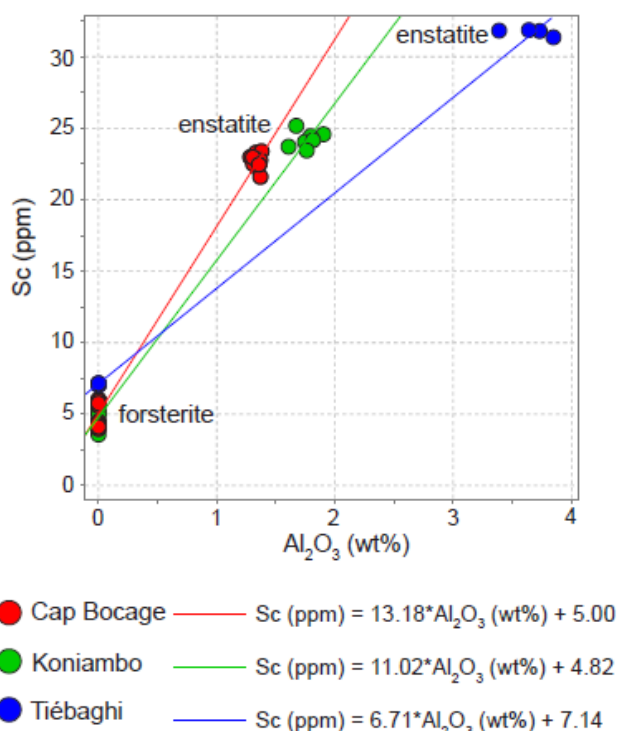
345 excluded from PCA calculations. (A) Scree plot. (B) PC1-PC2 biplot showing variable loadings (arrays)
346 and sample scores (circles). See Fig. 7 for lithology colour coding.

347

348 **6. Mineral Chemistry**

349 The mineral chemistry data obtained from LA-ICP-MS analyses (Supplementary Table 2) allow us to
350 assess the contribution of primary mantle silicates to the Al and Sc budget in the unweathered
351 peridotites. Forsterite has a low Sc content in all of the investigated sites, about 3-6 ppm at Ma-Oui
352 and Coquette Red and about 7 ppm at East Alpha (Fig. 9), together with Al below detection limits.
353 Enstatite yields higher Sc and Al concentrations, which vary from one site to another. Sc concentrations
354 in enstatite from Ma-Oui and Coquette Red are similar (24 and 22.5 ppm, respectively). Al_2O_3
355 concentrations in enstatite are slightly higher at Ma-Oui (about 1.8 wt%) than at Coquette Red (about
356 1.4 wt%). In contrast, enstatite from East Alpha is enriched in Sc (about 32 ppm) and Al_2O_3 (about 3.4
357 to 3.8 wt%). Importantly, Sc- Al_2O_3 regression lines obtained from enstatite and forsterite mineral
358 compositions in each investigated site (Fig. 9) closely match those obtained from whole-rock
359 geochemical analysis throughout the weathering sequences (Fig. 7). More specifically, regression
360 coefficients estimated from mantle silicate mineral chemistry *versus* global whole-rock geochemistry,
361 respectively, are (i) 12.03 vs 11.02 at Ma-Oui, (ii) 13.18 vs 12.84 at Coquette Red, and (iii) 6.71 vs 6.56
362 at East Alpha.

363



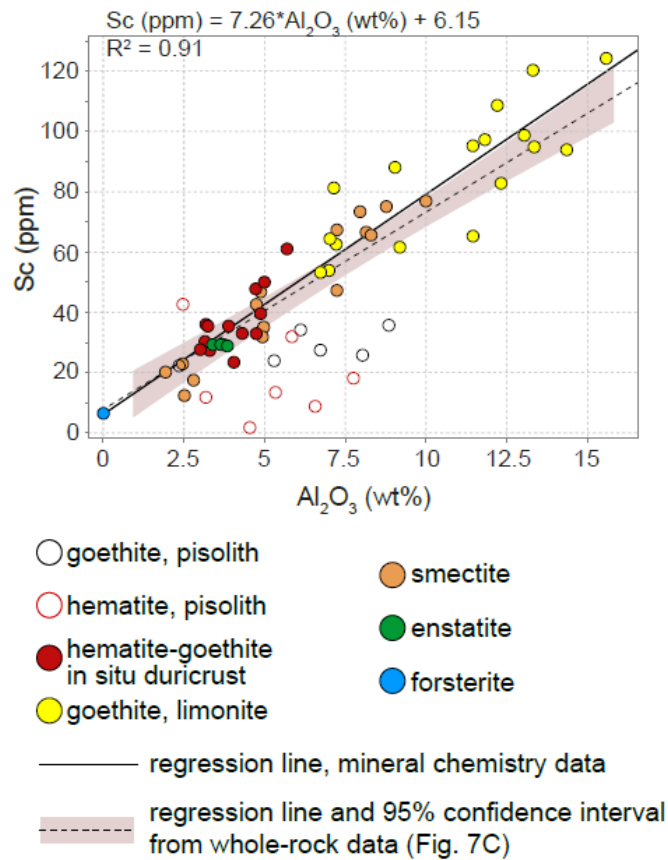
364

365 Fig. 9: Sc-Al₂O₃ scatterplot and regression lines obtained for mantle silicates (forsterite, enstatite) in
 366 peridotite bedrocks from Ma-Oui (Koniambo), Coquette Red (Cap Bocage) and East Alpha (Tiébaghi)
 367 from LA-ICP-MS analyses.

368

369 Further support for the intimate relationship between Sc-Al₂O₃ contents of peridotite mantle silicates
 370 and Sc-Al₂O₃ contents of peridotite-derived laterite samples is provided by the mineral chemistry data
 371 of secondary mineral phases along with laterite profiles as analysed at East Alpha (Fig. 10,
 372 Supplementary Table 2). Together with forsterite and enstatite, Sc and Al₂O₃ concentrations in
 373 smectite, ochreous goethite from the limonite zone, and goethite-hematite from the lateritic residuum
 374 appear to be strongly proportional, with a regression line closely similar to that obtained from whole-
 375 rock geochemistry. Smectite in the smectitic saprolite and ochreous goethite in the limonite exhibit
 376 variable yet proportional Sc and Al₂O₃ concentrations. Indeed, Sc and Al₂O₃ concentrations in smectite
 377 vary from 20 to 80 ppm and from 2.5 to 10 wt%, respectively, while Sc and Al₂O₃ concentrations in
 378 limonitic, ochreous goethite vary from 55 to 122 ppm and from 7 to 16 wt%, respectively. Goethite-
 379 hematite from the lateritic residuum is, comparatively, depleted both in Sc and Al₂O₃, yet it falls on or

380 close to the regression line. In contrast, goethite and hematite nodules and pisolitic cortexes from the
 381 ferricrete appear further depleted in Sc to fall below the regression line.



382

383 Figure 10: Sc-Al₂O₃ scatterplot and regression line obtained for silicates, smectite and iron oxides in
 384 the East Alpha deposit (Tiébaghi) from LA-ICP-MS analyses. The regression line calculation excluded
 385 spot analyses on goethite and hematite from the nodular/pisolitic duricrust.

386

387 7. Sequential extractions

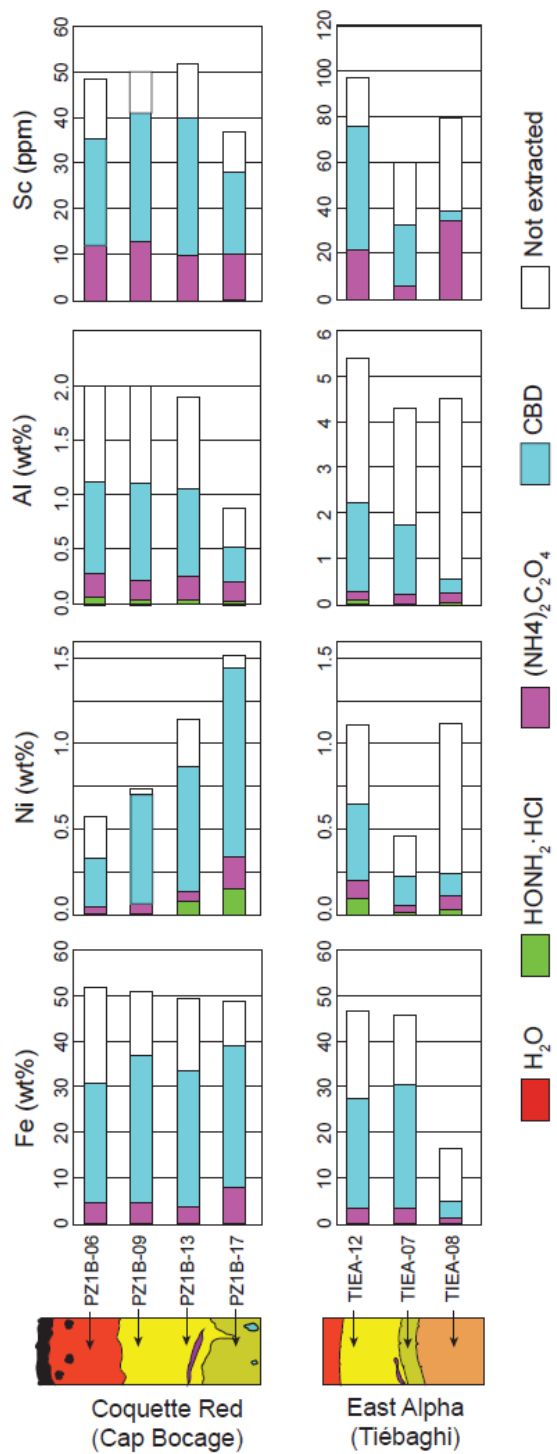
388 The sequential extractions for Fe, Al, Ni and Sc are given in Fig. 11. The ultrapure water did not permit
 389 solubilising these elements in any investigated samples during the first extraction step. With regards
 390 to Fe, the hydroxylamine hydrochloride extraction also proved unsuccessful. In iron-rich samples
 391 (earthy saprolite, yellow and red limonite), about 10-15% of the total Fe mass was extracted during
 392 the subsequent extraction step involving ammonium oxalate, while about 50-60% was removed during
 393 the last extraction step involving citrate-bicarbonate-dithionite (CBD). In iron-rich lithologies, the

394 overall procedure therefore permits the extraction of 60 to 80% of the total Fe content, and CBD
395 appears the most effective reagent to solubilise Fe. In contrast, the general approach only resulted in
396 the extraction of about 25% of the total Fe in the smectitic saprolite sample (TIEA-08) from East Alpha,
397 mainly through the action of CBD and, to a lesser extent, of ammonium oxalate. With regards to Al,
398 the overall procedure succeeded in solubilising 40-50% and 10% of the total Al (Fig. 10A) in iron-rich
399 and smectite-rich samples, respectively. The relative amount of extracted Al is higher in iron-rich
400 samples from Coquette Red (PZ1B-06, PZ1B-09, PZ1B-13 and PZ1B-17) compared to their equivalents
401 from East Alpha (TIEA-07 and TIEA-12). Among this fraction, a small portion (less than 5% of the total
402 Al extracted) was solubilised using hydroxylamine hydrochloride. The relative amount of Al removed
403 by ammonium oxalate is similar to that of Fe, about 10% or less. CBD remains the most efficient reagent
404 for Al extraction but seems less effective for solubilising Al than Fe. In addition, Al appears more
405 efficiently extracted by ammonium oxalate in iron-rich samples from Coquette Red (about 10% of the
406 total Al or 15-30% of the whole extracted Al) than in their equivalent from East Alpha (about 5% of the
407 total Al or 10% of the extracted Al).

408 Bulk Ni extraction is similar or higher to Fe extraction. It is, in particular, higher in iron-rich samples
409 from Coquette Red than in their equivalents from East Alpha. More specifically, two samples from
410 Coquette Red (PZ1B-09 and PZ1B-17) show almost complete Ni extraction, while Ni extraction in East
411 Alpha does not exceed 60%. In contrast, Ni is weakly extracted from the smectitic saprolite sample
412 from East Alpha. The relative proportion of Ni removed by hydroxylamine hydrochloride remains low
413 (5 to 15% of the total Ni extracted) yet higher than that observed for Al. The efficiency of Ni extraction
414 by ammonium oxalate appears similar to that of Fe (about 5 to 15% of the total Ni extracted) and
415 slightly lower than Al. As for Fe and Al, Ni is best extracted through the last extraction step using CBD.
416 Regarding Sc, the extraction procedure proves efficient in oxide-rich samples, resulting in about 75%
417 of the total Sc amount, except in one sample (60% extraction efficiency in TIEA-07). Like Fe, neither
418 the ultrapure water nor the hydroxylamine hydrochloride extraction proved successful in extracting Sc

419 from any of the samples. Sc extraction using ammonium oxalate, which accounts for about 20 to 30%
420 of the total Sc contained, appears significantly more efficient than Fe, Al and Ni in iron-rich samples.
421 Nevertheless, in these samples, CBD remains the most efficient reagent for Sc extraction. In contrast,
422 in the smectitic saprolite sample from East Alpha, Sc is almost exclusively extracted using ammonium
423 oxalate. However, the total amount of extracted Sc from this sample remains moderate (about 50% of
424 the bulk Sc content). To summarise, it should be noted that, in oxide-rich facies, (i) the extraction
425 procedure is globally efficient for solubilising Fe, Al, Ni and Sc, though significant differences in global
426 extraction efficiencies are observed depending on the considered element, and the sample
427 provenance (ii) only Al and Ni can be slightly extracted using hydroxylamine hydrochloride, (iii) Fe, Al,
428 Ni and Sc are best solubilised using CBD and, to a lesser extent, ammonium oxalate, (iii) the efficiency
429 of Sc extraction using ammonium oxalate is significantly greater than that of Fe, Al and Ni. In contrast,
430 the overall procedure is less well suited for the sequential extraction in smectitic saprolite, so the
431 greater extraction efficiency of ammonium oxalate relative to other reagents must be considered
432 cautiously.

433



434

435 Figure 11: Results of sequential extractions. Cumulative histograms showing the total quantities of Fe
 436 (wt%), Ni (wt%), Al (wt%) and Sc (ppm) extracted with the different reagents, as well as the quantities
 437 not extracted. H₂O = Ultrapure water (step 1), HONH₂-HCl = hydroxylamine hydrochloride 0.1 mol.L-1
 438 at pH 3.5 (step 2), (NH₄)₂C₂O₄ = ammonium oxalate 0.2 mol.L-1 at pH 3 (step 3), CBD = citrate-

439 bicarbonate-dithionite $\text{Na}_2\text{S}_2\text{O}_4$ (22% Na-citrate and 1 g Na-dithionite) (step 4). See Fig. 7 for lithology
440 colour coding.

441

442 **8. Discussion and implications for the evaluation of Sc in Ni-Co laterites**

443 This study aims to assess in which conditions Al may be reliably used as a geochemical proxy for a first-
444 order evaluation of Sc grades and distribution in Ni-Co lateritic ores. In the following, we discuss the
445 causes of the Al-Sc co-variation regarding the mineralogical evolution in lateritic profiles and the
446 relevance of using deposit-scale Sc- Al_2O_3 correlations to assess the distribution of Sc in Ni-Co laterites.

447

448 ***8.1 Co-evolution of Al and Sc concentration and speciation through weathering***

449 Analytical data documented in the present contribution reveal significant correlations, at the deposit
450 scale, between Sc and Al_2O_3 concentrations in some lateritic Ni deposits of New Caledonia. The high
451 proportionality between Sc and Al_2O_3 , observed in the investigated lateritic deposits from the bedrock
452 to the red limonite, is identified from whole-rock geochemistry (scatterplots of untransformed data
453 and PCA of centred log-ratio-transformed data) and mineral chemistry data (Fig. 7, 8, 10). Such
454 proportionality of whole-rock Sc and Al_2O_3 concentrations have already been documented by Teitler
455 et al. (2019), although the relevance of the Sc- Al_2O_3 correlation was not investigated at the deposit
456 scale. Also, the study conducted by Santoro et al. (2022) on trace element concentrations in goethite
457 from various Ni-laterite deposits showed a strong association between the Sc and Al contents of
458 goethite from the Wingellina deposit (Australia). The authors interpreted such association as being
459 primarily controlled by the composition of the parent rock, highlighting the influence of Al- and Sc-
460 bearing pyroxenite lenses on the composition of their goethite-bearing, weathered derivatives. The
461 Sc- Al_2O_3 proportionality, documented in the present contribution throughout the weathering
462 sequences of various Ni-laterites from New Caledonia (i.e. from the bedrock to the red limonite),
463 argues for a similar behaviour of Al and Sc during weathering.

464 In the unweathered mantle silicates, Ni is exclusively bound to forsterite. In contrast, virtually all of the
465 Al is hosted in pyroxenes (enstatite and diopside), and to a lesser extent, in chromiferous spinel, as it
466 is highly incompatible in forsterite. Sc is also predominantly hosted in pyroxenes, though forsterite
467 incorporates Sc up to a few ppm. Diopside contains significant concentrations of Sc (up to about 60
468 ppm; Teitler et al., 2019; Ulrich et al., 2019) but is not abundant (Table 1) and has a minor influence on
469 the bulk Sc content of unweathered Iherzolite. Teitler et al. (2019) proposed that serpentinisation of
470 the peridotite most likely has a marginal effect on Sc concentrations in the bedrock. Therefore, the
471 global Sc and Al₂O₃ contents in unweathered peridotite mainly depend on the relative proportion of
472 enstatite and its chemical composition.

473 In the lower part of the weathering sequence (saprock and smectitic saprolite), Sc and Al
474 concentrations co-increase with Fe and Cr concentrations, suggesting that Sc and Al enrichments are
475 essentially residual. Co-variations, along a quite extensive concentration range, of Al, Sc, Fe and Cr in
476 smectitic saprolite samples from East Alpha (Fig. 7) result from inherent co-variation of smectite
477 composition, as evidenced by mineral chemistry data (Fig. 10). The sequential extraction procedure
478 proved relatively ineffective in solubilising Fe, Ni and Al and from the smectitic saprolite. These
479 elements are typically present in octahedral and tetrahedral positions in nickeliferous smectite (Mano
480 et al., 2014; Ratié et al., 2018) and are not leached easily from smectite. However, the significant
481 amounts of Sc extracted from the smectite-rich saprolite using ammonium oxalate raise questions
482 regarding the speciation of Sc in this horizon. Together with the elevated Sc concentrations measured
483 in smectite from LA-ICP-MS analysis, the lack of Fe extraction by ammonium oxalate rules out any
484 significant contribution of amorphous iron oxides/oxyhydroxides to the Sc budget in the smectite-rich
485 zone. Based on the scandium K-edge XANES analysis, Chassé et al. (2019) proposed that Sc in the
486 plasmic horizon of the Syerston-Flemington Sc laterite (Australia) is efficiently trapped in smectite
487 through incorporation into octahedral sites. Such interpretation seems unable to account for the high
488 quantities of Sc extracted using ammonium oxalate. Further investigations remain necessary to
489 evaluate the Sc speciation in the smectitic saprolite from the East Alpha deposit.

490 Contrasting with the Fe-Al-Sc-Cr collinearity identified in the lower portion of the weathering
491 sequences, Sc and Al exhibit a relative enrichment compared to Fe in the earthy saprolite/yellow
492 limonite and a relative depletion in the red limonite. This distribution pattern, observed at Coquette
493 Red and East Alpha (Fig. 7B, 7C) as well as in several New Caledonian Ni-Co laterites (Teitler et al.,
494 2019), but not at Ma-Oui (Fig. 7A), supports specific mobility of Sc and Al. It is suggested that these
495 elements are, to some extent, remobilised from the red limonite and accumulated downwards in the
496 yellow limonite. The remobilisation of Sc and Al possibly result from the release of Sc and Al after the
497 dissolution/recrystallisation of increasingly crystallised goethite during the maturation of the lateritic
498 profile (Dublet et al., 2015; Teitler et al., 2019). Such a model is commonly accepted for explaining the
499 distribution pattern of Ni concentrations, which generally decrease gradually from the earthy saprolite
500 upwards in conjunction with an increase of the mean coherent domain (MCD) size of the goethite
501 crystallites (Dublet et al., 2012, 2015). This typical Ni distribution pattern is, for instance, well-
502 evidenced at Coquette Red, where a gradual decrease of Ni concentrations occurs from the earthy
503 saprolite (1.5 wt% Ni) to the red limonite (0.5 wt% Ni). There, Sc and Al distribute differently from Ni,
504 as Sc and Al concentrations are higher in the yellow limonite than in the earthy saprolite. Although the
505 release of Sc during dissolution/recrystallisation of goethite has been proposed as a relevant model
506 for explaining some elevated Sc concentrations in the yellow limonite (Chassé et al., 2019; Teitler et
507 al., 2019), the mobility of Sc released during this process must therefore be lower than that of Ni. In
508 addition, the formation of hematite at the expense of goethite in the red limonite likely results in the
509 downward redistribution of Sc and Al, as both Sc and Al substitute more easily for Fe in goethite than
510 in hematite (Levard et al., 2018; Schwertmann and Latham, 1986; Trolard et al., 1995), thus
511 contributing to Sc enrichment in the yellow limonite.

512 Sequential extraction provides further insights on the speciation of Sc and its association with other
513 elements in the earthy saprolite, yellow and red limonite. It is worth noting that the extraction
514 procedure here applied differs from the method used by Chassé et al. (2019) and Qin et al. (2020) on
515 ultramafic-derived laterites from the Syerston-Flemington (Australia) and the Berong (Philippines)

516 deposits, respectively. In these two studies, the extraction procedure is adapted from Hall et al. (1996)
517 and Sanematsu et al. (2011). It includes sodium acetate as the first reagent to assess the adsorbed and
518 exchangeable species. In contrast, we used ultrapure water, which only allows us to extract the easily
519 exchangeable species and therefore does not estimate the adsorbed species.

520 Nevertheless, the extracted Sc amounts obtained by Chassé et al. (2019) and Qin et al. (2020) from
521 sodium acetate treatment are low (10-15%) in the Syerston-Flemington laterites to very low (<5%) in
522 the Borong laterites. These two studies combine sequential extraction with XANES analysis. Chassé et
523 al. (2019) observed that the low proportion of exchangeable goethite-hosted Sc obtained from
524 sequential extraction (10-15%) is at odds with the results of XANES analysis. The latter is interpreted
525 to reflect an elevated contribution of adsorbed Sc (up to 80%) in the global Sc budget of iron
526 oxides/oxyhydroxides and only a small proportion of Sc being substituted in iron oxides or
527 oxyhydroxides. The authors favour better reliability of the XANES spectra interpretation than the
528 sequential extraction results and propose reconciling these data by arguing for the high stability of the
529 Sc adsorption complex on goethite, thus preventing the extraction of adsorbed Sc through sodium
530 acetate treatment. Similarly, in the Gorong deposit (Qin et al., 2020), the amounts of Sc adsorbed on
531 goethite appear more significant when estimated from XANES spectra (24-49%) than from sequential
532 extraction (below 5%).

533 Both of these studies then use hydroxylamine hydrochloride to extract amorphous iron oxides. In
534 contrast, we used hydroxylamine hydrochloride at lower concentrations to extract manganiferous
535 species. No Fe nor Sc, and only a very slight fraction of Ni and Al, are extracted using hydroxylamine
536 hydrochloride, highlighting the marginal presence of Mn oxides in the investigated samples and the
537 absence of detectable Sc in Mn oxides. Following hydroxylamine hydrochloride treatment, we used
538 ammonium oxalate to extract amorphous iron oxides. Ammonium oxalate has been reported as an
539 efficient and selective dissolving agent for amorphous and poorly crystalline ferric
540 oxides/oxyhydroxides, without significant dissolution of crystalline goethite and hematite, nor
541 attacking silicates (Leermakers et al., 2019; Poulton and Canfield, 2005). Chassé et al. (2019) and Qin

542 et al. (2020) did not pursue sequential extraction further than the amorphous iron
543 oxides/oxyhydroxides extraction step, hypothesizing that the residue is mostly representative of
544 crystalline iron oxides. In the present study, the use of CBD as the last extraction step unambiguously
545 demonstrates that crystalline iron oxides/oxyhydroxides predominates over amorphous iron
546 oxides/oxyhydroxides in oxide-rich horizons. Along with Fe, the elevated Ni, Al and Sc fractions
547 extracted using CBD confirm that these elements are mainly bound to crystalline goethite. At Coquette
548 Red, a slight decrease in the proportion of total extracted Fe is observed from the earthy saprolite to
549 the red limonite, from about 80 to 60% (Fig. 11). Such decrease, resulting from a slight lowering of
550 both CBD and ammonium oxalate extraction efficiencies (from about 60 to 50% and 15 to 8%,
551 respectively), may indicate the upwards increase in goethite crystallinity. Compared to Fe, Al extraction
552 appears globally less effective, especially at East Alpha, wherein the Al contents of oxide-rich facies are
553 higher than at Coquette Red. Such a discrepancy between the extraction efficiencies of Al and Fe
554 possibly results from the presence of extraction-resistant, Al-bearing minerals in the oxide-rich facies.
555 Chromiferous spinel, which is residually enriched in these horizons, contains about 15 wt% Al (Teitler
556 et al., 2019). Therefore, even in minor amounts, the presence of extraction-resistant Cr-spinel implies
557 that a non-negligible portion of the whole-rock Al content is hosted in Cr-spinel and cannot be
558 extracted through the used procedure. However, such quantities of unextractable Al are likely
559 insufficient to account for the apparent lower extractability of Al, nor for the differences in Al
560 extraction rates between Coquette Red and East Alpha, as both sites have similar Cr contents.
561 Alternatively, although not observed in any of the peridotite-derived limonite samples, the presence
562 of trace amounts of kaolinite in the lherzolite-derived limonite cannot be ruled out at East Alpha.
563 Similar to Cr-spinel, the used extraction procedure is ineffective in solubilising kaolinite, whose
564 potential presence in the East Alpha limonite may explain the lower extraction rate for Al. Regarding
565 Sc, total extraction rates in the Fe-rich horizons are similar to that of Fe (and therefore higher than that
566 of Al), supporting the strong association of Sc with iron oxides/oxyhydroxides, and in particular with
567 crystalline goethite. Nevertheless, ammonium oxalate appears relatively more efficient in extracting

568 Sc (about 20 to 35% of total Sc) than Fe (about 10% of the total Fe). The proportion of Sc extracted
569 from amorphous iron oxides in the present study is therefore slightly higher than that obtained by
570 Chassé et al. (2019), that is about 15-25%, and significantly higher than that obtained by Qin et al.
571 (2020), that is below 3%. This discrepancy possibly results from a better efficiency of ammonium
572 oxalate to extract Sc from amorphous iron oxides/oxyhydroxides than hydroxylamine hydrochloride.
573 Our results suggest that Sc may have a higher affinity for amorphous iron oxides/oxyhydroxides than
574 crystalline goethite. Significant amounts of Sc can be thus concentrated in amorphous iron
575 oxides/oxyhydroxides despite the predominance of crystalline goethite throughout the lateritic
576 sequence. The speciation of Sc in oxide-rich facies differs probably in part from that of Al. The latter is
577 mainly incorporated in the lattice of crystalline goethite and preserved in weathering-resistant Cr-
578 spinel. Yet, despite second-order differences between the speciation of Sc and Al₂O₃, these elements
579 show strong proportionality from the bedrock to the red limonite. As these elements (i) are both
580 mainly immobile during the weathering of peridotite, (ii) have a preferential affinity for goethite, and
581 (iii) are only moderately remobilised following recrystallisation and goethite replacement by hematite,
582 the composition of the parent rock remains the first-order control on their concentrations throughout
583 the weathering sequences. Thus, the Sc-Al₂O₃ regression lines obtained from forsterite-enstatite
584 mineral compositions are close to those obtained from weathering-related mineral compositions and
585 whole-rock geochemistry along weathering profiles. The slightly lower regression coefficients obtained
586 from whole-rock geochemistry than those obtained from mantle silicate mineral composition may
587 result from the second-order contribution of Cr-spinel to the global Al budget in whole-rock
588 geochemical compositions. These results indicate that (i) the Sc-Al₂O₃ content of enstatite in a given
589 peridotite bedrock drives the Sc-Al₂O₃ regression line within its weathered derivatives, and (ii) the
590 relative proportion of enstatite together with its Sc content primarily control the maximum Sc
591 concentrations reached in the yellow limonite.

592 Contrasting with the proportionality observed between Sc and Al₂O₃ from the bedrock up to the red
593 limonite, samples from the duricrust are out of the Sc-Al₂O₃ whole-rock correlation trends. Such offset,

594 previously documented by Teitler et al. (2019), possibly results from the contribution of allochthonous
595 material to the duricrust. Indeed, in situ Sc analysis of goethite-hematite in duricrust, were identified
596 as lateritic residuum, shows a good fit with the Sc-Al₂O₃ regression line obtained on saprolitic and
597 limonitic minerals. On the opposite, nodular and pisolitic goethite and hematite from the ferricrete
598 exhibit a relative depletion in Sc compared to Al, similar to the offsets identified in the whole-rock
599 geochemical dataset. In the East Alpha deposit, the offset of gabbro-derived saprolite from the Sc-
600 Al₂O₃ correlation trend also results from the allochthonous nature of the gabbro compared to the
601 peridotite-derived Ni-Co laterite, together with the specific mineral assemblage of the gabbro-derived
602 saprolite. The formation of kaolinite during the weathering of gabbro is related to its substantial Al
603 content (Schwertmann et al., 2000; Teitler et al., 2019; Trolard and Tardy, 1989). As Sc is typically
604 poorly concentrated into kaolinite (Chassé et al., 2017; Teitler et al., 2019; Ulrich et al., 2019), the
605 weathering of gabbros may lead to Sc remobilisation and trapping into nearby yellow limonite, while
606 Al remains concentrated in saprolitised gabbro as kaolinite. Consequently, Sc and Al₂O₃ may be
607 positively correlated in lateritic deposits if kaolinite, or other Al-bearing phases such as gibbsite, are
608 mostly absent from the lateritic profiles. The formation of kaolinite (or gibbsite) during the
609 lateritisation process requires that the parent rock contains significant amounts of Al, so that Sc-Al₂O₃
610 correlation trends may only be observed in ultramafic-derived laterites, wherein the Al content is low.

611

612 ***7.2 Implications for the assessment of Sc in Ni-laterites***

613 The relevance of using Al as a geochemical proxy to conduct a first-order estimation of Sc
614 concentration and distribution in a given Ni-Co deposit depends both on the specific reliability of the
615 Sc-Al₂O₃ correlation at the deposit scale and on the method used to characterise Al concentration and
616 distribution. The reliability of the Sc-Al₂O₃ correlation may be influenced by (i) potential
617 heterogeneities in the parent rock lithology, (ii) the occurrence of alteration facies containing Al-rich
618 phases such as kaolinite or gibbsite and (iii) the inherent data dispersion in Sc-Al₂O₃ scatterplots.
619 Interestingly, the alternance of harzburgite and dunite in the bedrock does not seem to significantly

620 affect the Sc-Al₂O₃ regression coefficient nor the dispersion of the data, providing that the composition
621 of enstatite remains similar in both facies. Nevertheless, lithological heterogeneities involving a change
622 in the composition of enstatite, elevated amounts of diopside and plagioclase (e.g. in some lherzolite
623 facies), or the occurrence of mafic intrusive dykes, may cause significant variations of the Sc/Al₂O₃
624 concentration ratio both in the parent rocks and in their weathered derivatives. These potential
625 variations of the parent rock lithology at the deposit scale may be tested by geological characterisation
626 and geochemical assay data analysis. In addition, alteration facies containing significant amounts of Al-
627 rich phases (e.g. kaolinite, gibbsite) are commonly characterised by a substantial deviation from the
628 Sc-Al₂O₃ correlation trend, established from smectite- and Fe-oxide-dominated lithologies. The
629 possible occurrence of Al-rich phases, typically poor in Sc, must be examined to prevent over-
630 estimation of the Sc content. Al-rich phases are commonly associated with weathered intrusive rocks
631 such as gabbros. Still, they may also form during the weathering of some peridotites that yield
632 significant Al concentrations. In particular, some plagioclase-bearing lherzolites (not investigated in the
633 present study) can exhibit Al₂O₃ contents up to ~4 wt% (Marchesi et al., 2009; Ulrich et al., 2010) and
634 may consequently alter to kaolinite or gibbsite.

635 Geochemical homogeneity and low Al-content of the parent rock are, therefore, necessary conditions
636 for the occurrence of a reliable Sc-Al₂O₃ correlation trend at the deposit scale. Determination of a
637 reliable, deposit-scale Sc-Al₂O₃ correlation requires assessing the range of Al₂O₃ concentrations for
638 which Sc is well correlated with Al₂O₃ through an adequate sampling strategy that encompasses the
639 whole range of Al₂O₃ concentrations and the mineralogical diversity throughout the deposit. Finally,
640 the inherent data dispersion in Sc-Al₂O₃ biplots may be variable depending on the investigated deposit.
641 Therefore, the number of samples used for establishing the Sc-Al₂O₃ correlation must be adapted to
642 the inherent data dispersion to develop a reliable correlation with a good correlation coefficient. Once
643 verified, deposit-scale Sc-Al₂O₃ correlations may first prove useful to estimate Sc concentrations on
644 surface outcrops or pit walls using portable devices such as pXRF. Indeed, the relatively low Sc
645 concentrations observed in Ni-laterites (<100 ppm) limit the use of pXRF to directly assess Sc (Lacroix

646 et al., 2021) whereas Al concentrations, typically about a few wt%, can be confidently estimated using
647 such a device. The slightly lower accuracy obtained on Al analysis from pXRF than from a classical assay
648 analysis would only marginally affect the estimation of Sc. More importantly, applying this approach
649 to deposits where Al is routinely assayed could provide a first-order Sc concentration and distribution
650 estimate. The reliability of such estimation would depend on the reliability of the Sc-Al₂O₃ correlation
651 and the reliability of the Al distribution model. Indeed, block models are developed firstly to estimate
652 the resource and distribution of Ni both in saprolitic and limonitic facies. They rely on statistical
653 variograms set explicitly for several metals (e.g. Si, Mg, Fe, Ni) but not necessarily Al. In such a case, a
654 specific evaluation of the variability of Al in the limonitic facies may be beneficial.

655

656 **Conclusion**

657 This contribution examines the relevance of using Al as a geochemical proxy for first-order estimates
658 of Sc distribution and concentration in some peridotite-hosted, Ni-Co laterites from New Caledonia.
659 Apparent correlations are identified at the deposit scale between Sc and Al₂O₃ concentrations from
660 the bedrock to the red limonite. These correlations put forward the similar behaviour of Al and Sc
661 during the peridotite weathering, which concentrations are primarily issued from the residual
662 enrichment. Local remobilisation from the uppermost horizons is shown. Al and Sc are both
663 predominantly hosted in crystalline goethite, but Sc has a relatively higher affinity for amorphous iron
664 oxides compared to Al. In all investigated deposits, the Sc-Al₂O₃ regression coefficient remarkably
665 depends on the Sc content in enstatite. Providing that the parent lithology is homogeneous and
666 relatively depleted in Al, reliable Sc-Al₂O₃ correlations may thus be determined at the deposit scale
667 after analysing a limited number of spatially and chemically representative samples. An adequate
668 sampling strategy is required to cover the range of Sc and Al₂O₃ concentrations throughout the deposit
669 and to take in account potential occurrences of specific alteration facies that may affect the relevance
670 of the deposit-scale correlation (ferricrete, weathered intrusive rocks, kaolinite- or gibbsite-bearing
671 alterite). Although the zones of maximum Sc enrichment are situated above the zones of maximum Ni

672 and Co enrichment, Sc-rich limonite may overlap the Co-rich transition zone, so that the base of the
673 limonite may yield elevated Co and Sc concentrations together with sub-economic Ni grades. In such
674 conditions, lateritic ores may be valuably exploited for Ni, Co and Sc assuming cost-effective co-
675 valorisation of these metals.

676

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865

866 **Appendix A**

867 ***Whole-rock geochemistry***

868 Batch 1 sample pulps were analysed for whole-rock major- and trace-element geochemistry using the
869 procedure of Carignan et al. (2001). Major element oxides and Sc were analysed using an iCap6500
870 ICP-OES with Li borate fusion. Trace elements were analysed using an iCapQ ICP-MS with Li borate
871 fusion followed by nitric acid digestion. Analytical accuracy (2s standard deviation) lies within the
872 typical uncertainty of the analytical data for both major element oxides and trace elements, which is
873 less than 1% for major oxides and less than 5% for most trace elements. Batch 2 samples were analysed
874 for major elements, Ni, Co and Sc, using an Axios FAST Wavelength Dispersive XRF spectrometer with
875 LiF200 crystal. The detection limit for Sc is 12 ppm, and analytical accuracy is less than 7% in the 50-

876 120 ppm concentration range. The relative analytical precision between the two datasets, tested by
877 duplicating the analysis of 3 samples in both laboratories, is better than 2% for Sc.

878

879 ***LA-ICP-MS***

880 LA-ICP-MS analysis of Sc in silicates and phyllosilicates was performed with the NIST60 reference
881 standard using Si concentration obtained from EMPA as internal standard. For oxides, analysis was
882 performed with the StdGoe 1.1 pelletised goethite standard developed and validated by Ulrich et al.
883 (2019) and using Fe concentration as an internal standard. Reference standards were analysed before
884 and after every 15 ablations conducted on samples. Before each analysis, the background signal, or
885 gas blank, was measured for a duration of 25 s. Ablation time, spot sizes and laser pulse frequency
886 were 45 s, 60 µm, and 5 Hz, respectively. Data processing was conducted using the SILLS program
887 (Guillong et al., 2008). The detection limit was below 1 ppm for most trace elements.

888

889 ***PCA on CLR-transformed geochemical data***

890 Principal Component Analysis (PCA) was conducted on whole-rock geochemical data using the atomic
891 weight percentages of Mg, Al, Si, Sc, Cr, Mn, Fe, Co, Ni and LOI following centred log-ratio (CLR)
892 transformation to avoid spurious proportionality and boundary effects (Aitchison, 1986; Tolosana-
893 Delgado & McKinley, 2016). PCA consists in transforming a multivariate dataset - here, each elemental
894 concentration represents a variable - into a lower-dimensional dataset while preserving as much of the
895 data's variation as possible. The dataset is projected into a new coordinate system based on the
896 principal components, which are orthogonal linear combinations of original variables and
897 corresponding to the eigenvectors of the covariance matrix. The advantage of such analysis is that
898 principal components are likely controlled by mineral stoichiometry, providing a more realistic
899 representation of geological variability. Centred log-ratio transformation of Mg, Al, Si, Sc, Cr, Mn, Fe,
900 Co, Ni concentrations and LOI performed before PCA has the benefit of removing the proportionality
901 effect (i.e. the predominance of major elements on the geochemical variability) and the boundary

902 effects (negative bias and spurious correlation effect; Chayes, 1960). Saproilitised gabbro samples from
903 East Alpha were excluded from PCA calculations to explore better the impact of weathering on
904 peridotite bedrocks alone. In a covariance biplot of log-ratio transformed data, a short distance
905 between the ray tips of two variables (i.e. coincident rays) indicates that these variables are highly
906 proportional (Tolosana-Delgado & McKinley, 2016).

907

908 ***Sequential extractions***

909 Sequential extractions were conducted on seven Sc-bearing samples from Cap Bocage and Tiébaghi,
910 encompassing earthy saprolite, smectitic saprolite, yellow and red limonite facies. For each extraction,
911 approximately 1 g of sample powder (<50 µm) was weighed into 50 mL of reagent solution and agitated
912 for 76 h. Each tube was then centrifugated at 10000 rpm, and the supernatant liquid was filtered at
913 0.2 µm before ICP-AES analysis. The residue was then rinsed with Milli-Q® water and used for
914 subsequent extraction after re-suspension.

915

916

917 ***Appendix A references***

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