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► **To cite this version:**

Thierry Augé, Laurent Bailly, Jean-Yves Roig. A double Fe-Ti oxide and Fe-sulphide liquid immiscibility in the Itsindro Gabbro Complex, Madagascar. *Journal of African Earth Sciences*, 2017, 135, pp.152-172. 10.1016/j.jafrearsci.2017.08.009 . hal-01816579

HAL Id: hal-01816579

<https://brgm.hal.science/hal-01816579>

Submitted on 21 Nov 2023

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1 **A double Fe-Ti oxide and Fe-sulphide liquid immiscibility in the Itsindro Gabbro**

2 **Complex, Madagascar**

3 June 6, 2017

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11

12 **Abstract**

13 The petrology and mineralogy of the Itsindro complex in south-central Madagascar has been
14 investigated through samples obtained from the 320.7 m-deep Lanjanina borehole. The
15 section consists of a 254 m-thick pyroxenite unit with interbedded gabbro layers that overlies
16 a gabbro unit and is itself overlain by a 19 m-thick granite unit. Most of the structures are
17 sub-horizontal. A weak magmatic layering is locally observed but at the scale of the core, the
18 intrusion does not appear to be a layered complex.

19 Pyroxenite and gabbro show a systematic disseminated mineralization consisting of Fe-Ti-P
20 oxides and Fe-(Cu-Ni) sulphides that takes the form of ilmenite-titanomagnetite±apatite and
21 pyrrhotite±chalcopyrite±pentlandite. In the upper zone, from 90 to 72 m, sub-massive
22 centimetre- to decimetre-sized layers of oxides and sulphides comprise a total of 16 m of
23 sub-massive sulphide (the main mineralized zone). In this mineralized zone the
24 oxide/sulphide ratio is close to 1/1. The sulphide is strongly dominated by pyrrhotite, which
25 may locally contain inclusions of molybdenite crystals with the Re sulphide rheniite (ReS_2).
26 Oxides are generally euhedral, included in or attached to the Fe-sulphide, and also locally
27 form sub-massive centimetre-sized bands.

28 Apatite as a cumulus phase is ubiquitous. Locally it may account for 30 % of the ore-rich
29 samples and some samples consist of apatite-Fe-Ti oxides-Fe-Cu-Ni sulphides with virtually
30 no silicate. Apatite is the main REE carrier but the total REE content remains low (<90 ppm).

31 Mineral compositions and whole rock geochemistry indicate that the rocks are highly
32 differentiated, and in spite of a relatively limited thickness, the differentiation process is
33 observed. Two zones can be distinguished: from the bottom to 162.8 m we see a decrease in
34 the Mg number of olivine and pyroxene, and a drop in TiO_2 and Al_2O_3 for the latter. A reverse
35 trend is then observed within the pyroxenite unit from the 162.8 m level upwards. The main
36 mineralized zone is located in the upper part of this unit, about 70 m above this discontinuity.

37 The highly differentiated Fe-Ti-P facies of the Lanjanina series in the Itsindro Gabbro
38 Complex have been interpreted as corresponding to the Fe-Ti-P rich, Si-poor member
39 remaining after an immiscible segregation of an evolved mafic magma. The granite dykes
40 and the overlying granite unit represent the second, Si-rich member of the immiscibility
41 process.

42 The presence of large amounts of sulphide is attributed to sulphur contamination of the Fe-
43 Ti-rich liquid. Fe-Ti oxides will tend to crystallize on the sulphide droplets and the
44 accumulation of dense Fe-sulphides (liquid) and associated Fe-Ti oxides (solid) will result in
45 this complex and unusual association taking the form of a net texture.

46 **Keywords** Fe-Ti oxide ores, Fe-(Cu-Ni) sulphides, Fe-Ti-P-rich liquid immiscibility, sulphide
47 liquid immiscibility, mafic-ultramafic intrusion, Itsindro Gabbro, Madagascar

48

49

50 **1. Introduction**

51 The Itsindro massif (south-central Madagascar, Fig. 1) was known to contain an Fe-Cu-Ni
52 sulphide mineralization dominated by pyrrhotite with minor chalcopyrite and rare pentlandite.
53 Previous work (Martel-Jantin, 1991) mentioned a cumulative thickness of 16 m of sub-
54 massive pyrrhotite between 72 and 90 m in the only drill hole completed in the mafic-
55 ultramafic rocks of the complex. Further work in the area was abandoned because of the lack
56 of Cu-Ni mineralization.

57 Following a recent 1/1,000,000-scale geologic and metallogenic synthesis of Madagascar
58 geology (Roig et al., 2012; Peters et al., 2012), interest in this massif was rekindled and new
59 studies were carried out. As part of a research project aimed at understanding the
60 parameters controlling the composition of magmatic sulphide assemblages (and specifically
61 their Ni-Cu-PGE contents), the sulphide mineralization was reinvestigated by the

62 examination of borehole samples. Selected samples were characterized in terms of
63 petrography, ore paragenesis and geochemistry.

64 Detailed investigation of borehole samples revealed the presence of a systematic
65 accumulation of Fe-Ti oxides (forming locally dm-sized sub-massive layers), closely
66 associated with the Fe-Cu-Ni sulphides together with--in most samples--magmatic apatite in
67 mafic (ferrogabbro) and ultramafic (ferropyroxenite) cumulates. This type of ore mineral
68 association seems to be very uncommon, although it presents some similarities with mineral
69 occurrences described in the Duluth Complex, Minnesota (Ripley et al., 1998).

70 The aim of this paper is to describe the mineralized drill core and to propose an original
71 genetic model in which by combining textural, mineralogical and chemical evidence, we
72 interpret the coexistence of the Fe-Ti-oxide-apatite mineralization and the Fe-sulphide
73 mineralization (with virtually no Ni-Cu) as a result of a complex immiscibility process
74 preceding a crustal S contamination of the Fe-Ti-(P)-rich magma.

75

76 **2. Geological environment and previous work**

77

78 The Itsindro gabbro massif, located in the Itremo region, belongs to the southern part of a
79 nearly continuous 450 km-long belt of mafic and granitic plutons of Neoproterozoic age
80 (Tucker et al., 1999) interpreted as the root of a continental magmatic arc emplaced between
81 804 and 776 Ma, during or slightly preceding the breakup of the Rodinian supercontinent
82 (Archibald et al., 2016). Mafic-ultramafic bodies belonging to this belt, such as the Itsindro
83 massif or the Ambodilafa complex (located 120 km E of the Itsindro massif) have all the
84 characteristics of anorogenic plutons (Tucker et al., 2012). The Itremo region (Fig. 1) is
85 characterized by late undifferentiated Archean migmatitic gneisses and schists (Tucker et al.,
86 1999) and metamorphosed Mesoproterozoic sedimentary rocks of the *Quartzto-Schisto-*
87 *Calcaire* series (Moine, 1968; 1974). The Itsindro gabbro gives an age of 790.1 ± 0.9 Ma (U-
88 Pb on zircon and baddeleyite) and the age range obtained for other plutons in the region is

89 compatible with the ages obtained in western Madagascar, thus defining a nearly continuous
90 belt of plutonic rocks interpreted as a continental magmatic arc (Handke et al., 1999).

91 The Itsindro massif is elongated, about 40 x 8 km, with a N-S orientation (Fig. 1), and
92 emplaced in the Itremo "*Quartzto-schisto-calcaire*" series. Detailed mapping of the massif was
93 carried out in 1968 (Coulombeau, 1969) under difficult conditions, owing to the lack of access
94 and outcrop. The massif was interpreted as a series of gabbro-forming sills or laccoliths in
95 the metamorphosed sedimentary series.

96 Other mafic-ultramafic facies have been sporadically observed but the difficult field
97 conditions did not allow their relationships with the gabbro units to be defined. They include
98 plagioclase lherzolite, clinopyroxenite, orthopyroxenite and dunite. The gabbro units are cut
99 by various felsic facies, such as syenite and various generations of granite, but again, their
100 relationships with the gabbros are not known.

101 The Itsindro massif was studied in the 1970s for its potential in Cu, after the discovery of
102 malachite and azurite in a gossan developed on a magnetite-rich gabbro. A geochemical
103 exploration survey identified an anomalous zone where the highest Ni and Cu values were
104 superposed. This zone, corresponding to an area of about 0.07 km², includes the mineralized
105 occurrence known as "Lanjanina". A ground geophysical exploration survey conducted in the
106 gossan area gave positive results and the superposition of the geochemical and geophysical
107 anomalies was interpreted as indicating the existence of massive sulphides at depth.

108 A deep vertical borehole was drilled where the geochemical and geophysical anomalies were
109 optimally superposed (Fournié, 1970). The LJ1 hole was stopped at a depth of 320.75 m
110 (Fig. 2). The results were considered to be negative, in spite of the abundance of sub-
111 massive sulphides: largely dominated by pyrrhotite, they yielded correspondingly low Cu and
112 Ni values.

113

114 **3. Borehole description**

115

116 The drill core recovered in 1969 was well preserved and a detailed log at 1/100 scale was
117 available with macroscopic descriptions (Fournié, 1970). Moreover from 34 to 320.7 m, every
118 one-metre interval had been analyzed for Ni and Cu.

119 The log is relatively simple at the macroscopic scale and shows five main units (Fig. 2):

120 - 0 – 8.2 m: oxidized iron cap (“gossan”),

121 - 8.2 – 15.35 m: gabbro (saprolite) unit,

122 - 15.35 – 34.02 m: granite unit (heterogeneous, weathered, and strongly fractured),

123 - 34.02 – 287.6 m: pyroxenite unit with dm- to m-thick dykes of fine grained granite and
124 syenite above 120 m, and metre-sized gabbro layers throughout the unit,

125 - 287.6 – 320.73 m: main gabbro unit, with 3- to 7 m-thick pyroxenite layers.

126 Most of the pyroxenite and gabbro facies are isotropic. In some cases however, a magmatic
127 fabric was observed, suggesting that the complex is not strongly deformed and is preserved
128 in its original position with a sub-horizontal layering. Similarly, when preserved, contacts
129 between pyroxenite and gabbro, and massive ore and mafic-ultramafic rocks, tend to be
130 horizontal. A weak hydrothermal alteration is developed in the first 130 m, with occurrences
131 of secondary amphibole (locally forming amphibolite), biotite, chlorite, and carbonate.

132 Disseminated sulphides are observed throughout the borehole, in all rock types. From 72 to
133 90 m massive to sub-massive sulphide concentrations form centimetre- to decimetre-thick
134 accumulations corresponding to the equivalent of about 16 m of the “massive sulphides
135 layer” (Martel-Jantin, 1991). In this Fe-Cu-Ni sulfide-rich zone (hereafter “the main
136 mineralized zone”), 50-cm intervals were analyzed for Ni and Cu. The maximum Ni value
137 obtained is 2600 ppm, the maximum Cu, 2800, and there is a weak correlation between the
138 two, with a Ni/Cu ratio close to 1/2.

139

140 **4. Sampling and petrography**

141 Thirty-three samples were collected throughout the drill core, from 34.8 m to 316.7 m. A
142 systematic sampling was supplemented by a specific sampling of the mineralized facies.
143 Table 1 summarizes the main characteristics of the samples. Sampling was focused on the
144 mafic-ultramafic rocks; granitic facies were not collected.

145 All the rock types consist of various proportions of clinopyroxene, plagioclase, olivine,
146 apatite, mica, rare small zircon and secondary amphibole. Orthopyroxene is totally lacking. In
147 the pyroxenite unit; pyroxenite with various proportions of ore minerals is generally coarse-
148 grained, exhibiting a mesocumulate texture (Figs. 3A, D). Olivine was found in four
149 pyroxenite samples (out of 17), and does not exceed 5 % in volume (Figs. 3H, K). In some
150 samples olivine forms a rim around the ore minerals, in contact with clinopyroxene,
151 resembling a reaction texture (Figs. 3I, L). Some pyroxenites contain up to 10 % interstitial
152 plagioclase; plagioclase also locally forms a very thin (20 μm) rim between ore minerals and
153 silicates. Gabbro interlayered in the pyroxenite unit exhibits either a fine-grained equant
154 texture, with a relatively low (20 %) proportion of plagioclase, or a pegmatitic facies in which
155 plagioclase dominates over pyroxene.

156 In the gabbro unit, gabbro seems to show a more pronounced magmatic mineral layering
157 (Figs. 3B, E), marked by a preferred orientation of the plagioclase laths, and various types of
158 gabbro are observed, from leucogabbro with 60 % plagioclase to mafic gabbro (close to
159 plagioclase wehrlite). Olivine is common in the basal gabbro and may be more abundant
160 than in the pyroxenite unit. Pyroxenite layers in the basal gabbro are olivine bearing. Their
161 contacts with the host gabbro are sharp, and parallel to the magmatic layering.

162 Throughout the drill core, apatite occurs as a cumulus phase. It is ubiquitous, euhedral, and
163 included in the magmatic silicates, in the oxide phases, in the Fe-(Cu-Ni) sulphides (Figs.
164 3G, H, J, K), and in the oxide- sulphide association. Locally it forms aggregates of crystals up

165 to 1.5 mm in size. Its volume may locally reach 30 % of the sample in the Fe-Ti oxide-rich
166 facies and some samples consist of apatite-Fe-Ti oxides and Fe-Cu-Ni sulphides with
167 virtually no silicate.

168 A weak, late hydrothermal alteration affects most of the gabbro and pyroxenite, and is
169 characterized by amphibolization of pyroxene and the local development of carbonates This
170 episode does not affect the ore minerals and is not accompanied by the deposition of
171 metallic minerals. At hand-specimen scale we see no rhythmic layering anywhere in the
172 borehole, and no evidence of a “layered complex” but rather two main units, suggesting that
173 the borehole corresponds to two “mega-cyclic” units.

174

175 **5. Mineralization**

176 5.1. Textures

177 Disseminated Fe-Cu-Ni sulphides and Fe-Ti oxides occur throughout the LJ1 borehole and
178 there are no occurrences of oxide without sulphide or sulphide without oxide. The collected
179 samples exhibit various proportions of Fe-Cu-Ni sulphides and Fe-Ti oxides (as reflected by
180 whole-rock composition) and in spite of local variations the average proportion may be
181 estimated at 50/50. At centimetre scale, nearly massive Fe-Cu-Ni sulphides with inclusions of
182 Fe-Ti oxides alternate with sub-massive Fe-Ti oxides containing Fe-Cu-Ni sulphide
183 inclusions.

184 In most cases, disseminated oxides and sulphides tend to be interstitial with respect to
185 silicates. Sulphide and oxide crystals are generally adjacent rather than forming separate
186 patches, and we observe “droplets” of Fe-Cu-Ni sulphides included in oxides and inclusions
187 of euhedral oxide in Fe-Cu-Ni sulphides, suggesting that S immiscibility occurred before or
188 contemporaneously with the oxide crystallization, and that the S liquid was still present when

189 the Fe-Ti oxides crystallized. Rare rounded inclusions of oxides and sulphides are also
190 observed in silicates,.

191 When the content of ore mineral reaches about 30 %, the ore begins to display a
192 characteristic net texture and the oxide-sulphide association generally appears interstitial
193 with respect to euhedral magmatic silicates and apatite (Figs. 3C, F). This net texture is
194 typical of Fe-Ti oxide rock (Dymek and Owens, 2001). The net and massive textures clearly
195 show euhedral to subhedral oxides enclosed in the Fe-Cu-Ni sulphides, both oxides and
196 sulphides forming a network surrounding isolated cumulus silicate grains (Figs. 4A, B, C, D),
197 very similar to the interconnected network around isolated silicate grains shown by Liu et al.
198 (2014) for an Fe-Ti mineralization in a context without Fe-Cu-Ni sulphides.

199 Graphite flakes ubiquitous, but always in very minor proportions (<1 %). Graphite generally
200 occurs as small clusters (<100 μm) of fibres closely associated with the ore minerals.

201 5.2. Sulphides

202 Pentlandite is sparsely developed, mainly as large crystals and flame-like inclusions found
203 along cracks in pyrrhotite. Chalcopyrite appears as lamellar exsolutions in pyrrhotite as well
204 as larger grains between pyrrhotite crystals. Cobaltite-gersdorffite group minerals form
205 rounded inclusions in pyrrhotite. Tiny crystals of sphalerite were observed in a few samples.
206 Very small (max. 10 μm long) molybdenite flakes are commonly included in or adjacent to
207 Fe-(Cu-Ni) sulphides. A tiny Re-sulphide (rheniite) is very commonly found next to or partly
208 included in molybdenite (Figs. 4H, I).

209 5.3. Oxides

210 Most oxide grains are two-phase associations, composed of ilmenite free of exsolution
211 lamellae, and titanomagnetite everywhere exhibiting complex subsolidus exsolution textures.
212 Titanomagnetite is recrystallized into magnetite containing a complex network of oriented
213 exsolutions and intergrowths of ilmenite and aluminous spinel-group minerals (Figs. 4E, G).

214 Ilmenite largely dominates over titanomagnetite. We never observed magnetite crystals free
215 of exsolution.

216 The contact between ilmenite and titanomagnetite is highly irregular and marked by a fringe
217 up to 120 μm in width of tiny Al-spinel crystals, titanite and biotite (Fig. 4F). Lozenge-shaped
218 spinel crystals are also seen in titanomagnetite crystals. Such features have been described
219 elsewhere, for example by Charlier et al. (2007) in the Tellnes deposit in Norway and by Liu
220 et al. (2015) in Fe-Ti mineralization in a layered mafic intrusion in China.

221

222 **6. Analytical techniques**

223 Among the thirty-two samples collected throughout the section (all prepared in polished thin
224 sections), twenty-two were selected for mineralogical analyses and fifteen for whole rock
225 analyses (Table 1). Major and trace elements were analysed by ALS Minerals (Ireland).
226 Major elements were analysed by ICP-AES after lithium borate fusion; Ag, Cu, Cd, Co, Mo,
227 Ni, Pb, Sc, and Zn by ICP-AES after four-acid dissolution; other trace elements and rare
228 elements by ICP-MS after lithium borate fusion; C and S by combustion furnace; and As, Bi,
229 Hg, Sb, Se, and Te by ICP-MS after aqua regia dissolution.

230 Silicates and oxides were analysed by electron probe microanalyser (EPMA) with the
231 CAMECA SXFive operated by the "*Plateforme analytique régionale*" (BRGM - Université
232 d'Orléans - CNRS Orléans) equipped with 5 WDS spectrometers under the following
233 conditions: acceleration voltage of 15 keV, beam current of 12 nA, counting time of 10 sec.
234 Natural in-house minerals were used as standards. $K\alpha$ lines were used for all the elements.
235 Apatite analyses were performed with a CAMECA SX100, at the GeoRessources Laboratory,
236 Université de Lorraine. For Cl, P, and Ca a standard apatite was used with an acceleration
237 voltage of 15 keV, a beam current of 12 nA and a counting time of 10 sec. All the values
238 given below are above the detection limit.

239 In each thin section, usually five points were analysed on a given mineral species to test
240 potential zoning and compositional variability. As expected in such a context, no significant
241 differences were observed and average compositions were calculated and used in most of
242 the diagrams below except for olivine, in which large compositional variations were obtained
243 from one crystal to another within a given sample (see below).

244 7. Litho-geochemistry

245 Whole-rock analyses were performed on 15 selected representative samples to characterize
246 their major, trace and rare earth element contents (Table 2). Their geochemistry, and more
247 especially their contents of Ti (reported as TiO_2) and Fe (reported as Fe_2O_3), are strongly
248 influenced by their contents of oxides (ilmenite, titanomagnetite) and sulphides
249 (pyrrhotite±chalcopyrite±pentlandite). Note that as the samples are cumulates; the
250 compositions obtained are not representative of liquid compositions.

251 7.1. Major elements

252 The SiO_2 content of pyroxenite samples ranges between 13.3 and 47.2 wt. %. Highly variable
253 contents of Fe_2O_3 and TiO_2 are also observed, between 14.25 and 54.4 wt. % and 1.91 and
254 14.2 wt. % respectively. These variations reflect the varying proportions of Fe-Ti oxides and
255 Fe-sulphides. Some ten samples have an S content lower than 2 %, some showing TiO_2
256 contents greater than 11 % (corresponding to S-poor oxide-rich mineralized samples). This is
257 the case for some gabbros, generally relatively poor in sulphides (less than 1.36 wt. % S) but
258 locally rich in Fe-Ti oxides (TiO_2 up to 9.2 %). Two pyroxenite samples show extremely high
259 S contents (11.4 and 17.9 %) and a TiO_2 content ranging between 4.3 and 9.2 wt. %,
260 corresponding to samples mineralized by oxides and sulphides. Some samples are
261 characterized by TiO_2 contents above 12 % (ilmenite-rich samples) and variable but high
262 sulphide contents between 2.3 and 9.5 % (sulphide-rich samples).

263 SiO_2 and Fe_2O_3 are negatively correlated, sulphide-bearing samples showing the highest
264 Fe_2O_3 contents (Fig. 5G). SiO_2 is also negatively correlated with TiO_2 although the correlation

265 is not perfect (Fig. 5B). TiO_2 and Fe_2O_3 are positively correlated (reflecting the proportion of
266 Fe-Ti oxides, Fig. 5F). Similarly, and for the same reason, MgO and Fe_2O_3 are negatively
267 correlated (Fig. 5D).

268 SiO_2 and MgO are positively correlated and two trends are observed (Fig. 5A). The first one
269 is defined by pyroxenite samples characterized by an SiO_2/MgO ratio of 3.4, the second is
270 defined by gabbro samples with a higher SiO_2/MgO ratio (around 6.3). Only one pyroxenite
271 sample (LJ 31) shows Mg enrichment ($\text{SiO}_2/\text{MgO} = 1.6$). A similar evolution is observed for
272 CaO, positively correlated with SiO_2 (Fig. 5C). Both trends reflect an increasing proportion of
273 clinopyroxene (together with a decreasing proportion of ore minerals).

274 In pyroxenite, Al_2O_3 remains low, and is not correlated with the SiO_2 variations. High Al_2O_3
275 values are seen only in the gabbros (Fig. 5E). Despite the presence of graphite, observed in
276 nearly all thin sections, the total C content remains low, ranging between 0.10 and 0.54 %
277 (Table 2).

278 7.2. Trace elements

279 Only a few trace elements exhibit significant and distinguishing contents. The V content
280 ranges between 176 and 1440 ppm without significant difference between pyroxenite and
281 gabbro. Its abundance reflects the amount of titanomagnetite, this being the main V carrier
282 (1.12 % V_2O_3 on average, EPMA data). A positive correlation is observed between V and
283 Fe_2O_3 (Fig. 5H) except for samples having the highest pyrrhotite contents (corresponding to
284 S contents ranging from 7.43 to 17.95 %). Ba, mainly hosted by plagioclase, is significantly
285 enriched in gabbro (81 to 348 ppm) compared to pyroxenite (2.8 to 68 ppm). The same
286 behaviour is observed for Sr, which ranges between 357 and 425 ppm in gabbro and
287 between 12.8 and 52.4 ppm in pyroxenite. The Sc content ranges between 33 and 100 ppm,
288 and Zr is below 60 ppm.

289 Base metals are mainly represented by Cu, ranging between 44 and 5460 ppm in correlation
290 with the variable, but always low content of chalcopyrite. Ni (22 to 1350 ppm), mainly carried

291 by rare pentlandite exsolutions in pyrrhotite and the cobaltite-gersdorffite mineral series, is
292 positively correlated with Co (47 to 596 ppm, Fig. 6C), and with Cu (Fig. 6D). Note that the Ni
293 content of olivine is typically low, <0.05 wt.%. Both Cu and Ni are positively correlated with S
294 (Figs. 6A, B).

295 Few crystals from the cobaltite-gersdorffite mineral series have been identified, but no
296 correlation is observed between Ni, Co and As. Zn, mainly carried by Al spinel (2.75 % on
297 average, EPMA data) and by rare sphalerite crystals, ranges from 57 to 454 ppm. For such
298 an ultramafic environment the Cr content is low, ranging between 10 and 310 ppm (no
299 chromite crystals have been identified and the Cr content in clinopyroxene and
300 titanomagnetite is extremely low. In spite of the presence of molybdenite, the Mo content is
301 low, around 1 ppm, except in the three samples that have the highest S content (LJ4, 17.95
302 wt.% S, LJ16, 11.40 and LJ22, 7.43) where it reaches 5-6 ppm, confirming that molybdenite
303 is associated with the sulphide phase.

304 7.3. Rare Earth Elements

305 The REE content of the 15 analysed samples is low, ranging from 12 to 89.92 ppm in
306 pyroxenite and 15.72 to 32.42 ppm in gabbro (Table 2). Apatite-rich samples are
307 characterized by the highest REE contents and a positive correlation is observed between
308 the amount of P_2O_5 and the sum of REE, confirming that the majority of the REE are carried
309 by apatite (Fig. 7A). LREE are dominant and the LREE/HREE ratio ranges from 1.56 to 3.74.

310 The chondrite-normalized REE profiles are reported in Figures 7B, C, D. The REE patterns
311 are slightly fractionated, with a low La/Lu ratio ranging between 1.1 and 6.7. LREE are poorly
312 fractionated ($0.53 < La/Sm < 1.37$) compared to HREE ($1.84 < Gd/Lu < 5.25$). The Eu anomaly
313 ranges from 0.86 to 1.41 in pyroxenite and 1.79 to 2.45 in gabbro. Sample LJ9 containing
314 about 10 % of interstitial plagioclase also exhibits a positive Eu anomaly (Fig. 7B). The LREE
315 enrichment observed in samples LJ22, 16, 11, 26 and 10 is in accordance with their contents
316 of apatite.

317

318 **8. Mineral chemistry**

319 Four main types of sample were distinguished in the log: “barren” pyroxenite and its
320 oxide/sulphide mineralized equivalent, and “barren” gabbro and its oxide/sulphide
321 mineralized equivalent

322 8.1. Clinopyroxene

323 Clinopyroxene was analyzed in 21 samples (out of 22) and shows a wide range of
324 compositions (Table 3). In the Ca-Mg-Fe triangular diagram (not shown), clinopyroxene plots
325 in the augite field, close to the salite domain, and is marked by large Mg-for-Fe substitution.
326 The most Mg-rich clinopyroxene is found in gabbro, but there is a large compositional
327 overlap in clinopyroxene compositions from pyroxenite and gabbro (Fig. 8).

328 As regards minor elements, large variations are observed: Al_2O_3 content ranges between
329 3.04 and 1.91 wt.% and TiO_2 between 1.08 and 0.53, whereas Cr_2O_3 is generally below the
330 detection limit (around 0.01 wt.%) with a maximum of 0.06 wt.%.

331 There is a significant decrease in the Al_2O_3 and TiO_2 contents in the pyroxenites and gabbros
332 correlated to an Mg decrease (Fig. 8) but the presence of ore minerals does not seem to
333 influence the mineral composition.

334 The Mg number ($\text{Mg}/(\text{Mg}+\text{Fe})$ at. conc.) of the clinopyroxene was plotted as a function of
335 depth (Fig. 9) and two domains appear: the first, from the bottom (316 m) to 162.8 m, is
336 marked by a regular decrease in the Mg number (and a correlated drop in TiO_2 and Al_2O_3);
337 the second, observed from 162.8 m to the top, is characterized by a reverse trend occurring
338 within the pyroxenite unit with a sudden increase in the Mg number, followed by a complex
339 and irregular evolution up to the top of the pyroxenite unit. The first trend cuts across the
340 petrographic and macroscopic units described in the log, and is compatible with an
341 undisturbed fractional crystallization process. In the second domain of the section, the Al_2O_3

342 in the pyroxene seems to remain fairly constant whereas TiO_2 appears to vary erratically
343 (Fig. 9).

344 8.2. Olivine

345 Olivine was analysed in nine samples: four pyroxenites and five gabbros (Table 4). Contrary
346 to the other silicates, olivine exhibits large compositional variations within a given sample.
347 The maximum range is for the gabbro LJ28 where the Fo values range between 39.80 and
348 50.40 % (average 46.38 on 6 analytical points). In terms of average values per sample, the
349 Fo content ranges from 62.85 (lowermost olivine gabbro LJ31) to 37.2 (uppermost olivine
350 pyroxenite LJ11). There is no relationship between the nature of the host rock and the olivine
351 composition. Plotted versus depth, the Fo content tends to decrease from the bottom to the
352 marker level (discontinuity) near 163 m. The same trend is shown by the clinopyroxene
353 composition (Fig. 9). Interestingly, as with clinopyroxene, above this point the Mg number
354 increases again, suggesting that the level corresponds to a significant horizon in the
355 evolution of the complex.

356 Considering minor elements, the NiO content in the olivine appears typically low, <0.05 wt.%,
357 whereas MnO, correlated with Mg number (Fig. 10), decreases from 1.13 (Fo 40.18 %) to
358 0.36 wt.% (Fo 62.85 %).

359 The Fe-Mg distribution between olivine and clinopyroxene has been studied experimentally
360 (Perkins and Vielzeuf, 1992). The experimental curve is plotted in Figure 11, together with
361 olivine (average values) coexisting with clinopyroxene from the Lanjanina drill core. The
362 observed trend partly overlaps the experimental one, the former tends to be more Mg-rich
363 than the composition expected from equilibrium with the olivine. This suggests that there is
364 no significant re-equilibration between the silicates and the Fe-Ti oxides.

365 As mentioned above, olivine is seen either as individual subhedral crystals or as thin rims
366 between clinopyroxene – Fe-Ti-oxide or clinopyroxene – Fe-sulphide (Figs. 3I, L).
367 Heterogeneity in composition is observed within a single crystal and olivine rimming the Fe-

368 rich minerals does not show any specific Fe-enrichment that could be interpreted as
369 subsolidus re-equilibration. Olivine composition may have been locally modified at a late
370 magmatic stage but we do not have any evidence of such a mechanism.

371 8.3. Plagioclase

372 Plagioclase was analysed in three gabbros from the basal gabbro unit and in three
373 plagioclase pyroxenites and two gabbros from the pyroxenite unit (Table 5). Plagioclase
374 tends to be interstitial in pyroxenite, and to form laths in the gabbro. In some mineralized
375 facies, it also occurs as a thin rim between clinopyroxene and ore minerals.

376 Plagioclase is relatively homogeneous in composition within a single sample, but at the scale
377 of the drill core variations from An 50.22 to An 98.14 have been recorded. In greater detail,
378 plagioclase from the basal gabbro unit appears very homogeneous (An57-An58) and fairly
379 similar to plagioclase from the gabbro in the pyroxenite unit (An ca. 53), whereas interstitial
380 plagioclases in pyroxenite are more An-rich but also have more variable compositions (An
381 74.3 for sample LJ14 and An 96-97 for sample LJ12-JL13).

382 Plotted versus depth (Fig. 9), the An composition seems to reflect changes in the mineral
383 composition already observed around 163 m but there is no obvious correlation between the
384 plagioclase and pyroxene compositions.

385 8.4. Amphiboles

386 Most amphiboles derive from hydrothermal alteration of clinopyroxene, and locally their
387 proportion may exceed that of clinopyroxene. As a result, they are calcic ferromagnesian
388 amphiboles and various compositions have been obtained in the magnesiohornblende and
389 tschermakite fields, corresponding to various Si/Al ratios. Some are locally enriched in TiO₂
390 (up to 2.85 wt.%). Rare magmatic amphiboles have been observed, occurring as colourless
391 interstitial crystals, with a composition close to the actinolite-tremolite boundary.

392 8.5. Apatite

393 Apatite was analysed in the two samples where it is most abundant (Table 6). Their
394 composition is relatively homogeneous, and at the crystal scale no zoning was observed.
395 The major-element content is similar in the two samples (P_2O_5 around 42.2 wt.% and CaO
396 55.9-56.5), with FeO ranging between 0.5 and 0.35 wt.%, and MnO, MgO and SrO remaining
397 close to the detection limits of 0.15, 0.05 and 0.05 wt.% respectively. A slight difference
398 appears in the halogen contents with an X^F value of 1.21 for sample LJ19 and 0.90 for LJ22.
399 The presence of REE (La, Ce, Pr, Nd, Sm, Eu, Gd and Dy) was tested with a detection limit
400 of 0.05 % for the rare-earth oxides; only Pr appears to be above the detection limit (Pr_2O_3
401 ranging between 0.15 and 0.2 wt. %).

402 8.6. Fe-Ti oxides

403 Magnetites were analysed in homogeneous areas devoid of ilmenite and spinel exsolution.
404 Their compositions are quite homogeneous and no evolution with depth is observed (Table
405 7). They are characterized by low TiO_2 (less than 1 wt. %), Al_2O_3 (0 to 1.32 wt. %) and Cr_2O_3
406 (0 to 0.87 wt. %) contents, whereas V_2O_3 ranges between 0.36 and 2.45 wt. %.

407 Like titanomagnetite, ilmenite (either as exsolution lamellae within titanomagnetite or as
408 discrete grains) exhibits a homogeneous composition characterized by average contents of
409 MgO and MnO of 0.84 and 0.81 wt. % respectively (Table 8). The V_2O_3 content is low,
410 between 0 and 0.35 wt. %. Cr_2O_3 is very low, and generally not detected

411 The spinel-group minerals range in composition between spinel s.s. and hercynite; their
412 $Fe^{2+}/(Fe^{2+}+Mg)$ ratios ranging between 0.48 and 0.80 (Table 9). Their ZnO contents range
413 between 1.51 and 6.92 % (avg. 2.49 %). No correlation was observed between the
414 composition of the oxides and the depth of sampling.

415

416 9. Phase proportion

417 Knowing the mineral composition (EPMA data) and the bulk analysis, we have estimated the
418 theoretical proportion of each ore mineral in the analysed samples.

419 For the oxides, the calculation is based on the following assumptions:

- 420 - All TiO_2 is carried by ilmenite (discrete crystals and exsolution in titanomagnetite); the
421 TiO_2 content of associated magnetite, about 0.50 % on average, has been neglected;
- 422 - The contents of TiO_2 , FeO , MnO and MgO in ilmenite are based on its average
423 composition obtained by EPMA analysis (Table 8);
- 424 - The proportion of FeO in the bulk analysis due to the titanomagnetite contribution has
425 been estimated on the basis of the relative proportion of V_2O_3 (magnetite being the
426 only V carrier). The contents of FeO and V_2O_3 in magnetite are estimated on the
427 basis of its average EPMA analyses (Table 7).

428 The estimated proportions of ilmenite and magnetite are reported in Table 10.

429 For the Fe-Cu-Ni sulphides (pyrrhotite, chalcopyrite and pentlandite):

- 430 - All sulphur is distributed between these three minerals. The amount of sphalerite and
431 other minerals is considered to be negligible;
- 432 - The composition of the sulphides corresponds to the theoretical composition
433 (chalcopyrite – 34.63 wt. % Cu, 30.43 wt. % Fe, 34.94 wt. % S; pentlandite – 32.56
434 wt. % Fe, 34.21 wt. % Ni, 33.23 wt. % S; pyrrhotite – 62.33 wt. % Fe, 37.67 wt. % S).

435 S was first distributed to chalcopyrite and pentlandite. The remaining sulphur was then
436 attributed to pyrrhotite. The estimated proportions of the main sulphides are reported in Table
437 10.

438 Similarly, based on the average composition of apatite (P_2O_5 : 42.2 wt. % and CaO : 56.2 wt.
439 %, Table 6), and assuming that all P is contained in this mineral, the calculated amount of
440 apatite ranges between 0.05 and 5.7 % in the 15 analysed samples. The silicate proportion is
441 estimated by difference to total 100 %.

442

443 **10. Discussion**

444 10.1. Emplacement and differentiation

445 The 320.7 m of the Lanjanina drill core approximately correspond to the true thickness of the
446 cumulate pile sampled, which is very small compared to the whole Itsindro complex, whose
447 outcrop area is about 40 x 8 km. Moreover this drill core, emplaced on geophysical and
448 geochemical anomalies, cannot be representative of the whole complex, although it
449 constitutes a key zone for understanding the mineralizing processes.

450 The drill core consists of a 254-m-thick pyroxenite unit resting on a gabbro unit (of unknown
451 thickness) and overlain by 19 m of granite, capped by a weathered gabbro unit. Ore minerals
452 are found throughout the drill core but are concentrated in a 19 m-thick zone near the top of
453 the pyroxenite unit. We clearly see that although the dominant facies in the Itsindro complex
454 is a gabbro, the Lanjanina section is dominated by pyroxenite.

455 Pyroxenite occurrences are interlayered in the basal gabbro, as are gabbro horizons in the
456 pyroxenite unit. The upper third of the pyroxenite unit is cut by granitic dykes, which seem to
457 be feeders for the upper granite unit. A magmatic layering is locally observed, but at the
458 scale of the core mineral layering is generally lacking and most facies are isotropic.

459 Mineral chemistry indicates that the rocks are highly differentiated, and in spite of their
460 relatively limited thickness, the differentiation process is observed within the core. Two zones
461 can be distinguished: from the bottom to 162.8 m, we see a decrease in the Mg number of
462 olivine (0.63 to 0.40) and pyroxene (0.72 to 0.57), and a drop in TiO_2 and Al_2O_3 for the latter.
463 This evolution cuts across the petrographic and macroscopic units described in the log and is
464 compatible with an undisturbed fractional crystallization process. This suggests that the basal
465 gabbro unit and the bottom half of the pyroxenite unit belong to the same magmatic system.
466 A reverse trend is then observed above the 162.8 m level, within the pyroxenite unit, followed

467 by a complex and irregular trend in the Mg number of olivine (0.53 to 0.37) and pyroxene
468 (0.68 to 0.61). In the upper part of the drilled section, Al_2O_3 in pyroxene seems to remain
469 fairly constant whereas TiO_2 seems to vary erratically. This reversed and disturbed trend
470 could reflect physical and/or chemical disturbances in the magma chamber, such as the
471 incorporation of a less differentiated magma and seems to be marked by the local presence
472 of gabbro. Note that the main mineralized zone is located in this upper part of the unit, about
473 70 m above the marker level. Duchesne et al. (2006) invoke such an inverse evolution
474 resulting from crystallization downwards from the roof in the case of the Fedorivka layered
475 intrusion.

476 The silicate composition is not related to the content of ore minerals, Fe-Ti oxides or Fe-Cu-
477 Ni sulphides, suggesting that the magmatic system is relatively independent of the
478 mineralizing systems and that they are all in equilibrium. Thus, the mineral composition
479 suggests that the magmatic pile corresponds to two magmatic cycles in a single magma
480 chamber.

481 10.2. Ore mineral composition

482 Fe-Ti oxides have an almost constant composition throughout the drill core. Titanomagnetite
483 everywhere contains ilmenite exsolutions resulting from subsolidus re-equilibration. In most
484 cases the ilmenite and titanomagnetite crystals are adjacent, suggesting a genetic link
485 between them. Their contacts are irregular, with complex interfingerings of magnetite into
486 ilmenite (defined as symplectite, see McEnroe et al., 2000), with the systematic presence of
487 Al-Zn spinel surrounding the interfingered magnetite. Al spinel is also common as exsolution
488 lamellae in magnetite. Magnetite is characterized by a high V-content (up to 1.7 % V) which
489 according to Duchesne et al. (2006) is an indication of a high V^{3+} content in the melt,
490 revealing crystallization under low $f\text{O}_2$ conditions Unlike ilmenite in anorthosite-related
491 deposits (where ilmenite is an early liquidus phase crystallizing after plagioclase), which have
492 a high MgO content (2.5 - 4.0 wt.% for example in the Tellnes Fe-Ti deposits, Charlier et al.,
493 2007), ilmenite from the Lanjanina area has a low MgO content (< 1.5 wt.%, except in one

494 basal gabbro where it reaches 2.7 wt.%). The low MgO is consistent with the derivation of
495 the Fe-Ti oxide from a fairly evolved Fe-rich Mg-poor liquid, MgO in ilmenite being directly
496 related to the Mg number of the magma (Charlier et al., 2007).

497 Fe-(Cu-Ni) sulphides were not analysed with the EPMA, but only qualitatively characterized
498 using an SEM equipped with an EDS detector. During this checking, we found small
499 molybdenite crystals included in the Fe-Cu-Ni sulphides. In most cases they take the form of
500 elongated particles, 10 x 2 μm . In almost every case, a very small rheniite grain is adjacent to
501 the molybdenite flakes or interlayered in the molybdenite structure. Owing to the size of both
502 minerals, EPMA analyses were not possible. However, qualitative analyses enabled the
503 detection of Re in solid solution in molybdenite. Rheniite and Re-rich molybdenite are typical
504 of certain porphyry-type ore deposits and sublimes derived from volcanic gases. Obviously
505 we are in a very different setting here, and although molybdenite is a common mineral in
506 magmatic Ni-Cu sulphides in mafic-ultramafic environments (Garuti et al., 2001; Helmy,
507 2004), as far as we know rheniite has never been described in a similar context.

508 In the magmatic sulphide deposit in Wetlegs, Duluth Complex, occurrences of molybdenite
509 associated with Co-Ni arsenides are interpreted as proving the presence of hydrothermal
510 fluids related to country-rock assimilation (Raic et al., 2015). The molybdenite-rheniite
511 assemblage described here shows some similarities with occurrences described by
512 Voudouris et al. (2009) in a porphyry-type Mo-Cu prospect in northern Greece. The authors
513 suggested that rheniite and molybdenite coprecipitated from a vapour phase. The close
514 relationships between them could suggest that the Re sulphide may have exsolved from the
515 Mo sulphide, but detailed examination of the SEM images (Figs. 4H, I), and rare occurrences
516 of rheniite without molybdenite preclude this possibility.

517 10.3. Ore mineral texture

518 A typical net texture characterizes the mineralized samples. This texture, very common in
519 magmatic sulphide ores, has also been recognized in many Fe-Ti oxide deposits. Wang and
520 Zhou (2013) suggested that net-textured ores formed from immiscible Fe-Ti-(P)-rich melts

521 segregated from an evolved magma. Using 3-D CT reconstruction, Liu et al. (2014)
522 demonstrated that in the net-textured ores, Fe-Ti oxides form an interconnected network
523 enclosing silicate cumulates, as a result of the crystallization of Fe-Ti oxides from an Fe-Ti-
524 rich liquid percolating throughout an unconsolidated silicate pile.

525 Wang and Zhou (2013) underlined the analogy between sulphide and Fe-Ti net-textured
526 ores. There is however a major difference: in the case of sulphide ore, it is accepted that the
527 Fe-Cu-Ni sulphides crystallized directly from an immiscible sulphide liquid, whereas given the
528 existence of an immiscible Fe-Ti-rich melt percolating through the silicates, the Fe-Ti oxides
529 must crystallise from this magmatic liquid and be segregated in the interstices between the
530 silicates; the residual liquid must then be evacuated, probably through a filter-press process.
531 The special feature of the Lanjanina net-textured ore is its association of Fe-(Cu-Ni)
532 sulphides and Fe-Ti oxides within the same facies.

533 An alternative hypothesis has been proposed to explain the typical net-texture of the Fe-Ti
534 oxides. This model considers that the Fe-Ti oxides are cumulus minerals crystallized from a
535 Fe-Ti-P- rich magma, the net-texture resulting from sub-solidus reequilibration of the oxides
536 (see Duchesne, 1996; 1999; Charlier et al., 2015). These authors suggested that high
537 temperature deformation enhances the process. This model was developed for Fe-Ti
538 deposits in anorthosites where deformation is related to the diapiric emplacement of the
539 anorthosite plutons. In the specific case of the Lanjanina mineralisation we do not have
540 evidences of deformation features such as the strongly foliated rocks commonly described in
541 anorthosite bodies (Charlier et al., 2015). Net-textures similar to textures described for Fe-Ti
542 oxides are very common in chromite ore from stratiform (Bailly et al., 2011) or ophiolite
543 complexes (Cassard et al., 1981) where subhedral chromite crystals fill interstices between
544 undeformed olivine crystals. This texture is interpreted as a primary magmatic texture and we
545 favour the same origin for the net texture of the Lajanina mineralization.

546 10.4. The Fe-Ti-P mineralization and the immiscibility question

547 Horizons of gabbro mineralized by Fe–Ti-(V) oxides and apatite are commonly observed in
548 layered intrusions of various types, such as the Bushveld (Eales and Cawthorn, 1996),
549 Skaergaard (McBirney, 1975), Duluth (Ripley et al., 1998), Bjerkreim-Sokndal (Duchesne
550 and Charlier, 2005), Panzihua (Zhou et al., 2005), and Sept-Iles (Namur et al., 2012).
551 Ferrogabbros with large Fe-Ti-(V) deposits are also commonly associated with massif-type
552 anorthosites (Duchesne, 1999; Duchesne et al., 2006; Charlier et al., 2015).

553 Several hypotheses have been proposed for their origin. Cawthorn and Ashwal (2009) listed
554 five possible mechanisms from the literature to account for the formation of the magnetite
555 layers in the Bushveld Complex: liquid immiscibility (Reynolds, 1985); magma addition and/or
556 mixing (Harney et al., 1990); settling and sorting of minerals (Wager and Brown, 1968);
557 change in oxygen content (Klemm et al., 1985); and changes in pressure (Cawthorn and
558 McCarthy, 1985). They concluded that liquid immiscibility cannot be the operating process,
559 because this process cannot generate monomineralic layers with a sharp contact to the
560 underlying anorthosite. They favour changes in pressure to explain the origin and
561 characteristics of the layers of magnetite.

562 Charlier et al. (2008) considered that the Fe-Ti-P ores in the Grader intrusion (Havre-Saint
563 Pierre Anorthosite, Quebec) represent cumulates rather than crystallized Fe–Ti–P-rich
564 immiscible melts and resulted from successive appearances of a liquidus phase in a
565 fractional crystallization process, followed by gravitational segregation. They concluded that
566 there is no evidence for an origin of the oxide ore by liquid immiscibility.

567 On the other hand, based on mineralogical and textural constraints Wang and Zhou (2013)
568 considered that the Fe-Ti oxide deposit in the Panxi region (SW China), occurring in
569 plagioclase pyroxenite, had formed from an Fe-Ti-(P)-rich melt segregated from a
570 differentiated ferrobaltic magma as a result of liquid immiscibility. The mineralization
571 consists of titanomagnetite, ilmenite and apatite interstitial to clinopyroxene and plagioclase,

572 forming a net texture. They emphasized the similarity between this texture and the magmatic
573 sulphide ores.

574 The question of liquid immiscibility has also been highlighted by the study of melt inclusions.
575 Fe- and Si-rich liquids are known as inclusions trapped in apatite and olivine in the Upper
576 Zone of the Skaergaard intrusion, showing signs of liquid immiscibility in the late-stage
577 evolution of the magma. Jacobsen et al. (2011) conclude that a significant part of the
578 Skaergaard intrusion crystallized from an “emulsion” of Fe- and Si-rich immiscible melts, and
579 explained the heterogeneous composition of the melt inclusions in plagioclase from the
580 Lower Zone by the entrapment of various proportions of Si-rich and Fe-rich liquid. In the
581 Upper Zone, most of the inclusions in apatite are composed of end-member liquids. Metre-
582 sized pods and layers of melanogranophyre in the upper part of the intrusion are believed to
583 represent pooled bodies of the immiscible Si-rich liquid.

584 If we accept the existence of liquid immiscibility, the question then becomes the mode of
585 segregation of the two liquids. Charlier et al. (2011) and Jakobsen et al. (2011) considered
586 that evolved Fe–Ti–P gabbros from the Skaergaard and Sept-Iles layered intrusions have
587 crystallized from a “liquid emulsion”. For Namur et al. (2012) the question concerning the
588 origin of these rocks is not whether they are “cumulates” or “solidified immiscible liquids” but
589 whether they are cumulates formed from a homogenous melt or from a mixture of two
590 immiscible liquids.

591 Charlier et al. (2015) in a review paper describing Fe-Ti-V-P ore deposits in anorthosites
592 listed five possible ore-forming processes: (1) fractional crystallization, crystal sorting and
593 plagioclase buoyancy, (2) immiscibility, (3) magma mixing (4) filter-press compaction and (5)
594 hydrothermal remobilization. They concluded that immiscibility of an Fe-Ti-(P)-rich melt
595 should be more carefully examined. Duchesne and Liégeois (2015) suggested that high REE
596 values in whole rocks and apatites in the Hestnes deposit (Rogaland anorthosite province,

597 Norway) coexisting with high values of Cr in magnetites indicates that the Hestnes cumulates
598 were derived from an Fe-rich liquid resulting from an immiscibility process.

599 What are the main evidences in the Lanjanina mineralisation in favour of one of these five
600 processes? The very high proportion of Fe-Ti oxide is compatible with fractional
601 crystallization and crystal sorting, but the lack of anorthosite in the Itsindro complex does not
602 permit us to invoke plagioclase buoyancy. Trends in the evolution of the mineral composition
603 in the cumulate pile could suggest magma mixing, but since the ore minerals are distributed
604 along the section, such a process cannot be responsible for the formation of the Fe-Ti
605 oxides. Filter pressing can be invoked as a mechanism causing the removal of trapped
606 interstitial liquid but cannot have a major role in the mineralizing process. Finally we have no
607 evidence of hydrothermal remobilization.

608 Thus, with reference to some of the literature data we favor the hypothesis of immiscibility
609 between two silicate melts with (1) an Fe-Ti-(P)-rich liquid crystallizing to form the
610 ferrogabbro and the ferropyroxenite, plus the Fe-Ti oxides and apatite, and (2) an Si-rich
611 liquid taking the form of granitic dykes, intruding the top 120 m of the pyroxenite unit (like the
612 granophyre veins in the Skaergaard Intrusion) and forming a sill or layer. The separation of
613 the two immiscible liquids must have been facilitated by the density contrast between the
614 heavier, Fe-rich liquid and the lighter Si-rich viscous one. The Fe-Ti-(P)-rich liquid will
615 undergo fractional crystallization and crystal sorting, leading to the abnormally high
616 concentration of apatite and Fe-Ti oxides. This model also provides an explanation for the
617 presence of Si-rich dykes in the gabbro and pyroxenite units.

618 Accepting that the Lanjanina sequence corresponds to the two end-members of the
619 immiscibility process, nothing explains the mechanism leading to the formation of Fe-
620 sulphide. Such a high proportion of disseminated and locally sub-massive sulphides must be
621 the crystallization product of a sulphide liquid, and such a liquid must result from immiscibility
622 between sulphide and silicate liquids. Mechanisms leading to the formation of an immiscible

623 sulphide liquid are well documented *e.g.*, Naldrett, 1981, 1989; Leshner, 1989. In such a
624 context, *i.e.*, an evolved magma, an S enrichment in the magma attributable to crustal
625 contamination must be envisaged but has not so far been demonstrated.

626 10.5. Sulphide immiscibility in an Fe-Ti-P liquid: evidence from the Duluth Complex as a possible
627 analogue

628 Although occurrences of apatite Fe-Ti-rich oxide rocks (“nelsonites”) are common in gabbroic
629 and ultramafic rocks, the complex association of apatite, Fe-Ti oxide, Fe sulphide and mafic
630 silicates observed in the Lanjanina drill hole is fairly uncommon. As far as we know, however,
631 the occurrence of apatite- and Fe-Ti oxide-rich rocks containing sulphide minerals in
632 amounts up to several volume percent has been described only in the Boulder Lake area in
633 the Southern part of the Duluth Complex. In this complex, apatite and Fe-Ti oxide minerals
634 are also found in the massive sulphide mineralization at the Babbitt deposit. These
635 occurrences led Ripley et al. (1998) to compare the two types of mineralization and to
636 speculate about their origin.

637 The Boulder Lake area is composed of several intrusive bodies in the troctolitic rocks of the
638 Duluth Complex. These intrusions are either apatite- and Fe-Ti oxide-rich ultramafic bodies
639 or apatite-poor oxide-rich ultramafic bodies, both showing the same geometry and position.

640 The intrusions range from lenses up to 25 m in thickness to large ovoid bodies as much as
641 500 x 150 x 200 m in size. The ultramafic facies are composed of olivine and pyroxene, in
642 various proportions from dunite to pyroxenite, with local gradations between both. Apatite
643 content ranges from 2 to 30 % and Fe-Ti oxides from 10 to 25 % with a few massive oxide
644 zones up to 40 m thick. Ilmenite is generally the dominant oxide, always accompanied by
645 titanomagnetite. Plagioclase accounts for less than 10 % in most Fe-Ti oxide ultramafic
646 intrusions, but may reach 50 % in oxide-rich troctolitic portions. Sulphide minerals are found
647 as interstitial phases or as inclusions in apatite and silicates. Accessory minerals include Zn-
648 rich hercynite, biotite, zircon and baddeleyite; alteration minerals include chlorite, serpentine
649 and actinote.

650 The Babbitt area, located in the north of the complex (about 60 km N of the Boulder Lake
651 area) contains a vein-like massive sulphide mineralization (with pyrrhotite, cubanite and
652 chalcopyrite) known as the Babbitt deposit. It is also characterized by the presence of apatite
653 as up to 10 volume % of euhedral crystals. The nature of the apatite, included in massive
654 sulphide, is identical to that in Fe-Ti oxides from the Boulder Lake area. Moreover the
655 minerals found in the massive sulphide mineralization at Babbitt are identical to those found
656 in the nelsonite occurrences in the Boulder Lake area, but in different proportions: ilmenite,
657 magnetite, Zn-hercynite, biotite, zircon and baddeleyite occurring as accessory minerals.

658 For Ripley et al. (1998), the presence of rounded sulphide droplets in apatite and oxide as
659 well as interstitial grains of sulphide in a framework of oxide and apatite crystals suggest that
660 an immiscible sulphide liquid accompanied the apatite-oxide liquid, which itself is most
661 consistent with an origin through Fe-Ti-P liquid immiscibility. The fact that both the nelsonite
662 and sulphide occurrences contain accessories such as biotite, Zn-rich spinel, zircon and
663 baddeleyite suggests that small amounts of incompatible elements may be found in both
664 immiscible sulphide and Fe-Ti-P liquids

665 Ripley et al. (1998) concluded that the apatite-bearing sulphide mineralization at Babbitt and
666 the sulphide-bearing apatite-Fe-Ti oxide rock occurrences at Boulder Lake represent end
667 members of immiscible liquids formed during crystallization of tholeiitic magmas, most likely
668 in the presence of a volatile phase. Nelsonite at Boulder Lake and massive sulphide at
669 Babbitt are associated with a ferrogabbro host rock and derivation of each type of
670 mineralization from such a parental melt is a strong possibility, but the nature of the parental
671 magma from which the immiscible liquids were derived remains poorly constrained.

672 The Lanjanina mineralization probably represents the same processes but with sulphide
673 immiscibility occurring within the oxide-apatite rich liquid. The sulphide composition,
674 dominated by Fe-sulphide, confirms that S immiscibility occurred in an evolved liquid, having
675 a composition close to the Fe-Ti-P gabbro, strongly impoverished in Ni and Cu.

676 The geology of the Itsindro gabbro massif is poorly constrained, and we have no field
677 observations showing the relationships between the “Lanjanina” facies and the other gabbro
678 facies. The geochemical and geophysical exploration campaign conducted in the Itsindro
679 massif enabled evaluation of the extensions of two anomalies caused by the sulphide and
680 Fe-Ti-P mineralization, covering an area of a few ha. Only the southern one (Lanjanina) was
681 drilled.

682 We speculate that these two anomalies trace the outline of the Lanjanina facies,
683 corresponding to a quite limited volume at the scale of the Massif. Thus, by analogy with the
684 Duluth Complex’s Boulder Lake area, it is suggested that the Lanjanina type ultramafic
685 mineralized facies form intrusive bodies within the gabbroic rocks corresponding to a specific
686 magmatic evolution.

687 10.6. Contamination and S immiscibility

688 A common feature for a large number of sulphide deposits is the presence of graphite
689 associated with ore, with graphite-sulphide-bearing schist in the vicinity of intrusions (Boyd
690 and Mathiesen, 1979; Mainwaring and Naldrett, 1977; Peltonen, 1995).
691 Assimilation/contamination processes, and in particular assimilation of graphite-sulphur-
692 bearing rocks, appear to be important in the formation of sulphide ore deposits (Naldrett,
693 1999), because of the modifications of magmatic processes they imply. Note however that
694 graphite can also be a primary magmatic phase precipitated from the partially outgassed
695 residual liquid trapped between silicate crystals, when saturation of the liquid in carbon is
696 reached (Pineau et al., 1987). This process of crystallisation of graphite under magmatic
697 conditions from a carbon outgassed melt is also applicable to mineralised samples. The role
698 of the host-rock is important because the carbon contamination of magma enhances the
699 crystallisation of graphite from the residual (Pineau et al., 1987). Study of carbon isotopes
700 allows the contribution of contamination to be established (Lerouge et al., 2001).

701 The strong sulphide enrichment in the Lanjanina area associated with highly differentiated
702 facies must arise from the incorporation of S from the country rock. This is clearly not the
703 case, for example, for the PGE-poor Fe-Ni-Cu sulphides described as tiny blebs (1 to 3 vol.
704 %) in Fe-Ti oxide-bearing layered intrusions in the Tarim igneous province, NW China, for
705 which a mantle origin has been demonstrated, with sulphide saturation occurring at a late
706 stage of the fractional crystallization process (Cao et al, 2016).

707 The host "*schisto-quartzo-calcaire*" series is the probable source of the S contamination. We
708 have no evidence however that the molybdenite, associated with the sulphides, reflects this
709 contamination episode. Moreover Re, almost systematically associated with molybdenite in
710 the form of rheniite, is generally interpreted as evidence of a magmatic hydrothermal
711 process.

712 10.7. A tentative model

713 Several papers have recently proposed models to account for the formation of Fe-Ti oxide
714 deposits. Some are focused on the large Permian Emeishan igneous province (ELIP, SW
715 China, Liu et al., 2014; She et al., 2014; Xing et al., 2014; Zhou et al., 2005; 2008; 2013).
716 They first consider a deep-seated magma chamber into which is injected a high-Ti picritic
717 mantle-derived magma that will accumulate ultramafic minerals. The residual liquid will be
718 Fe-Ti enriched. After immiscible separation, the two magma compositions will evolve
719 separately.

720 By analogy with the ELIP, the model proposed (Fig. 12) considers a mantle-derived primitive
721 magma. This magma, stored in a deep-seated magma chamber, will crystallize ultramafic
722 cumulates. Analogues of such ultramafic facies are known in the area, such as the
723 Ambodilafa complex (Tucker et al. 2012). The residual liquid will be an evolved Fe-Ti-rich
724 magma that will continue its fractional crystallization process and generate the various
725 pyroxenite and gabbro units that form the Itsindro complex. Part of this magma (or a different
726 pulse) will have a different evolution and follow two compositional trends after immiscible

727 separation: an Si-rich magma and an Fe-Ti-P-rich, Si-poor magma. The Si-rich magma will
728 be expelled from the Si-poor melt and form syenitic and granitic dykes and lenses in the
729 complex. Owing to crustal contamination, the Fe-Ti oxide-rich magma will become enriched
730 in S, and at a certain stage of its evolution (cooling, changes in physical and chemical
731 parameters), S saturation will result in the formation of an immiscible sulphide liquid. The
732 massive crystallization of Fe-Ti oxides will drag down droplets of sulphide liquid, resulting in
733 various mineralized Fe-Ti oxide and Fe-(Cu-Ni) sulphide-rich ore types. The Fe-rich nature
734 of this evolved magma explains the composition of the Fe-Cu-Ni sulphides, largely
735 dominated by pyrrhotite.

736

737 **11. Conclusion**

738 The Lanjanina series drilled in the Itsindro Gabbro Complex corresponds to a mineralized
739 part of the complex. As such, it is not possible to extrapolate the result obtained here to the
740 whole complex. The Lanjanina series provides an illustration of complex immiscibility and
741 contamination processes. The first immiscibility affecting an evolved mafic magma results in
742 the segregation of two liquids, a “light” Si-rich magma that will tend to coalesce and be
743 evacuated through dykes (conduits) to form an upper granitic layer, and a dense Fe-Ti-rich,
744 Si-poor magma. At a certain stage, this magma will be contaminated by S. The dense
745 magma will start to crystallize according to a normal fractional crystallization process, with
746 cumulus olivine, apatite, pyroxene, and cumulus to intercumulus plagioclase. Early in its
747 evolution, S saturation will result in sulphide immiscibility, with formation of sulphide droplets.
748 Fe-Ti oxides will tend to grow on the S droplets and both heavy phases will accumulate
749 locally to form layers. The Fe-Ti-rich composition of the magma explains both the abundance
750 of Fe-Ti oxides, and the composition of the sulphide (the magma being totally impoverished
751 in Cu, Ni and PGE).

752 The mineral composition exhibits two trends in the ultramafic units. The first, observable from
753 the bottom to 163 m, reflects a normal fractionation trend, whereas the second marks an
754 abrupt change reflecting perturbations in the system. The main mineralized zone is found in
755 the second part, but there is no evidence of a link between the two.

756 By definition, the Lanjanina area is an “anomaly” in the complex (it corresponds to a
757 geochemical anomaly). The relationship between this series and the whole complex has not
758 been established. The complex has been interpreted as a series of gabbro-forming sills or
759 laccoliths in a metamorphosed sedimentary series, with at least four gabbro units. It is further
760 envisaged that the evolved mafic magma from which the Lanjanina series has been derived
761 could be related to one of these magma pulses.

762

763 **Acknowledgements**

764 We thank Guillaume Wille for the EPMA analyses obtained with the Cameca SXFive at the
765 “Plateforme analytique régionale” (BRGM - University – CNRS, Orléans), O. Rouer and D.
766 Ohnenstetter for the EPMA analyses of apatite and Prof. J.C. Duchesne, Prof. H.G. Dill and
767 an anonymous reviewer for their critical comments. The English text was edited by J.V. Guy-
768 Bray.

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929 and associated Fe-Ti-V oxide deposits, Sichuan Province, SW China. *Journal of Petrology*
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931 **List of Figures**

932 Fig. 1. Geological map of the Itremo region, showing the Itsindro gabbro and the position of
933 the LJ1 drilling (star). After Handke et al. (1999).

934 Fig. 2. Simplified stratigraphic section of the Itsindro gabbro in the Lanjanina area showing
935 the location of the analysed samples collected in borehole LJ1 (after Fournié 1970).

936 Fig. 3. Photomicrographs illustrating the rock types and ore textures of the Lanjanina
937 borehole. Vertically, same image in plane-polarized light (top) and cross-polarized light
938 (bottom). A, D Pyroxenite (sample LJ14); B, E Olivine gabbro showing a magmatic layering
939 (sample LJ30). C, F Typical net texture in an olivine pyroxenite. Opaque minerals are Fe-Ti
940 oxides (dominant) and Fe-Cu-Ni sulphides (sample LJ31); G, J Euhedral apatite enclosed in
941 ore minerals. Olivine gabbro LJ28. H, K Detail of the net-texture, with interstitial ore minerals,
942 euhedral apatite, pyroxene and olivine (sample LJ19). I, L Detail of the net texture, with
943 interstitial ore minerals, euhedral pyroxene and olivine forming a thin rim between
944 clinopyroxene and the ore minerals (sample LJ19). Scale bar is 2 mm, except for H, I, K, L
945 where it is 0.5 mm. Abbreviations: Opa undifferentiated opaque minerals, Cpx –
946 clinopyroxene, Ol – olivine, Ap – apatite.

947 Fig. 4. Scanning electron microscope images (backscattered electron mode). A, Typical net-
948 texture showing the interstitial ore minerals (euhedral Fe-Ti oxides – grey– in a Fe-Cu-Ni
949 sulphides matrix – white) surrounding cumulus silicates – black (sample LJ4); B, detail of A
950 showing the relationships between the ore minerals and the cumulus silicates; C, euhedral
951 Fe-Ti oxides (grey) enclosed in Fe-Cu-Ni sulphides (white), adjacent silicates in black
952 (sample LJ6); D. euhedral (elongated) apatite (dark grey) and euhedral Fe-Ti oxide (grey)
953 enclosed in Fe sulphide (sample LJ10); E, titanomagnetite (Mag) with ilmenite exsolutions
954 adjacent to ilmenite (Ilm). Silicate in black, sulphide droplets (BMS) in white (sample LJ12).
955 F, Detail of the complex contact between titanomagnetite (with ilmenite exsolution) and
956 ilmenite (dark grey, sample LJ12). In black, Al-Zn spinel surrounding the interfingering of

957 titanomagnetite in ilmenite. G, Detail of the complex ilmenite exsolution system in
958 titanomagnetite (sample LJ4). H, I, molybdenite (Mol) and rheniite (Re) included in pyrrhotite
959 (samples LJ10 and LJ12 respectively).

960 Fig. 5. Binary diagrams showing the correlation between major elements in pyroxenite (open
961 diamond) and gabbro (grey square).

962 Fig. 6. Binary diagrams showing the correlation between minor and trace elements in
963 pyroxenite (open diamond) and gabbro (grey square).

964 Fig. 7. Rare earth element content in selected samples of the Lanjanina bore hole. A
965 correlation of REE vs P_2O_5 , B, C and D chondrite-normalized REE patterns for gabbro (B),
966 apatite-poor pyroxenite (C) and apatite-rich pyroxenite (D). Tm is below the detection limit.
967 Normalization according to McDonough and Sun (1995).

968 Fig. 8. Plots of (A) TiO_2 in wt percent and (B) Al_2O_3 in wt percent vs. $Mg/(Mg+Fe)$ in molar
969 percent from clinopyroxenes in pyroxenite and gabbro from the Itsindro Complex.

970 Fig. 9. Clinopyroxene, olivine and plagioclase compositions along stratigraphic height. MMZ,
971 main mineralized zone, ML, marker level.

972 Fig. 10. Plot of MnO in wt. percent vs $Mg/(Mg+Fe)$ in molar percent in olivine in pyroxenite
973 and gabbro from the Itsindro Complex.

974 Fig. 11. Distribution of $Mg/(Mg+Fe)$ in molar percent between olivine and clinopyroxene.
975 Experimental values from Perkins and Viezeuf (1992).

976 Fig. 12. Schematic model showing the various liquid immiscibility processes and crustal
977 contamination leading to the formation of the complex Fe-Ti oxide Fe-(Cu-Ni) sulphide
978 mineralization in the Itsindro Complex, Madagascar.

979

980 **List of Tables**

981 Table 1

982 Characteristics of the samples analysed in the Itsindro intrusion. For Fe-Cu-Ni sulphides
983 (undifferentiated sulphides) and Fe-Ti oxides (titanomagnetite, ilmenite and spinel), the
984 number and size of “X” reflect the relative proportions of each. MMZ, main mineralized zone,
985 from 72 to 90 m in the pyroxenite unit. Stars at 162.8 correspond to the marker level. Code: 1
986 pyroxenite, 2, mineralized pyroxenite, 3 gabbro, 4, mineralized gabbro.

987

988 Table 2

989 Major and trace element compositions of selected samples from the Lanjanina borehole.

990 Table 3

991 Selected electron microprobe analyses of clinopyroxene.

992 Table 4

993 Selected electron microprobe analyses of olivine.

994 Table 5

995 Selected electron microprobe analyses of plagioclase.

996 Table 6

997 Selected electron microprobe analyses of apatite. OH calculated assuming full site
998 occupancy.

999 Table 7

1000 Selected electron microprobe analyses of magnetite. Fe_2O_3 calculated assuming
1001 stoichiometry.

1002 Table 8

1003 Selected electron microprobe analyses of ilmenite.

1004 Table 9

1005 Selected electron microprobe analyses of Al-Zn spinel. Fe_2O_3 calculated assuming
1006 stoichiometry.

1007 Table 10

1008 Calculated proportions (percent) of chalcopyrite (Ccp), pentlandite (Pn), pyrrhotite (Po),
1009 ilmenite (Ilm), magnetite (Mag), apatite (Ap) and silicates in pyroxenite and gabbro (see text
1010 for explanation).

Table1.xlsx

Stratigraphic depth (m)	Sample no.	Petrography and code	Mineralogy						ore texture	EPMA	whole-rock analyses	
			ol	cpx	plag	apatite	sulphides	Fe-Ti oxides				
MMZ	36.9	LJ3	Pyroxenite/2		X		X	XX	XXX	net-texture	X	X
	39.3	LJ4	Pyroxenite/2		X		x	XXX	XXX	net-texture	X	X
	50.7	LJ6	Pyroxenite/2		X		x	XXX	XXX	massive/net-texture	X	
	74.1	LJ8	Massive ore				x	XXX	X	massive	X	
	80.0	LJ9	Gabbro/3		X	X	x	X	XX	net-texture	X	X
	82.7	LJ10	Gabbro/4		X	X	X	XX	X	massive/disseminated	X	X
	106.5	LJ11	Pyroxenite/1	X	X		X	X	X	disseminated	X	X
Pyroxenite Unit	133.8	LJ12	Gabbro/4		X	X	x	XXX	XXX	net-texture	X	
	135.3	LJ13	Plag pyroxenite/2		X	X	X	XXX	XXX	net-texture	X	X
	140.9	LJ14	Plag pyroxenite/1	X	X	X	x	X	X	disseminated	X	X
	162.8	***** LJ16	Pyroxenite/2		X		X	X	XX	net-texture	X	X
	163.9	LJ17	Pyroxenite/2		X		X	XXX	X	net-texture	X	
	185.8	LJ19	Pyroxenite/2	X	X		X	X	XXX	net-texture	X	
	189.6	LJ20	Pyroxenite/2	X	X		X	XXX	XX	net-texture	X	X
	211.0	LJ22	Pyroxenite/2		X		X	XX	XX	net-texture	X	X
	230.5	LJ24	Pyroxenite/2		X		X	X	XX	net-texture	X	X
	260.4	LJ26	Pyroxenite/2		X		x	X	X	disseminated	X	X
	286.9	LJ28	Gabbro/3	X	X	X	x	X	X	disseminated	X	X
	Gabbro Unit	294.2	LJ29	Gabbro/4	X	X	X	x	X	XX	disseminated	X
303.2		LJ30	Gabbro/3	X	X	X	x	X	X	disseminated	X	X
309.0		LJ31	Pyroxenite/2	X	X		x	X	XXX	net-texture	X	X
316.7		LJ32	Pyroxenite/2	X	X		x	X	XX	net-texture	X	

Table2.xlsx

Sample	LJ3	LJ4	LJ9	LJ10	LJ11	LJ13	LJ14	LJ16	LJ20	LJ22	LJ24	LJ26	LJ28	LJ30	LJ31
Depth	36.9	39.3	80.0	82.7	106.5	135.3	140.9	162.8	189.6	211.0	230.5	260.4	286.9	303.2	309.0
Rock/code	Px/2	Px/2	Gab/3	Gab/4	Px/1	Px/4	Px/3	Px/2	Px/2	Px/2	Px/2	Px/2	Gab/3	Gab/3	Px/2
Major elements (wt.%)															
SiO ₂	30.80	18.00	20.40	38.70	43.00	21.20	47.20	26.10	38.40	13.30	27.90	34.40	46.70	48.20	24.70
Al ₂ O ₃	3.16	1.08	2.03	10.80	2.38	2.44	3.77	1.47	2.06	2.00	2.38	2.03	14.95	15.45	2.03
Fe ₂ O ₃	30.10	54.10	47.60	22.00	21.60	47.20	14.25	42.70	25.70	54.40	39.10	30.70	13.00	12.05	42.00
CaO	12.50	6.89	7.83	12.10	17.05	8.27	19.60	13.00	15.15	8.48	11.30	14.80	13.05	12.70	5.49
MgO	7.98	4.72	5.76	5.80	10.80	6.33	12.45	6.13	9.77	3.90	7.30	8.96	7.37	8.35	15.00
Na ₂ O	0.42	0.18	0.16	1.69	0.30	0.13	0.38	0.14	0.21	0.06	0.16	0.18	2.09	2.24	0.11
K ₂ O	0.12	0.09	0.03	0.26	0.02	<0,01	0.03	<0,01	0.01	<0,01	0.02	<0,01	0.21	0.22	0.02
TiO ₂	13.90	9.20	12.20	9.20	3.99	12.75	1.91	4.27	7.30	14.20	10.60	9.57	1.54	0.75	11.65
MnO	0.37	0.19	0.30	0.26	0.37	0.35	0.26	0.28	0.37	0.40	0.42	0.39	0.17	0.17	0.32
P ₂ O ₅	0.03	0.02	0.06	0.36	0.59	0.02	0.02	1.80	0.02	2.40	0.03	0.68	0.07	0.04	0.03
SrO	<0,01	<0,01	<0,01	0.02	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0.03	0.03
LOI	0.33	5.62	2.10	0.00	0.52	0.33	0.68	3.04	0.00	1.41	0.00	0.00	0.38	1.05	0.00
Total	99.71	100.09	98.47	101.17	100.62	99.02	100.55	98.93	98.99	100.55	99.21	101.71	99.53	101.22	101.35
Mg#	0.34	0.15	0.19	0.34	0.50	0.21	0.63	0.22	0.43	0.12	0.27	0.37	0.53	0.58	0.41
C	0.27	0.14	0.22	0.16	0.54	0.20	0.26	0.18	0.20	0.21	0.17	0.14	0.21	0.25	0.10
S	2.30	17.95	9.50	1.36	0.62	4.83	0.22	11.40	1.54	7.43	0.60	1.01	0.25	0.27	0.60
Trace elements (ppm)															
Ba	68.1	17.1	14.2	348	32.8	10.1	19.1	6.3	12.6	2.8	10.1	3.5	123	81.3	4.2
Y	10	6.5	7.4	10	18.5	8.3	17.7	22.9	12.9	20.3	9.8	17.2	10	6.3	4.7
Cr	50	80	200	100	40	310	30	80	100	160	90	60	190	30	10
Cs	0.41	0.76	0.04	0.12	0.03	0.04	0.06	0.02	0.05	0.05	<0,01	0.04	0.05	0.17	0.02
Ga	7.7	4.9	11.9	13	6.2	19.1	7.7	8.1	6.9	18.2	16.4	11	17.5	13.7	14.1
Hf	1.6	1	1.1	1.2	1.1	1.2	1.8	1	1.1	1.1	1.2	1.1	0.8	0.4	1
Nb	15.7	18.5	13.7	10.3	4.3	9.7	2.6	1.9	6.9	5.8	3	6.6	<0,2	<0,2	5.4
Rb	2.9	5.7	0.5	1.6	0.7	0.4	1	0.2	0.8	0.4	0.5	0.4	1.6	1.5	0.5

Table2.xlsx

Sr	48.1	12.8	27.3	357	51.1	18.3	52.4	44.4	28.4	41.1	19.5	33	425	412	13.5
Ta	2.6	5.6	4.1	2	1.2	2.4	1.3	0.5	1.1	1.1	0.7	1.3	0.4	0.6	1.3
Th	1.07	0.63	0.43	0.65	0.45	0.78	0.78	0.39	0.31	0.59	0.26	0.38	0.26	0.31	0.59
U	0.1	0.09	0.05	0.07	0.07	<0,05	0.17	0.14	<0,05	0.19	0.1	0.11	<0,05	<0,05	<0,05
V	544	286	754	398	264	1440	354	305	484	1150	1010	705	644	176	1270
Zr	59	36	37	39	38	42	44	31	43	37	33	41	21	11	33
As	0.5	1.4	0.2	0.3	0.2	0.1	0.1	0.5	<0,1	0.9	0.1	0.1	<0,1	0.9	0.3
Bi	0.06	1.21	0.04	0.04	0.01	0.12	0.01	0.02	0.01	0.63	0.01	0.01	0.02	<0,01	0.01
Se	1	14.4	6.2	0.6	0.5	1.6	0.3	10.6	0.7	5.5	0.4	0.8	0.2	0.3	0.3
Cd	<0,5	1.2	1	<0,5	<0,5	<0,5	<0,5	<0,5	0.5	<0,5	1	<0,5	<0,5	<0,5	<0,5
Co	105	596	305	74	70	177	47	319	84	232	89	90	59	62	193
Cu	423	5460	839	510	118	940	44	1800	549	569	117	193	47	55	134
Mo	1	5	2	<1	1	3	1	6	1	5	3	1	<1	<1	1
Ni	172	1350	711	117	77	346	34	592	102	394	62	80	46	42	22
Sc	70	49	58	56	95	64	79	75	99	50	88	100	44	33	46
Zn	101	109	219	77	84	307	57	116	91	454	218	125	70	58	201
Rare earth elements (ppm)															
La	3.7	2.2	2	3.7	4.7	2.5	3.8	8.8	2.1	10.9	1.6	4.4	2.8	1.9	1.8
Ce	8.5	4.6	4.5	8.7	12.7	5.5	10.6	23.1	5.5	27.5	4.2	11.9	6.2	3.8	3.3
Pr	1.28	0.72	0.72	1.31	2.17	0.87	1.84	3.79	1.12	4.21	0.84	2.15	0.94	0.54	0.51
Nd	6.8	3.9	4.2	7.3	12	4.8	9.6	20.9	6	22.6	5.2	11.8	5.1	3.1	2.6
Sm	2.08	1.24	1.27	2.1	4.05	1.68	3.3	5.78	2.41	5.73	1.88	3.74	1.54	0.97	0.82
Eu	1.02	0.44	0.7	1.86	1.81	0.61	1.21	2.45	1.07	2.31	0.93	1.8	1.05	0.81	0.27
Gd	2.55	1.58	1.8	2.56	5.4	1.97	4.34	7	2.99	7.22	2.58	4.69	2.08	1.41	1.11
Tb	0.42	0.23	0.26	0.34	0.69	0.29	0.62	0.91	0.46	0.85	0.36	0.66	0.35	0.26	0.15
Dy	2.21	1.25	1.45	2.11	3.93	1.88	3.97	4.87	2.65	4.39	2.34	3.69	2.14	1.32	0.96
Ho	0.42	0.24	0.29	0.38	0.76	0.35	0.68	0.86	0.51	0.79	0.39	0.68	0.38	0.21	0.17
Er	1.16	0.76	0.76	1.04	1.99	0.95	1.87	2.23	1.32	1.9	1.14	1.71	1.08	0.69	0.56
Tm	0.12	0.06	0.08	0.11	0.22	0.08	0.23	0.24	0.16	0.17	0.11	0.16	0.12	0.06	0.04
Yb	0.99	0.6	0.57	0.8	1.58	0.72	1.6	1.51	1.07	1.18	0.78	1.2	0.96	0.57	0.41
Lu	0.12	0.08	0.09	0.11	0.24	0.12	0.22	0.24	0.2	0.17	0.15	0.21	0.14	0.08	0.06
Total REE	31.37	17.9	18.69	32.42	52.24	22.32	43.88	82.68	27.56	89.92	22.5	48.79	24.88	15.72	12.76

Hg<0,005, Sn <1, W<1, Pb<2, Sb<0,05, Tl<0,02, Li<10, Ag< 0,5, Te<0,01 ppm, BaO<0,01%

Sample	LJ3	LJ4	LJ9	LJ10	LJ11	LJ13	LJ14	LJ16	LJ20	LJ22	LJ24	LJ26	LJ28	LJ30	LJ31
Depth	36.9	39.3	80.0	82.7	106.5	135.3	140.9	162.8	189.6	211.0	230.5	260.4	286.9	303.2	309.0
Rock/code	Px/2	Px/2	Gab/3	Gab/4	Px/1	Px/2	Px/1	Px/2	Px/2	Px/2	Px/2	Px/2	Gab/3	Gab/3	Px/2
Major elements (wt.%)															
SiO ₂	30.80	18.00	20.40	38.70	43.00	21.20	47.20	26.10	38.40	13.30	27.90	34.40	46.70	48.20	24.70
Al ₂ O ₃	3.16	1.08	2.03	10.80	2.38	2.44	3.77	1.47	2.06	2.00	2.38	2.03	14.95	15.45	2.03
Fe ₂ O ₃ (1)	30.10	54.10	47.60	22.00	21.60	47.20	14.25	42.70	25.70	54.40	39.10	30.70	13.00	12.05	42.00
CaO	12.50	6.89	7.83	12.10	17.05	8.27	19.60	13.00	15.15	8.48	11.30	14.80	13.05	12.70	5.49
MgO	7.98	4.72	5.76	5.80	10.80	6.33	12.45	6.13	9.77	3.90	7.30	8.96	7.37	8.35	15.00
Na ₂ O	0.42	0.18	0.16	1.69	0.30	0.13	0.38	0.14	0.21	0.06	0.16	0.18	2.09	2.24	0.11
K ₂ O	0.12	0.09	0.03	0.26	0.02	<0,01	0.03	<0,01	0.01	<0,01	0.02	<0,01	0.21	0.22	0.02
TiO ₂	13.90	9.20	12.20	9.20	3.99	12.75	1.91	4.27	7.30	14.20	10.60	9.57	1.54	0.75	11.65
MnO	0.37	0.19	0.30	0.26	0.37	0.35	0.26	0.28	0.37	0.40	0.42	0.39	0.17	0.17	0.32
P ₂ O ₅	0.03	0.02	0.06	0.36	0.59	0.02	0.02	1.80	0.02	2.40	0.03	0.68	0.07	0.04	0.03
SrO	<0,01	<0,01	<0,01	0.02	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0.03	0.03	0.00
LOI	0.33	5.62	2.10	0.00	0.52	0.33	0.68	3.04	0.00	1.41	0.00	0.00	0.38	1.05	0.00
Total (2)	99.71	100.09	98.47	101.17	100.62	99.02	100.55	98.93	98.99	100.55	99.21	101.71	99.53	101.22	101.35
FeOT	27.0842	48.6796	42.8309	19.7958	19.4359	42.4709	12.8223	38.4218	23.1251	48.9496	35.1825	27.6241	11.6975	10.8427	37.7919
Fe ²⁺	0.37696	0.67752	0.59612	0.27552	0.27051	0.59111	0.17846	0.53475	0.32185	0.68127	0.48967	0.38447	0.1628	0.15091	0.52598
Mg ²⁺	0.19792	0.11706	0.14286	0.14385	0.26786	0.15699	0.30878	0.15203	0.24231	0.09673	0.18105	0.22222	0.18279	0.20709	0.37202
Mg#	0.34428	0.14733	0.19332	0.34302	0.49754	0.20986	0.63373	0.22137	0.42951	0.12433	0.26994	0.36629	0.52891	0.57847	0.41428
C	0.27	0.14	0.22	0.16	0.54	0.20	0.26	0.18	0.20	0.21	0.17	0.14	0.21	0.25	0.10
S	2.30	17.95	9.50	1.36	0.62	4.83	0.22	11.40	1.54	7.43	0.60	1.01	0.25	0.27	0.60
Trace elements (ppm)															
Ba	68.1	17.1	14.2	348	32.8	10.1	19.1	6.3	12.6	2.8	10.1	3.5	123	81.3	4.2
Y	10	6.5	7.4	10	18.5	8.3	17.7	22.9	12.9	20.3	9.8	17.2	10	6.3	4.7
Cr	50	80	200	100	40	310	30	80	100	160	90	60	190	30	10
Cs	0.41	0.76	0.04	0.12	0.03	0.04	0.06	0.02	0.05	0.05	<0,01	0.04	0.05	0.17	0.02

Ga	7.7	4.9	11.9	13	6.2	19.1	7.7	8.1	6.9	18.2	16.4	11	17.5	13.7	14.1
Hf	1.6	1	1.1	1.2	1.1	1.2	1.8	1	1.1	1.1	1.2	1.1	0.8	0.4	1
Nb	15.7	18.5	13.7	10.3	4.3	9.7	2.6	1.9	6.9	5.8	3	6.6	<0,2	<0,2	5.4
Rb	2.9	5.7	0.5	1.6	0.7	0.4	1	0.2	0.8	0.4	0.5	0.4	1.6	1.5	0.5
Sr	48.1	12.8	27.3	357	51.1	18.3	52.4	44.4	28.4	41.1	19.5	33	425	412	13.5
Ta	2.6	5.6	4.1	2	1.2	2.4	1.3	0.5	1.1	1.1	0.7	1.3	0.4	0.6	1.3
Th	1.07	0.63	0.43	0.65	0.45	0.78	0.78	0.39	0.31	0.59	0.26	0.38	0.26	0.31	0.59
U	0.1	0.09	0.05	0.07	0.07	<0,05	0.17	0.14	<0,05	0.19	0.1	0.11	<0,05	<0,05	<0,05
V	544	286	754	398	264	1440	354	305	484	1150	1010	705	644	176	1270
Zr	59	36	37	39	38	42	44	31	43	37	33	41	21	11	33
As	0.5	1.4	0.2	0.3	0.2	0.1	0.1	0.5	<0,1	0.9	0.1	0.1	<0,1	0.9	0.3
Bi	0.06	1.21	0.04	0.04	0.01	0.12	0.01	0.02	0.01	0.63	0.01	0.01	0.02	<0,01	0.01
Se	1	14.4	6.2	0.6	0.5	1.6	0.3	10.6	0.7	5.5	0.4	0.8	0.2	0.3	0.3
Cd	<0,5	1.2	1	<0,5	<0,5	<0,5	<0,5	<0,5	0.5	<0,5	1	<0,5	<0,5	<0,5	<0,5
Co	105	596	305	74	70	177	47	319	84	232	89	90	59	62	193
Cu	423	5460	839	510	118	940	44	1800	549	569	117	193	47	55	134
Mo	1	5	2	<1	1	3	1	6	1	5	3	1	<1	<1	1
Ni	172	1350	711	117	77	346	34	592	102	394	62	80	46	42	22
Sc	70	49	58	56	95	64	79	75	99	50	88	100	44	33	46
Zn	101	109	219	77	84	307	57	116	91	454	218	125	70	58	201
Rare earth elements (ppm)															
La	3.7	2.2	2	3.7	4.7	2.5	3.8	8.8	2.1	10.9	1.6	4.4	2.8	1.9	1.8
Ce	8.5	4.6	4.5	8.7	12.7	5.5	10.6	23.1	5.5	27.5	4.2	11.9	6.2	3.8	3.3
Pr	1.28	0.72	0.72	1.31	2.17	0.87	1.84	3.79	1.12	4.21	0.84	2.15	0.94	0.54	0.51
Nd	6.8	3.9	4.2	7.3	12	4.8	9.6	20.9	6	22.6	5.2	11.8	5.1	3.1	2.6
Sm	2.08	1.24	1.27	2.1	4.05	1.68	3.3	5.78	2.41	5.73	1.88	3.74	1.54	0.97	0.82
Eu	1.02	0.44	0.7	1.86	1.81	0.61	1.21	2.45	1.07	2.31	0.93	1.8	1.05	0.81	0.27
Gd	2.55	1.58	1.8	2.56	5.4	1.97	4.34	7	2.99	7.22	2.58	4.69	2.08	1.41	1.11
Tb	0.42	0.23	0.26	0.34	0.69	0.29	0.62	0.91	0.46	0.85	0.36	0.66	0.35	0.26	0.15
Dy	2.21	1.25	1.45	2.11	3.93	1.88	3.97	4.87	2.65	4.39	2.34	3.69	2.14	1.32	0.96
Ho	0.42	0.24	0.29	0.38	0.76	0.35	0.68	0.86	0.51	0.79	0.39	0.68	0.38	0.21	0.17
Er	1.16	0.76	0.76	1.04	1.99	0.95	1.87	2.23	1.32	1.9	1.14	1.71	1.08	0.69	0.56

Tm	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Yb	0.99	0.6	0.57	0.8	1.58	0.72	1.6	1.51	1.07	1.18	0.78	1.2	0.96	0.57	0.41
Lu	0.12	0.08	0.09	0.11	0.24	0.12	0.22	0.24	0.2	0.17	0.15	0.21	0.14	0.08	0.06
Total REE	31.25	17.84	18.61	32.31	52.02	22.24	43.65	82.44	27.4	89.75	22.39	48.63	24.76	15.66	12.72
[La/Yb] _n	2.54	2.49	2.38	3.14	2.02	2.36	1.61	3.96	1.33	6.28	1.39	2.49	1.98	2.26	2.98
Eu/Eu*	1.35	0.96	1.41	2.45	1.18	1.02	0.97	1.17	1.22	1.09	1.29	1.31	1.79	2.11	0.86

Hg<0,005, Sn <1, W<1, Pb<2, Sb<0,05, Tl<0,02, Li<10, Ag< 0,5, Te<0,01 ppm, BaO<0,01%

- Below detection limit

(1) All Fe expressed in oxide form as Fe₂O₃ (2) Analytical total recalculated without C and S

[La/Yb]_n La/Yb after normalization McDonough & Sun (1995)

Eu/Eu* [(Sm x Gd)^{1/2}]/Eu_n

Table3.xlsx

Sample	LJ3	LJ4	LJ6	LJ9	LJ10	LJ11	LJ12	LJ13	LJ14	LJ16	LJ16	LJ17	LJ19	LJ20	LJ22	LJ24	LJ26	LJ28	LJ29	LJ30	LJ31	LJ32
Depth (m)	36.9	39.3	50.7	80.0	82.7	106.5	133.8	133.8	140.9	162.8	162.8	163.9	185.8	189.6	211.0	230.5	260.4	286.9	294.2	303.2	309.0	316.7
Code	2	2	2	3	4	1	4	4	3	2	2	2	2	2	2	2	2	3	4	3	2	2
SiO ₂	50.49	50.74	49.56	50.29	50.34	49.58	50.53	51.48	50.77	50.08	50.20	49.73	49.15	50.27	49.91	50.47	50.37	50.96	49.86	50.18	49.91	50.21
FeO	12.47	11.42	14.18	13.89	13.61	13.06	12.53	10.25	10.25	13.72	16.35	14.73	18.74	13.18	16.66	12.40	12.43	11.56	11.58	11.61	9.59	12.02
CaO	20.96	21.39	19.44	20.25	19.36	20.54	21.19	22.74	21.61	21.22	18.68	20.16	17.05	21.02	18.28	21.27	20.65	21.00	20.53	20.29	21.34	21.03
Na ₂ O	0.33	0.48	0.30	0.33	0.32	0.33	0.32	0.20	0.32	0.35	0.31	0.33	0.27	0.40	0.39	0.30	0.31	0.40	0.46	0.33	0.42	0.29
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.02	0.03	0.04	0.00	0.00	0.04	0.00	0.00
TiO ₂	0.95	0.93	0.87	1.03	0.88	0.90	0.82	0.36	0.84	0.94	0.74	1.00	0.55	0.68	0.77	0.72	0.62	0.75	0.91	1.68	1.19	0.67
Al ₂ O ₃	2.21	2.53	2.17	2.35	2.30	2.30	2.20	2.14	2.87	2.19	2.39	2.14	1.78	2.23	1.81	2.15	2.28	2.59	2.83	2.65	3.37	2.64
MnO	0.39	0.22	0.28	0.23	0.34	0.34	0.22	0.12	0.00	0.33	0.44	0.33	0.32	0.33	0.43	0.40	0.53	0.24	0.30	0.19	0.07	0.29
Cr ₂ O ₃	0.02	0.00	0.00	0.03	0.00	0.02	0.05	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.01	0.01
MgO	12.20	12.16	12.40	11.94	12.11	11.97	12.15	13.18	13.32	11.17	11.11	11.49	12.17	11.91	11.62	11.59	12.60	13.20	13.35	13.05	14.00	13.13
NiO	0.00	0.11	0.09	0.06	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.10	0.00	0.16	0.05	0.02	0.05	0.00	0.06	0.00
Total	100.02	100.02	99.29	100.44	99.28	99.17	100.03	100.52	100.01	99.99	100.29	99.95	100.08	100.20	99.90	99.52	99.91	100.80	99.93	100.07	99.96	100.34
Atomic concentration on the basis of 6 oxygens																						
Si	1.917	1.918	1.906	1.909	1.925	1.906	1.918	1.928	1.906	1.915	1.922	1.907	1.903	1.913	1.922	1.928	1.915	1.909	1.888	1.893	1.873	1.897
Fe	0.396	0.361	0.456	0.441	0.435	0.420	0.398	0.321	0.322	0.439	0.523	0.472	0.607	0.419	0.537	0.396	0.395	0.362	0.367	0.366	0.301	0.380
Ca	0.852	0.866	0.801	0.824	0.793	0.846	0.862	0.912	0.869	0.869	0.766	0.828	0.707	0.857	0.754	0.870	0.841	0.843	0.833	0.820	0.858	0.851
Na	0.024	0.035	0.022	0.024	0.024	0.025	0.024	0.015	0.023	0.026	0.023	0.025	0.020	0.030	0.029	0.022	0.023	0.029	0.034	0.024	0.031	0.021
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.002	0.002	0.000	0.000	0.002	0.000	0.000
Ti	0.027	0.027	0.025	0.029	0.025	0.026	0.024	0.010	0.024	0.027	0.021	0.029	0.016	0.019	0.022	0.021	0.018	0.021	0.026	0.048	0.034	0.019
Al	0.099	0.113	0.098	0.105	0.103	0.104	0.098	0.094	0.127	0.099	0.108	0.097	0.081	0.100	0.082	0.097	0.102	0.114	0.126	0.118	0.149	0.117
Mn	0.013	0.007	0.009	0.007	0.011	0.011	0.007	0.004	0.000	0.011	0.014	0.011	0.011	0.011	0.014	0.013	0.017	0.008	0.009	0.006	0.002	0.009
Cr	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000
Mg	0.690	0.685	0.711	0.676	0.691	0.686	0.688	0.736	0.745	0.637	0.634	0.657	0.703	0.676	0.667	0.660	0.714	0.737	0.754	0.734	0.783	0.740
Ni	0.000	0.003	0.003	0.002	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.003	0.000	0.005	0.002	0.001	0.001	0.000	0.002	0.000
Total	4.018	4.015	4.030	4.019	4.008	4.026	4.019	4.021	4.017	4.022	4.014	4.027	4.049	4.029	4.028	4.014	4.028	4.023	4.038	4.012	4.033	4.034
En	0.356	0.358	0.361	0.348	0.360	0.351	0.353	0.374	0.385	0.327	0.330	0.336	0.348	0.346	0.341	0.343	0.366	0.380	0.386	0.382	0.403	0.375
Fs	0.204	0.189	0.232	0.227	0.227	0.215	0.204	0.163	0.166	0.226	0.272	0.241	0.301	0.215	0.274	0.206	0.203	0.187	0.188	0.191	0.155	0.193
Wo	0.440	0.453	0.407	0.424	0.413	0.433	0.443	0.463	0.449	0.447	0.398	0.423	0.351	0.439	0.385	0.452	0.431	0.434	0.426	0.427	0.442	0.432

Table4.xlsx

Sample	LJ11	LJ14	LJ19	LJ20	LJ28	LJ28	LJ29	LJ30	LJ31	LJ32	LJ32
Depth (m)	106.5	140.9	185.8	189.6	286.9	286.9	294.2	303.2	309.0	316.7	316.7
Code	1	3	2	2	3	3	4	3	4	2	2
SiO ₂	33.49	34.37	32.50	34.09	33.48	34.63	35.31	35.41	36.53	33.90	34.39
FeO	48.63	40.35	48.96	43.54	48.13	41.24	39.05	38.00	32.61	44.94	40.83
MnO	0.98	1.05	1.48	0.87	0.70	0.39	0.44	0.52	0.25	0.63	0.52
MgO	17.04	24.47	17.05	22.06	17.84	23.24	26.43	26.85	31.37	22.54	25.82
CaO	0.02	0.03	0.00	0.00	0.04	0.04	0.02	0.02	0.08	0.01	0.03
TiO ₂	0.10	0.04	0.00	0.04	0.00	0.00	0.07	0.08	0.10	0.00	0.05
Al ₂ O ₃	0.00	0.03	0.00	0.03	0.00	0.00	0.04	0.02	0.00	0.00	0.02
Cr ₂ O ₃	0.00	0.00	0.01	0.00	0.04	0.00	0.01	0.00	0.01	0.00	0.00
Na ₂ O	0.00	0.03	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03
NiO	0.00	0.00	0.00	0.00	0.13	0.12	0.15	0.07	0.05	0.00	0.00
Total	100.25	100.37	100.03	100.65	100.39	99.73	101.54	100.96	101.00	102.03	101.73
Atomic concentration on the basis of 4 oxygens											
Si	0.999	0.982	0.980	0.986	0.995	0.997	0.985	0.988	0.990	0.972	0.968
Fe	1.214	0.964	1.234	1.053	1.196	0.993	0.911	0.887	0.739	1.077	0.961
Mn	0.025	0.025	0.038	0.021	0.018	0.010	0.010	0.012	0.006	0.015	0.012
Mg	0.758	1.042	0.767	0.951	0.790	0.997	1.099	1.117	1.268	0.963	1.084
Ca	0.001	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.002	0.000	0.001
Ti	0.002	0.001	0.000	0.001	0.000	0.000	0.002	0.002	0.002	0.000	0.001
Al	0.000	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.001
Cr	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Ni	0.000	0.000	0.000	0.000	0.003	0.003	0.003	0.002	0.001	0.000	0.000
Total	2.999	3.018	3.021	3.012	3.004	3.001	3.013	3.009	3.008	3.028	3.030
Fo	38.45	51.95	38.31	47.46	39.80	50.12	54.68	55.74	63.17	47.21	53.00

Sample	LJ9	LJ10	LJ12	LJ13	LJ14	LJ28	LJ29	LJ30
Depth (m)	80.0	82.7	133.8	135.3	140.9	286.9	294.2	303.2
Code	3	4	4	4	3	3	4	3
SiO ₂	55.26	54.70	43.91	43.52	48.62	54.60	53.01	52.84
TiO ₂	0.02	0.00	0.06	0.00	0.15	0.00	0.09	0.04
Al ₂ O ₃	28.47	28.61	35.47	35.38	31.89	28.84	29.22	28.98
FeO	0.21	0.23	0.10	0.00	0.22	0.10	0.10	0.03
MgO	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.00
CaO	10.67	10.76	19.85	19.74	15.49	11.45	12.02	12.28
Na ₂ O	5.28	5.00	0.41	0.43	2.76	4.83	4.88	4.70
K ₂ O	0.05	0.32	0.00	0.02	0.00	0.38	0.22	0.18
MnO	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.02
NiO	0.10	0.03	0.00	0.07	0.00	0.00	0.12	0.08
Total	100.05	99.68	99.80	99.17	99.13	100.22	99.67	99.14
Atomic concentration on the basis of 8 oxygens								
Si	2.488	2.475	2.038	2.033	2.245	2.461	2.413	2.417
Ti	0.001	0.000	0.002	0.000	0.005	0.000	0.003	0.001
Al	1.510	1.526	1.940	1.948	1.735	1.532	1.567	1.562
Fe	0.008	0.009	0.004	0.000	0.008	0.004	0.004	0.001
Mg	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000
Ca	0.515	0.522	0.987	0.988	0.766	0.553	0.586	0.602
Na	0.461	0.438	0.037	0.039	0.247	0.422	0.431	0.417
K	0.003	0.018	0.000	0.001	0.000	0.022	0.012	0.010
Mn	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001
Ni	0.004	0.001	0.000	0.003	0.000	0.000	0.004	0.003
Total	4.988	4.990	5.008	5.013	5.006	4.995	5.022	5.014
Ab	47.10	44.82	3.64	3.82	24.36	42.37	41.85	40.50
An	52.61	53.31	96.36	96.07	75.64	55.44	56.94	58.48

Table6.xlsx

Sample	LJ19	LJ19	LJ19	LJ19	LJ22	LJ22	LJ22	LJ22
Depth (m)	185.8	185.8	185.8	185.8	211.0	211.0	211.0	211.0
Code	2	2	2	2	2	2	2	2
P ₂ O ₅	41.87	41.56	42.08	41.50	42.42	42.07	42.43	42.32
Pr ₂ O ₃	0.17	0.21	0.23	0.17	0.13	0.16	0.19	0.20
CaO	56.19	56.33	55.91	56.23	55.52	56.07	55.47	55.58
SrO	0.06	0.05	0.07	0.06	0.02	0.07	0.07	0.09
FeO	0.14	0.08	0.18	0.11	0.00	0.12	0.10	0.00
MnO	0.00	0.00	0.00	0.00	0.02	0.00	0.08	0.00
MgO	0.06	0.05	0.00	0.00	0.06	0.05	0.03	0.04
F	2.18	2.47	2.19	2.34	1.60	1.76	1.71	1.20
Cl	0.06	0.07	0.07	0.06	0.15	0.25	0.22	0.25
H ₂ O calc.	0.74	0.59	0.73	0.65	1.00	0.89	0.93	1.16
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	101.47	101.41	101.46	101.12	100.92	101.44	101.23	100.84
O=F, Cl	0.93	1.06	0.94	1.00	0.71	0.80	0.77	0.56
Total	100.54	100.36	100.53	100.13	100.21	100.65	100.46	100.28
Atomic concentration on the basis of 25 O, OH, Cl, F								
P	5.939	5.917	5.964	5.921	6.004	5.956	6.002	5.995
Pr	0.010	0.013	0.014	0.010	0.008	0.010	0.012	0.012
Ca	10.086	10.150	10.029	10.153	9.945	10.045	9.930	9.964
Sr	0.006	0.005	0.007	0.006	0.002	0.007	0.007	0.009
Fe	0.020	0.011	0.025	0.016	0.000	0.017	0.014	0.000
Mn	0.000	0.000	0.000	0.000	0.003	0.000	0.011	0.000
Mg	0.015	0.013	0.000	0.000	0.015	0.012	0.007	0.010
F	1.155	1.314	1.160	1.247	0.846	0.931	0.904	0.635
Cl	0.017	0.020	0.020	0.017	0.042	0.071	0.062	0.071
OH	0.828	0.666	0.821	0.736	1.112	0.998	1.034	1.294
Total	18.076	18.109	18.039	18.106	17.976	18.047	17.983	17.990

Table7.xlsx

Sample	LJ3	LJ4	LJ6	LJ9	LJ12	LJ16	LJ17	LJ19	LJ22	LJ24	LJ26	LJ29	LJ32
Depth (m)	36.9	39.3	50.7	80.0	133.8	162.8	163.9	185.8	211.0	230.5	260.4	294.2	316.7
Code	2	2	2	3	4	2	2	2	2	2	2	4	2
TiO ₂	0.21	0.47	0.49	0.44	0.56	0.53	0.40	0.75	0.78	0.61	0.39	0.63	0.79
Al ₂ O ₃	0.40	0.19	0.15	0.54	0.48	0.54	0.70	0.48	0.28	0.51	0.47	0.85	0.47
Cr ₂ O ₃	0.13	0.26	0.39	0.25	0.24	0.15	0.16	0.07	0.00	0.00	0.53	0.00	0.83
Fe ₂ O ₃	66.94	66.51	66.90	66.33	66.24	67.26	66.72	66.12	66.60	66.56	65.51	64.98	63.43
FeO	31.56	31.46	31.84	31.65	31.69	31.85	31.48	31.85	31.87	31.70	31.63	31.74	31.70
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.08
V ₂ O ₃	1.51	0.89	1.21	1.10	1.25	0.41	1.01	0.81	0.63	0.63	1.82	2.20	2.43
Total	100.74	99.78	100.97	100.30	100.55	100.74	100.76	100.08	100.17	100.00	100.35	100.56	99.73
Atomic concentration on the basis of 4 oxygens													
Ti	0.006	0.014	0.014	0.013	0.016	0.015	0.011	0.022	0.023	0.018	0.011	0.018	0.023
Al	0.018	0.008	0.007	0.024	0.021	0.024	0.031	0.022	0.013	0.023	0.021	0.038	0.021
Cr	0.004	0.008	0.012	0.008	0.007	0.005	0.005	0.002	0.000	0.000	0.016	0.000	0.025
Fe ³⁺	1.920	1.929	1.917	1.909	1.901	1.929	1.910	1.908	1.923	1.923	1.884	1.859	1.833
Fe ²⁺	1.006	1.014	1.014	1.013	1.011	1.015	1.002	1.022	1.023	1.018	1.011	1.009	1.018
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.005
V	0.046	0.028	0.037	0.034	0.038	0.012	0.031	0.025	0.019	0.019	0.056	0.067	0.075
Total	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Usp (mol%)	0.006	0.014	0.014	0.013	0.016	0.015	0.011	0.022	0.023	0.018	0.011	0.018	0.023
Mag (mol%)	0.994	0.986	0.986	0.987	0.984	0.985	0.989	0.978	0.977	0.982	0.989	0.982	0.977

Table8.xlsx

Sample	LJ3	LJ4	LJ6	LJ8	LJ9	LJ11	LJ12	LJ13	LJ16	LJ17	LJ19	LJ20	LJ22	LJ24	LJ26	LJ28	LJ29	LJ30	LJ31	LJ32
Depth (m)	36.9	39.3	50.7	74.1	80.0	106.5	133.8	135.2	162.8	163.9	185.8	189.6	211.0	230.5	260.4	286.9	294.2	303.2	309.0	316.7
Code	2	2	2	2	3	1	4	4	2	2	2	2	2	2	2	3	4	3	2	2
TiO ₂	51.14	51.27	51.16	51.32	51.70	52.23	52.50	53.06	50.80	52.36	51.87	52.74	51.94	53.15	52.17	51.01	53.16	52.71	52.84	53.92
FeOt	47.31	47.71	45.68	47.68	47.11	47.01	45.17	45.25	48.01	46.50	46.60	45.63	47.38	45.16	46.38	47.86	44.67	47.13	44.27	44.86
MnO	0.83	0.62	1.05	0.48	0.63	0.71	1.01	0.73	0.76	0.78	1.19	0.85	0.90	0.88	0.80	0.57	0.70	0.78	0.69	0.00
MgO	0.53	0.32	0.75	0.47	0.62	0.63	1.39	1.08	0.58	0.65	0.82	1.37	0.58	0.82	0.76	0.35	1.20	0.65	2.65	1.62
V ₂ O ₃	0.25	0.09	0.00	0.03	0.11	0.09	0.18	0.01	0.00	0.05	0.02	0.13	0.00	0.00	0.18	0.25	0.11	0.26	0.00	0.00
Total	100.07	100.01	98.64	99.99	100.17	100.67	100.24	100.13	100.15	100.33	100.50	100.71	100.81	100.02	100.28	100.05	99.83	101.53	100.45	100.39
Atomic concentration on the basis of 3 oxygens																				
Ti	0.965	0.970	0.978	0.970	0.974	0.980	0.983	0.998	0.957	0.986	0.973	0.983	0.973	1.003	0.981	0.964	1.002	0.980	0.978	1.008
Fe ⁺³	0.065	0.059	0.044	0.060	0.049	0.039	0.030	0.004	0.086	0.028	0.054	0.031	0.054	-0.006	0.034	0.067	0.000	0.034	0.044	0.000
Fe ⁺²	0.927	0.944	0.927	0.942	0.938	0.941	0.911	0.942	0.919	0.945	0.917	0.915	0.932	0.954	0.936	0.939	0.942	0.940	0.866	0.948
Mn	0.018	0.013	0.023	0.010	0.013	0.015	0.021	0.016	0.016	0.016	0.025	0.018	0.019	0.019	0.017	0.012	0.015	0.016	0.014	0.000
Mg	0.020	0.012	0.029	0.018	0.023	0.024	0.051	0.040	0.021	0.024	0.030	0.051	0.022	0.031	0.028	0.013	0.045	0.024	0.097	0.060
V	0.005	0.002	0.000	0.001	0.002	0.002	0.003	0.000	0.000	0.001	0.000	0.002	0.000	0.000	0.004	0.005	0.002	0.005	0.000	0.000
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Ilm (mol%)	0.965	0.970	0.978	0.970	0.974	0.980	0.983	0.998	0.957	0.986	0.973	0.983	0.973	1.000	0.981	0.964	1.000	0.980	0.978	1.000
Hem (mol%)	0.035	0.030	0.022	0.030	0.026	0.020	0.017	0.002	0.043	0.014	0.027	0.017	0.027	0.000	0.019	0.036	0.000	0.020	0.022	0.000

Sample	LJ12	LJ13	LJ17	LJ19	LJ24	LJ29	LJ31
Depth (m)	133.8	135.3	163.9	185.8	230.5	294.2	309
Code	4	4	2	2	2	4	2
TiO ₂	0.00	0.29	1.98	0.44	0.00	1.97	0.36
Al ₂ O ₃	59.02	58.62	55.70	57.64	60.59	58.23	62.13
Cr ₂ O ₃	0.31	0.21	0.28	0.00	0.00	0.00	0.00
V ₂ O ₃	0.19	0.14	0.13	0.17	0.00	0.21	0.00
Fe ₂ O ₃	4.96	4.75	2.25	5.88	2.41	6.08	3.45
FeO	22.72	24.15	28.42	27.59	27.83	20.77	19.05
MnO	0.00	0.22	0.00	0.00	0.30	0.00	0.00
MgO	11.09	9.77	5.44	8.60	7.82	14.30	14.29
ZnO	1.90	2.78	6.78	1.51	1.96	1.45	1.68
Total	100.19	100.93	100.97	101.82	100.91	103.01	100.95
Atomic concentration on the basis of 4 oxygens							
Ti	0.000	0.006	0.042	0.009	0.000	0.039	0.007
Al	1.887	1.882	1.858	1.856	1.950	1.797	1.918
Cr	0.007	0.005	0.006	0.000	0.000	0.000	0.000
V	0.002	0.002	0.002	0.002	0.000	0.003	0.000
Fe ³⁺	0.101	0.097	0.048	0.121	0.050	0.120	0.068
Fe ²⁺	0.515	0.550	0.672	0.630	0.635	0.455	0.417
Mn	0.000	0.005	0.000	0.000	0.007	0.000	0.000
Mg	0.448	0.396	0.229	0.350	0.318	0.558	0.558
Zn	0.038	0.056	0.142	0.030	0.040	0.028	0.032
Total	2.999	2.998	2.999	2.999	3.000	2.999	3.000

Table10.xlsx

Sample	LJ3	LJ4	LJ11	LJ13	LJ14	LJ16	LJ20	LJ22	LJ24	LJ26	LJ31	LJ9	LJ10	LJ28	LJ30
	Pyroxenite											Gabbro			
Sulphides															
Ccp	0.12	1.58	0.03	0.27	0.01	0.52	0.16	0.16	0.03	0.06	0.04	0.24	0.15	0.01	0.02
Pn	0.05	0.39	0.02	0.10	0.01	0.17	0.03	0.12	0.02	0.02	0.01	0.21	0.03	0.01	0.01
Po	5.95	45.84	1.59	12.48	0.56	29.63	3.91	19.47	1.55	2.61	1.55	24.81	3.44	0.64	0.69
Oxides															
Ilm	27.10	17.94	7.78	24.86	3.72	8.33	14.23	27.69	20.67	18.66	22.71	23.79	17.94	3.00	1.46
Mag	7.14	3.75	3.47	18.90	4.65	4.00	6.35	15.09	13.26	9.25	16.67	9.90	5.22	8.45	2.31
Apatite															
Ap	0.07	0.05	1.41	0.05	0.05	4.30	0.05	5.74	0.07	1.63	0.07	0.14	0.86	0.17	0.10
Silicates	59.57	30.45	85.69	43.34	91.00	53.05	75.26	31.73	64.41	67.77	58.95	40.91	72.35	87.71	95.41





















