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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 ( $\text{ReS}_2$ ).  
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  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  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  $790.1 \pm 0.9$  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 km<sup>2</sup>, 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  $\mu\text{m}$ ) 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  $\mu\text{m}$ ) 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  $\mu\text{m}$  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  $\mu\text{m}$  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  $\text{TiO}_2$ ) and Fe (reported as  $\text{Fe}_2\text{O}_3$ ), 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  $\text{SiO}_2$  content of pyroxenite samples ranges between 13.3 and 47.2 wt. %. Highly variable  
253 contents of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  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  $\text{TiO}_2$   
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 ( $\text{TiO}_2$  up to 9.2 %). Two pyroxenite samples show extremely high  
259 S contents (11.4 and 17.9 %) and a  $\text{TiO}_2$  content ranging between 4.3 and 9.2 wt. %,   
260 corresponding to samples mineralized by oxides and sulphides. Some samples are  
261 characterized by  $\text{TiO}_2$  contents above 12 % (ilmenite-rich samples) and variable but high  
262 sulphide contents between 2.3 and 9.5 % (sulphide-rich samples).

263  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  are negatively correlated, sulphide-bearing samples showing the highest  
264  $\text{Fe}_2\text{O}_3$  contents (Fig. 5G).  $\text{SiO}_2$  is also negatively correlated with  $\text{TiO}_2$  although the correlation

265 is not perfect (Fig. 5B).  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  are positively correlated (reflecting the proportion of  
266 Fe-Ti oxides, Fig. 5F). Similarly, and for the same reason, MgO and  $\text{Fe}_2\text{O}_3$  are negatively  
267 correlated (Fig. 5D).

268  $\text{SiO}_2$  and MgO are positively correlated and two trends are observed (Fig. 5A). The first one  
269 is defined by pyroxenite samples characterized by an  $\text{SiO}_2/\text{MgO}$  ratio of 3.4, the second is  
270 defined by gabbro samples with a higher  $\text{SiO}_2/\text{MgO}$  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  $\text{SiO}_2$  (Fig. 5C). Both trends reflect an increasing proportion of  
273 clinopyroxene (together with a decreasing proportion of ore minerals).

274 In pyroxenite,  $\text{Al}_2\text{O}_3$  remains low, and is not correlated with the  $\text{SiO}_2$  variations. High  $\text{Al}_2\text{O}_3$   
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 %  $\text{V}_2\text{O}_3$  on average, EPMA data). A positive correlation is observed between V and  
283  $\text{Fe}_2\text{O}_3$  (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:  $\text{Al}_2\text{O}_3$  content ranges between  
329 3.04 and 1.91 wt.% and  $\text{TiO}_2$  between 1.08 and 0.53, whereas  $\text{Cr}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  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  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ );  
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  $\text{Al}_2\text{O}_3$

342 in the pyroxene seems to remain fairly constant whereas  $\text{TiO}_2$  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 TiO<sub>2</sub>  
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  $\text{TiO}_2$  is carried by ilmenite (discrete crystals and exsolution in titanomagnetite); the  
421  $\text{TiO}_2$  content of associated magnetite, about 0.50 % on average, has been neglected;
- 422 - The contents of  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{MnO}$  and  $\text{MgO}$  in ilmenite are based on its average  
423 composition obtained by EPMA analysis (Table 8);
- 424 - The proportion of  $\text{FeO}$  in the bulk analysis due to the titanomagnetite contribution has  
425 been estimated on the basis of the relative proportion of  $\text{V}_2\text{O}_3$  (magnetite being the  
426 only V carrier). The contents of  $\text{FeO}$  and  $\text{V}_2\text{O}_3$  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 ( $\text{P}_2\text{O}_5$ : 42.2 wt. % and  $\text{CaO}$ : 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  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  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,  $\text{Al}_2\text{O}_3$  in pyroxene seems to remain  
469 fairly constant whereas  $\text{TiO}_2$  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  $\text{V}^{3+}$  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  $\mu\text{m}$ . 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 sublimates 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

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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  
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953 enclosed in Fe sulphide (sample LJ10); E, titanomagnetite (Mag) with ilmenite exsolutions  
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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  
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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  
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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.

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1005 Selected electron microprobe analyses of Al-Zn spinel.  $\text{Fe}_2\text{O}_3$  calculated assuming  
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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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub>	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 <sub>2</sub> O <sub>5</sub>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub> (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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub>	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 <sub>2</sub> O <sub>5</sub>	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 <sup>2+</sup>	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 <sup>2+</sup>	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] <sub>n</sub>	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 Fe<sub>2</sub>O<sub>3</sub> (2) Analytical total recalculated without C and S

[La/Yb]<sub>n</sub> La/Yb after normalization McDonough & Sun (1995)

Eu/Eu\* [(Sm x Gd)<sup>1/2</sup>]/Eu<sub>n</sub>

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 <sub>2</sub>	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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub>	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 <sub>2</sub>	0.10	0.04	0.00	0.04	0.00	0.00	0.07	0.08	0.10	0.00	0.05
Al <sub>2</sub> O <sub>3</sub>	0.00	0.03	0.00	0.03	0.00	0.00	0.04	0.02	0.00	0.00	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.01	0.00	0.04	0.00	0.01	0.00	0.01	0.00	0.00
Na <sub>2</sub> 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 <sub>2</sub>	55.26	54.70	43.91	43.52	48.62	54.60	53.01	52.84
TiO <sub>2</sub>	0.02	0.00	0.06	0.00	0.15	0.00	0.09	0.04
Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	5.28	5.00	0.41	0.43	2.76	4.83	4.88	4.70
K <sub>2</sub> 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 <sub>2</sub> O <sub>5</sub>	41.87	41.56	42.08	41.50	42.42	42.07	42.43	42.32
Pr <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O calc.	0.74	0.59	0.73	0.65	1.00	0.89	0.93	1.16
CO <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sup>3+</sup>	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 <sup>2+</sup>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sup>+3</sup>	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 <sup>+2</sup>	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 <sub>2</sub>	0.00	0.29	1.98	0.44	0.00	1.97	0.36
Al <sub>2</sub> O <sub>3</sub>	59.02	58.62	55.70	57.64	60.59	58.23	62.13
Cr <sub>2</sub> O <sub>3</sub>	0.31	0.21	0.28	0.00	0.00	0.00	0.00
V <sub>2</sub> O <sub>3</sub>	0.19	0.14	0.13	0.17	0.00	0.21	0.00
Fe <sub>2</sub> O <sub>3</sub>	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 <sup>3+</sup>	0.101	0.097	0.048	0.121	0.050	0.120	0.068
Fe <sup>2+</sup>	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

























