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## Chemical and physical transfers in an ultramafic rock weathering profile: 2. Dissolution vs. accumulation of platinum group minerals

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1 **Revision 1 (including editorial corrections)**

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3 **Chemical and physical transfers in an ultramafic rock weathering profile: 2. Dissolution**  
4 **vs. accumulation of platinum group minerals**

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**ABSTRACT**

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The chemical weathering of ultramafic rocks has resulted in eluvial concentration of platinum-group minerals (PGM) in lateritic weathering profiles of southern New Caledonia. The Pt mineralization interpreted as being primary consists of platinum-group minerals included in chromite crystals. The occurrence of PGM as free particles in the weathering profile results from the supergene dissolution of Pt-bearing chromite (Traore et al. 2007). Following their release in the profile, supergene dissolution processes variably affect the PGM particles. The behavior of platinum-group elements in the weathering profile is characterized by significant loss of Pd and relative accumulation of Pt indicating that Pd is more mobile than Pt in the exogenous cycle. Unstable Pt-Fe-Cu-Pd alloys and PGE oxides undergo chemical and mineralogical changes to acquire the chemical configuration of the isoferroplatinum ( $Pt_3Fe$ ), which is the most stable Pt-phase in a lateritic environment. The isoferroplatinum phase may also be dispersed throughout the weathering mantle and/or accumulated in the lower parts of profiles according to a translocation mechanism of residual Pt-rich fine particles driven by percolation of water through the connected pore spaces.

*Keywords:* Platinum group minerals, platinum group elements, lateritic weathering, ultramafic rocks, New Caledonia.

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**INTRODUCTION**

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Lateritic weathering processes affect numerous regions of the intertropical zone (Pedro 1968; Nahon 1986; Tardy and Roquin 1992), where long term chemical weathering has led to the supergene accumulation of metals in profiles of 10 to 100 meters in thickness, and among them, precious metals such as Au and Pt. Previous studies concerning the behavior of Au and Pt have proven useful for tracing the geochemical evolution of lateritic weathering covers within which they are concentrated (Colin et al. 1993, 1997; Varajao et al. 2000).

Although hypotheses about the chemical mobilization of platinum-group elements (PGE) under supergene conditions are not new (Wagner 1929), the platinum-group minerals (PGM) are generally considered as resistant phases during weathering (Cabri and Harris 1975; Hattori and Cabri 1992). Much controversy remains, however, about the mobility of PGE, i.e., the geochemical and physical processes controlling their redistribution as PGM partial dissolution versus neo-formation processes in the surface-weathering environment. For example, Augustithis (1965) hypothesized the supergene formation of PGM in lateritic weathering materials from ultramafic rocks of Ethiopia. Two years later, Otteman et al. (1967) suggested that PGM formed during hydrothermal serpentinization. Over the last decades, numerous field and geochemical studies have shown the solubility of PGE in supergene environments (Bowles 1986; Middleworth and Wood 1999; Varajao et al. 2000; Azaroual et al. 2001; Oberthür et al. 2003). We investigate the geochemical behavior of the PGE and the physical-chemical processes controlling the PGM mineralogy under the influence of supergene conditions in a lateritic weathering profile from New Caledonia to characterize the dissolution and/or the accumulation of those minerals.

Previous studies at this site have shown that a lateritic mantle has developed at the expense of the primary mineralization and that it is systematically characterized by higher Pt and Pd

71 contents than the bedrock (Augé et al. 1995). The most common PGM identified in the  
72 secondary mineralization are the Pt minerals, mainly isoferroplatinum,  $Pt_3Fe$ , which  
73 represents about 60 percent of PGM (Augé and Legendre 1994). The other major alloys  
74 identified are tulameenite ( $Pt_2FeCu$ ) and tetraferroplatinum ( $PtFe$ ). Accessory cooperite and  
75 Rh-Ir-Pt-Fe oxides were also found (Augé and Legendre 1994). Previous studies at other  
76 sites have shown that PGM were, for the most part, included in chromite crystals (Augé  
77 and Maurizot 1995). A detailed mineralogical and micro chemical study of the PGM  
78 present in the weathering profile may be useful to characterize the physical and  
79 geochemical processes underlying the evolution of this profile.

#### 80 **GEOLOGICAL AND GEOMORPHOLOGICAL SETTING**

81 The Pirogues River dunite-gabbro unit of the New Caledonian Southern Massif (Fig.  
82 1) exhibits stratiform chromite-bearing rocks containing PGE at the base of a cumulate  
83 series. A lateritic weathering mantle is developed at the expense of the platinum  
84 mineralization under the influence of a warm and humid climate, which is characterized  
85 by a mean annual rainfall of 1700 mm with a wet season occurring from December to  
86 August, and a mean annual temperature of 22°C (Jaffré 1980).

87 The Pirogues River PGE mineralization (Fig. 1) is specifically related to chromitite in  
88 pyroxenite dikes crosscutting the basal ultramafic cumulate series, and in rare cases in  
89 decimetric scale chromite schlierens in the host wehrlite (Augé and Maurizot 1995).  
90 Chromitite occurs in the dikes as many local decimeter to meter scale segregations. Chromite-  
91 free facies are not mineralized in PGE. Platinum-group elements (Pt dominant) take the form  
92 of PGM that are, for the most part, included in chromite crystals (Augé and Maurizot 1995).  
93 The parent rock underwent strong lateritic weathering processes that has led to the dissolution  
94 of chromite, and thus, to the release of platinum-group minerals in the weathering mantle

95 (Traore et al. 2007). Previous studies have also shown a contrast in behavior between the  
96 PGE and chromite in the lateritic mineralization (Augé et al. 1995).

97 Natural weathering profiles exposed in deep gullies incising hillslopes. One of these  
98 profiles (also locally called “lavakas”) has been described and sampled *in situ* (Fig. 2a) for a  
99 thorough study of the PGM released in the weathering matrices. A companion paper  
100 addresses the mineralogical and geochemical nature of the profile (Traore et al. 2007). The  
101 weathering profile is developed from a wehrlite type ultramafic rock, and its thickness  
102 (to 4 m) has been divided into four main layers (Fig. 2a). At the base of the profile, the  
103 greenish-black parent rock changes to the brownish coarse saprolite that preserves the  
104 structure and the texture of bedrock. The mineralogical characterization indicates  
105 olivine, antigorite, diopside and goethite, with accessory chromite and enstatite. The  
106 coarse saprolite is progressively transformed into a fine saprolite, in which the texture and the  
107 structure of the parent rock are still preserved. The chromite grains are progressively  
108 dissolved that results in the depletion of chromium and the release of PGM (Traore et al.  
109 2007). At the top of the fine saprolite, the silicates are completely weathered into goethite.  
110 Toward the top of the profile, the fine saprolite changes to reddish laterites in which the  
111 original rock structures are no longer preserved. The mineral assemblage is dominated by  
112 goethite, with accessory hematite and chromite.

#### 113 MATERIAL AND METHODS

114 Fourteen samples of parent rock, laterite and soil were crushed and finely ground.  
115 According to the PGM-MS23 analytical procedure developed by the Australian Laboratory  
116 Services (ALS, Chemex), each prepared sample was fused with a mixture of lead oxide,  
117 sodium carbonate, borax and silica, inquarted with 6 mg of gold-free silver and then cupelled  
118 to yield a precious metal bead. The bead was digested for 2 minutes at high power by  
119 microwave in dilute nitric acid. The solution was cooled and hydrochloric acid was added.

120 The solution was digested for an additional 2 minutes at half power by microwave. The  
121 digested solution was then cooled, diluted to 4 ml with 2 % hydrochloric acid, homogenized  
122 and then analyzed for platinum and palladium by inductively coupled plasma – mass  
123 spectrometry (ICP-MS). Detection limits for Pd and Pt are 1 and 0.5 ppb, respectively.

124 Five hundred particles of PGM were extracted from three samples (1 sample = 50 kg) in  
125 different parts of the profiles (fine saprolite, mottled zone and nodular layer), before being  
126 examined by scanning electron microscopy (SEM) for morphological analysis, and by  
127 electron microprobe for micro-chemical analysis.

128 The samples were damped in a 20-liter drum, and then put in a concrete mixer to  
129 disaggregate the non-indurated nodules. The remaining non-indurated nodules were manually  
130 crushed and the resulting mix was sifted to 1 mm for eliminating fragments of rock and  
131 ferricrete prior to sorting with an automatic pan to separate out the heaviest particles. For each  
132 sample, heavy-mineral concentrates were separated into three grain-size fractions ( $< 65 \mu\text{m}$ ,  
133  $65\text{-}200 \mu\text{m}$  and  $> 200 \mu\text{m}$ ). Platinum-group mineral grains were isolated from the other heavy  
134 minerals. Because the PGM size ranges between 10 and  $40 \mu\text{m}$  (Augé and Legendre 1994;  
135 Augé and Maurizot 1995), the particle morphologies of the smaller grain-size fractions ( $< 65$   
136  $\mu\text{m}$ ) were directly examined using SEM. The fraction between 65 and  $200 \mu\text{m}$  was separated  
137 with a hand magnet into ferromagnetic and para- and non-magnetic fractions. The collected  
138 PGM grains were mounted on aluminum stubs for SEM morphoscopic examination and EDS  
139 semi-quantitative analysis.

140 Micro-chemical analyses of the PGM were made using a Cameca SX 50 electron  
141 microprobe under multiple analytical conditions in a single run. The analytical procedure was  
142 designed for routine analysis of PGM (Augé and Legendre 1992) including the quantitative  
143 analysis of oxygen. The analytical conditions (except for O) included an acceleration voltage  
144 of 25 keV, a beam current of 20 nA, and counting time of 6 s. The standards used are  $\text{Cr}_2\text{O}_3$

145 for Cr, AsGa for As, pyrite for Fe and S, stibnite for Sb, and pure metals for all other  
146 elements. The X-ray lines used were  $K\alpha$  for Ni, Cu, Cr and Mn,  $K\beta$  for Fe,  $L\alpha$  for Rh, Ir, Pt,  
147 and Ru, and  $L\beta$  for Os, Pd, and As. Oxygen was analyzed using the  $K\alpha$  line with an  
148 acceleration voltage of 10 kV. The change of acceleration voltage was made automatically  
149 during the analytical cycle. The Cameca PAP correction program was used.

## 150 **RESULTS AND DISCUSSION**

### 151 **Chemical and physical characterization of PGE and PGM**

152 **PGE bulk chemistry.** Figure 2 shows the variation of Pt and Pd contents and of  
153 the Pt/Pd ratio along the profile. Palladium concentration significantly increases in the  
154 upper fine saprolite (Fig. 2b), while Pt reaches a maximum of  $647 \mu\text{g.kg}^{-1}$  in the coarse  
155 saprolite, with a mean value of  $512 \mu\text{g.kg}^{-1}$  in the fine saprolite and decreases to  $240$   
156  $\mu\text{g.kg}^{-1}$  in the mottled zone and to  $196 \mu\text{g.kg}^{-1}$  in the soft nodular layer (Fig. 2c). The  
157 Pt/Pd ratio increases from 14 in the fresh wehrlite to 29 in the coarse saprolite, and  
158 decreases to 14 in the fine saprolite and to 10 in the mottled zone and soft nodular layer  
159 (Fig. 2d).

160 Although the absolute concentrations of Pt and Pd may not be directly comparable between  
161 the weathered profile and the parent rock, the increase of Pt/Pd ratio from the fresh rock to  
162 the saprolite and to the mottled zone (soft nodular layer being mostly a material transported  
163 mechanically on the hillslope) suggests that Pd is more mobile than Pt and dispersed  
164 chemically in the supergene environment (Fuchs and Rose 1974; Evans et al. 1994;  
165 Prichard and Lord 1994; Oberthür et al. 2003).

166 **PGM distribution and micro morphology.** Platinum-group metal distribution in the  
167 weathering profile is heterogeneous. Ninety five percent of the collected particles are in the  
168 fine saprolite, 4% in the mottled zone and only 1% in the nodular layer. Although the residual  
169 PGM particles present in the lateritic weathering profiles have various shapes and surface

170 aspects, the examination of PGM under electronic microscope allows for differentiation of  
171 three main morphological groups (Fig. 3). Euhedral PGM particles, with smooth surfaces and  
172 perfect crystal faces (Fig. 3a) are the least abundant and they are only found in the fine  
173 saprolite and the mottled zone. Rounded PGM particles are found in the fine saprolite and the  
174 mottled zone. Their crystal edges are smooth and their surfaces exhibit micrometric cracks  
175 and/or etching pits (Fig. 3b). The roughest PGM particles (Fig. 3c) were collected in the soft  
176 nodular layer and are strongly weathered. They have also been found in the fine  
177 saprolite and the mottled zone.. The size of etching pits on those particles increases from  
178 the lower to the upper horizons of the profile.

179 **Physical vs. chemical weathering signatures of PGM micromorphology.** The  
180 heterogeneous PGM distribution in the weathering profile and the significant concentration of  
181 round and rough PGM particles in the fine saprolite horizon can be explained by mechanical  
182 transfer and accumulation similar to the vertical translocation of small gold particles through  
183 relatively large porosity and higher groundwater hydrodynamic conditions (Michel 1987;  
184 Butt 1987; Colin et al. 1993; Hanlie 2000).

185 The size and shape of the cavities and/or etching pits in the PGM particles suggest that  
186 they result from a dissolution process. Deep in the saprolite, the pits are round and small; their  
187 sizes gradually increased upward in the weathering profile.

188 An additional change in PGM micromorphology consists of increasing rounding upward,  
189 from the saprolite to the soil surface. The rounding is most obvious in the mottled zone (Fig.  
190 3b) and soft nodular layer (Fig. 3c). The absence of striations and impact marks precludes  
191 smoothing by a transport mechanism. The roundness is therefore attributed entirely to a  
192 dissolution process.

193 The large cracks affecting the grains of PGM are interpreted to be a result of a change in  
194 volume due to chemical leaching in the oxidizing environment (Augé and Legendre 1994;

195 Oberthür et al. 2003). Our observations support this interpretation but the composite grains  
196 exhibit differential weathering patterns according to the PGM types. The Pt-Fe-(Cu-Pd) alloys  
197 and PGE oxides are effectively more weathered than isoferroplatinum in the lateritic  
198 weathering profiles as shown by microchemical analyses and SEM photographs (Figs. 4 and  
199 5).

200 **PGM micro chemical analysis.** Platinum-group elements of the Pirogues River lateritic  
201 mineralization zones are associated with platinum-iron alloys and oxides. A nomenclature of  
202 the PGM is proposed, based on their chemical composition and previous works (Augé and  
203 Legendre 1994; Augé and Maurizot 1995). Three species of PGM recognized are  
204 isoferroplatinum ( $\text{Pt}_3\text{Fe}$ ) that represents the majority of the PGM studied, and undetermined  
205 Pt-Fe-(Cu-Pd) alloys and PGE-oxides. See Tables 1 and 2 in the *American Mineralogist*  
206 *Online Background Dataset* for the microchemical composition of the different species of  
207 PGM.

208 The microchemical composition of isoferroplatinum is shown in Figure 4. Its Pt content  
209 varies between 58 and 69 at.%; Fe content ranges between 21 and 26 at.%; and Pd varies only  
210 from 0.2 to 2.7 at.%. While Cu does not enter in significant amounts into the isoferroplatinum  
211 composition, its content ranges from 0.2 to 4 at.%. The isoferroplatinum generally occurs as  
212 euhedral or subhedral grains (Fig. 5a), which are chemically homogeneous and form free  
213 particles, or is associated with other PGM (Fig. 5b and 5c). They may also constitute  
214 weathered rims around porous and rough particles (Fig. 6d).

215 The undetermined Pt-Fe-(Cu-Pd) alloys form euhedral and subhedral grains, and are  
216 sometimes characterized by an internal structure with concentric zoning (Fig. 6a). Another  
217 morphological type of the Pt-Fe-(Cu) system is a symplectic intergrowth with a phase that has  
218 not been preserved (Fig. 6b and 6c). The grains are isolated or associated with  
219 isoferroplatinum and/or PGM oxides in composite particles (Fig. 5b). Their reflectance is

220 lower than that of the isoferroplatinum. In many cases, the Pt-Fe-(Cu) grains present large  
221 cracks and/or weathered rims.

222 Microprobe analyses of Pt-Fe-(Cu) particles indicate a relatively wide range of  
223 compositions (Fig. 4). Platinum contents vary from 38 to 50 at.%; Fe from 20 to 28 wt.%; Pd  
224 from 1 to 12 at.%; and Cu from 12 to 26 at.%.

225 The existence of PGE-oxides has been widely established (Legendre and Augé 1993;  
226 Prichard and Lord 1994; Augé and Legendre 1994; Augé and Maurizot 1995; Jedwab 1995;  
227 Salpeteur et al. 1995; Garuti et al. 1997; Moreno et al. 1999; Hey, 1999; Oberthür et al. 2003).  
228 Platinum-group elements oxides are exceptionally abundant in the Pirogues River area where  
229 they form subhedral or rounded grains, which appear chemically heterogeneous (Fig. 7 and  
230 8). The oxidized compounds of PGE are associated with the other PGM in composites  
231 particles, or form free particles in the lateritic weathering profiles. Their reflectance is  
232 significantly lower than that of isoferroplatinum, and slightly lower than that of Pt-Fe-(Cu-Pd)  
233 alloys as shown in Figure 5b. PGE oxide particles are often cracked and/or present weathered  
234 rims (Fig. 5c and 6d).

235 Based on microprobe analyses, two compositional types of PGE oxides can be distinguished:

236 (1) Pt-Fe (Cu-Pd) oxides with Pt contents varying between 20 at.% and 46 at.%; Fe varies  
237 from 16 at.% to 30 at.%; Pd from 0 to 7 at.%; and Cu varies from 0 to 10 at.%. Representative  
238 analyses of the grains including oxygen are given in Figure 7. Oxygen contents indicate a  
239 relatively wide compositional range from 16 to 61 at.%, but with a relatively constant atomic  
240 ratio of (Pt+Pd)/(Fe+Cu).

241 (2) Rh-Ir-Pt-Fe oxides constitute small grains associated with Pt-Fe alloys and/or other  
242 PGE oxides (Fig. 5b, and 5c). Their main chemical components are Rh (12 to 36 at.%; Pt (0  
243 to 18 at.%; Ir (0 to 3 at.%; Fe (11 to 53 at.%; Pd (0 to 9 at.%). The oxygen content varies  
244 from 14 to 51 at. % (Fig. 8).

245 Detailed electron microprobe profiles have been performed on specific PGE oxides grains.  
246 The porous core of grain PGB7\_4h shows the presence of S (up to 12 at.%) (Fig. 9). The rest  
247 of the grains show significant amount of Si and Mg with 0.2 to 4 at.% and traces of Pd.

248 The frequent association of a PGE alloy and a PGE oxide suggests that the oxide does not  
249 derive from the Pt-Fe alloy. The systematic amount of S in the oxide (Fig. 9), though minor,  
250 suggests that the oxide could have been derived from a sulfide. A serpentinization process  
251 could have led to the desulfurization of primary PGE sulfides and contributed to the formation  
252 of an unstable oxidized phase (Stockman and Hlava 1984; Garuti and Zaccarini 1997). It is  
253 very likely that oxidation occurs at an early stage, as oxides are abundant in weakly weathered  
254 chromitite.

#### 255 **Selective dissolution of PGM**

256 The rough PGM grains exhibit weathering rims developed around a primary mineral.  
257 This is particularly evident in PGE oxides as well as for the undetermined Pt-Fe-(Cu-Pd)  
258 alloys, which can exhibit a weathered cortex that appears silver-white and porous on the SEM  
259 and backscattered electron imaging (Fig. 10). Microprobe analyses from the core to the  
260 weathered edge indicate a significant compositional change. The weathered rim has lower Cu  
261 content, which varies on average from 18.51 at. % in the core to 6.98 at. % in the weathered  
262 zone. Iron decreases on average from 23.32 at. % for the parent PGM to 19.96 at. % for the  
263 weathered external part. Platinum is relatively enriched and increases from 47.7 at. % to 68.18  
264 at. % from the core to the weathered edges of the grains. Palladium varies from 0.88 at. % in  
265 the core to 0.3 at. % in the weathered rim (Fig. 10).

#### 266 **Isoferroplatinum accumulation**

267 The Pt-Fe-(Cu-Pd) alloys and PGE oxides affected by the weathering process develop  
268 weathering rims, which are depleted in Cu, Pd and Fe, and relatively enriched in Pt. These Pt-  
269 minerals are thus impoverished in Cu, Pd and Fe and tend to acquire the chemical

270 composition of isoferroplatinum ( $\text{Pt}_3\text{Fe}$ ), which is a more stable mineralogical phase in the  
271 supergene environment. The weathered particles have generally preserved both the structure  
272 and the chemical signature (in the core of the grains) of the fresh PGM particles (Fig. 10).

273 This clearly demonstrates that the PGM particles are residual but are affected by dissolution.

274 The evidence of a supergene accumulation of isoferroplatinum is not new. Several field  
275 studies have reported the formation of Pt-Fe alloys of isoferroplatinum type from pre-existing  
276 unstable PGM under low-temperature conditions (Cousins and Kinloch 1976; Evans et al.  
277 1994; Salpeteur et al. 1995; Oberthür et al. 2003). Our observations indicate also that  
278 mineralogical changes occur in the supergene environment by the transformation of unstable  
279 PGM to porous and friable grains enriched in platinum as isoferroplatinum small particles that  
280 can be mechanically redistributed in the lateritic weathering profiles. Our results further  
281 indicate that Pt is dispersed mainly in particulate form by mechanical processes, whereas Pd  
282 is released mainly in solution (Wood and Vlassopoulos 1990; Cook and Fletcher 1994;  
283 Prichard and Lord 1994; Evans et al. 1994; Oberthür et al. 2003).

284

#### CONCLUSION

285 An eluvial concentration of platinum-group minerals was studied in a lateritic  
286 weathering profile, which developed at the expense of ultramafic rocks in southern New  
287 Caledonia. The PGE in the weathering profile take the form of PGM, which are mostly  
288 concentrated in the fine saprolite horizon. Our study confirms the abundance of PGE oxides  
289 in the Pirogues mineralized system and shows that they can derive from desulfurization of  
290 pre-existing PGE sulfides. Our results demonstrate that the PGE alloys of the Pt-Fe-(Cu)  
291 system and PGE oxides are weathered in a supergene environment. These PGM undergo  
292 selective partial dissolution according to a chemical eluviation gradient ( $\text{S} > \text{Cu} > \text{Pd} > \text{Fe} >$   
293  $\text{Pt}$ ) that leads to the formation of richer Pt-phases such as  $\text{Pt}_3\text{Fe}$ . The resulting  
294 isoferroplatinum grains are relatively stable regarding the supergene dissolution processes and

295 mostly transferred mechanically through the connected porosity lower in the weathering  
296 profiles, where they accumulate in a cementation zone.

297

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303

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404 **Figures Caption**

405

406 Figure 1. (a) geological map and location of studied area (after Augé and Maurizot, 1995).

407 The black star shows the location of the studied weathering profile (Fig. 2). (b) Inset of the

408 main Island of New Caledonia with its ultramafic massifs and location of (a) by the black

409 rectangle.

410

411 Figure 2. (a) Description of the weathered profile from a crosscut in a natural gully

412 (“lavaka”) and the location of studied samples (white squares). Vertical variations of contents

413 of (b) Pd, (c) Pt and of (d) ratio Pt/Pd along that profile are illustrated.

414

415 Figure 3. SEM photomicrographs of PGM grains with (a) euhedral, (b) smooth and (c) rough

416 morphologies.

417

418 Figure 4. Compositional variations in the Pt-Fe-Cu system of isoferroplatinum (black circles),

419 tetraferroplatinum (grey circles) and tulameenite (black stars). The analyses are plotted as

420 atomic percent (at%).

421

422 Figure 5. SEM photomicrographs of (a) automorphous isoferroplatinum, (b) composite PGM

423 of Pt-Fe-Pd alloy (light grey), isoferroplatinum (white) and Rh-Fe oxide (dark grey), and (c)

424 composite particle of isoferroplatinum (white), Rh-Fe oxide (dark grey) and Pt-Fe oxide.

425

426 Figure 6. SEM photomicrographs of (a) euhedral zoned Pt-Fe alloy, (b) and (c) symplectic

427 PGM composite grain, (d) PGM grain with weathering rim.

428

429 Figure 7. Compositional variation of Pt-Fe(Cu-Pd) oxides. The analyses are plotted as atomic

430 percent (at%).

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432 Figure 8. Compositional variation of Rh-Ir-Pt-Fe oxides shown in Figures 5b and 5c. The  
433 analyses are plotted as atomic percent (at%).

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435 Figure 9. Compositional variation through (a) a zoned particle with a porous core. The  
436 numbers represent the spot microanalyses given in (b). Light grey hexagons = Pt, black  
437 triangles = Fe, black circles = O, grey squares = S, and (c) grey triangles = Mg, light grey  
438 stars = Pd and black diamonds = Si.

439

440 Figure 10. Compositional variation from (a) a Pt-Fe-Cu alloy (light grey core) to a secondary  
441 isoferroplatinum (white rim). The numbers represent the spot microanalyses given in (b).

442 Light hexagons = Pt, light grey triangles = Fe, black circles = Cu and light grey stars = Pd.

443

444

445 **Table captions (for depository)**

446 TABLE 1. Microchemical composition of isoferroplatinum, tetraferroplatinum and  
447 tulameenite.

448

449 TABLE 2. Microchemical composition of platinum oxides.

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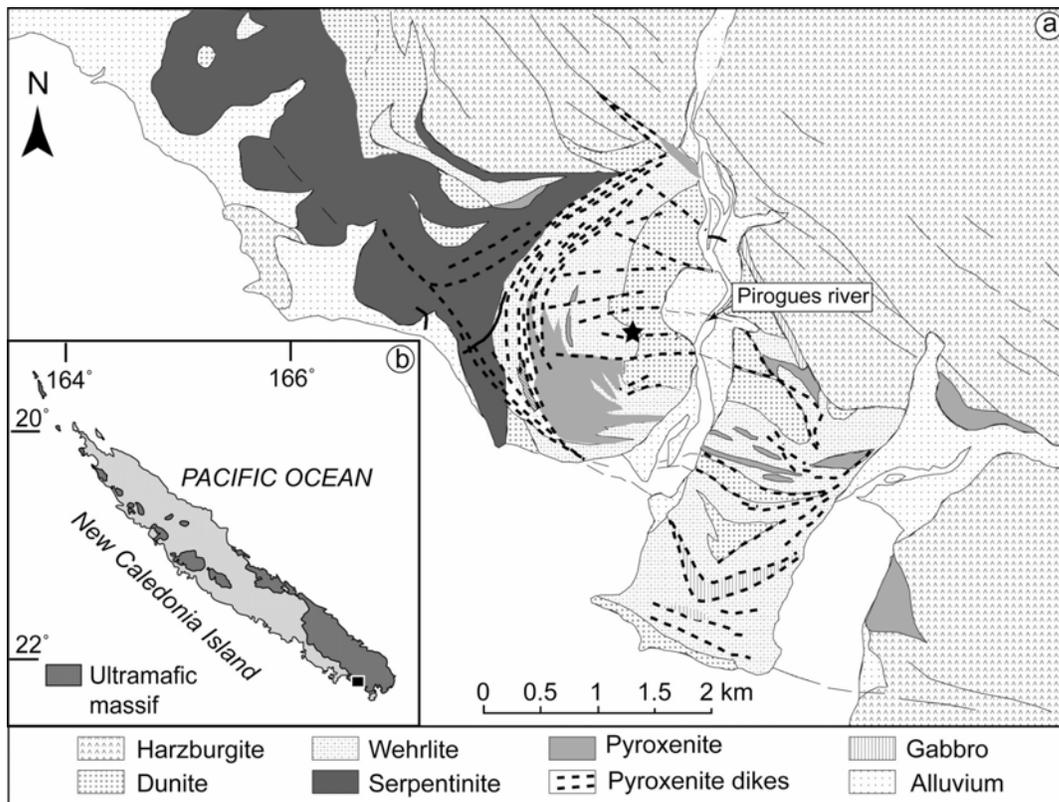


FIG. 1

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*Traore et al., 2007*

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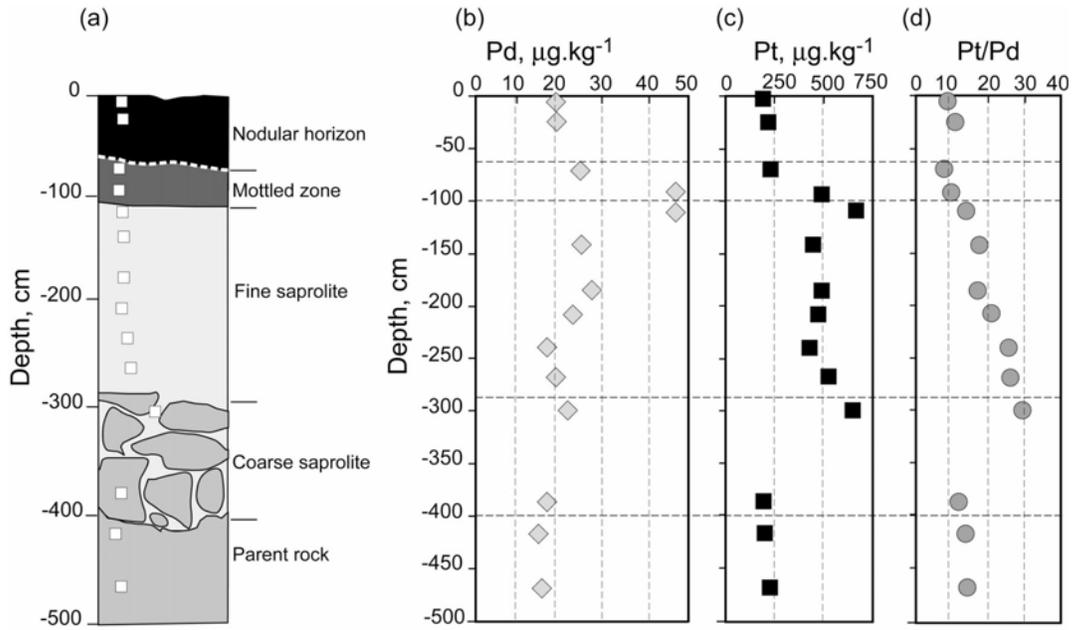


FIG. 2

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*Traore et al., 2007*

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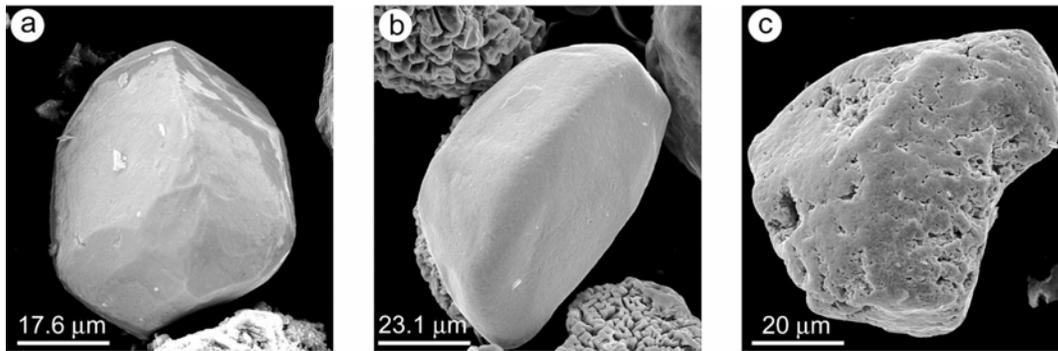


FIG. 3

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*Traore et al., 2007*

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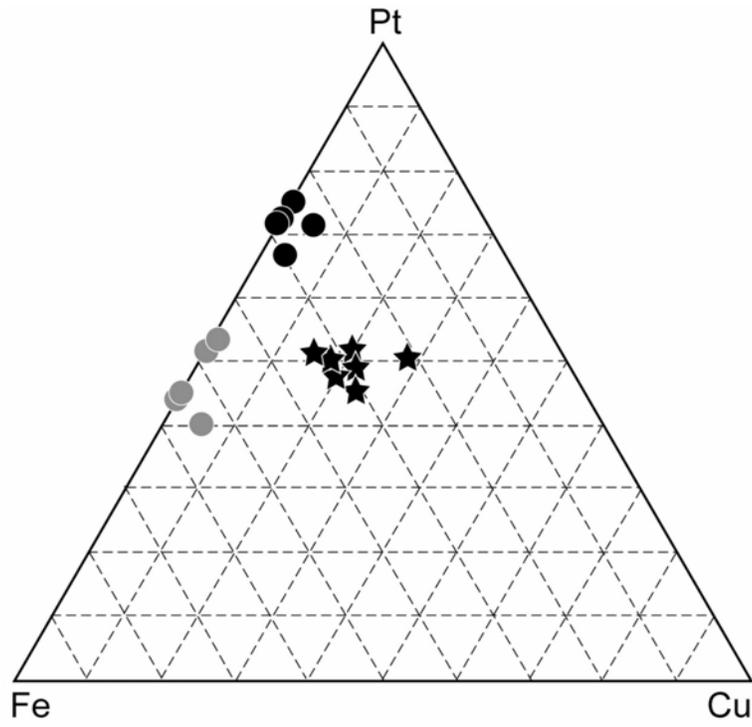


FIG. 4

*Traore et al., 2007*

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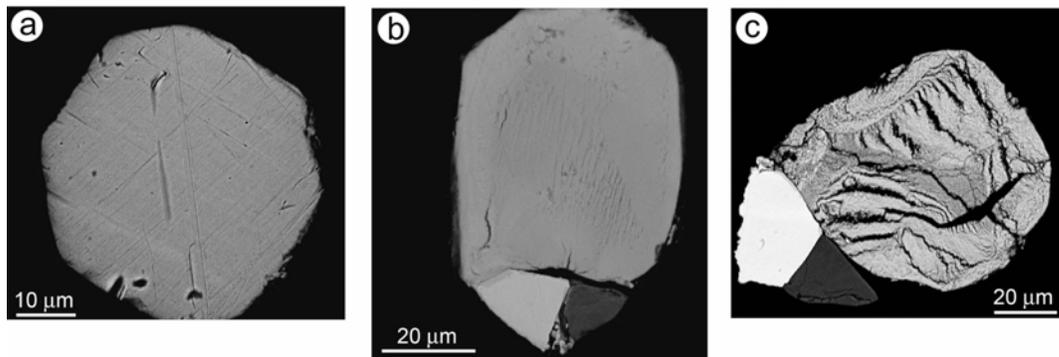


FIG. 5

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*Traore et al., 2007*

*Traore et al., 2007*

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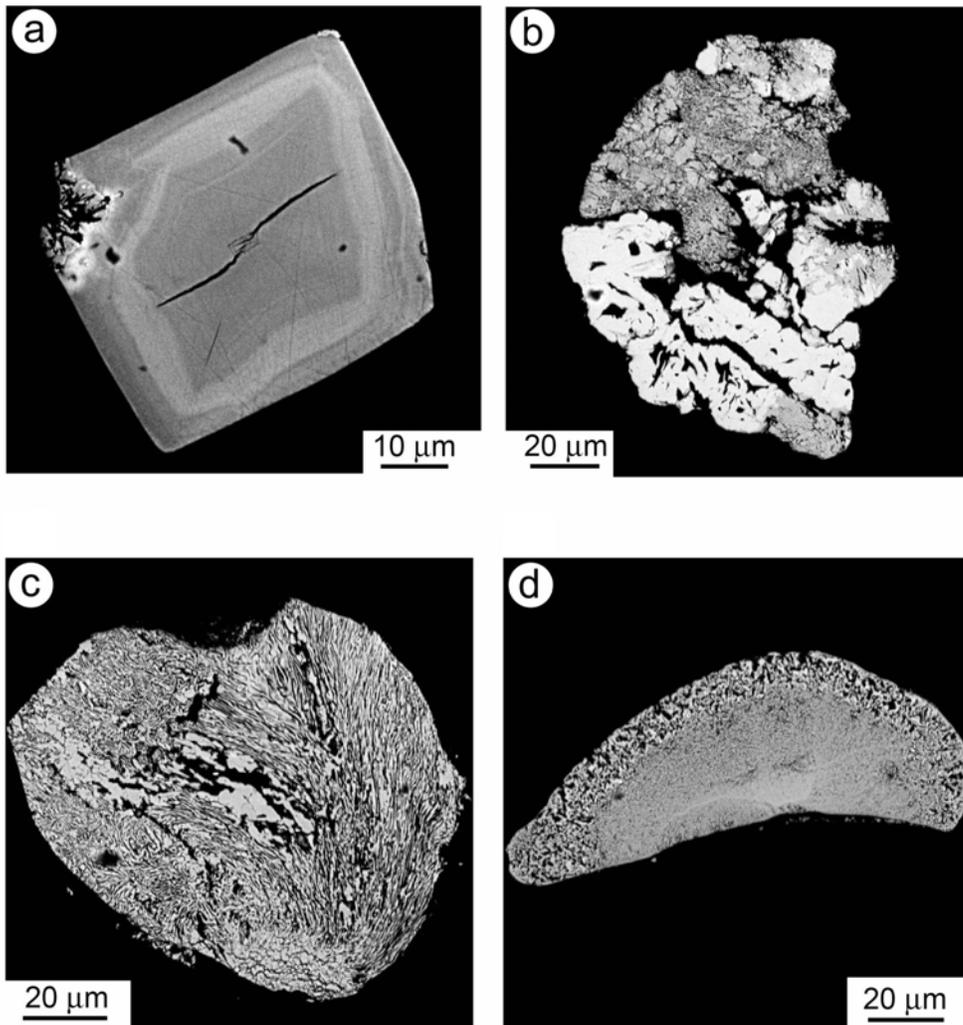


FIG. 6

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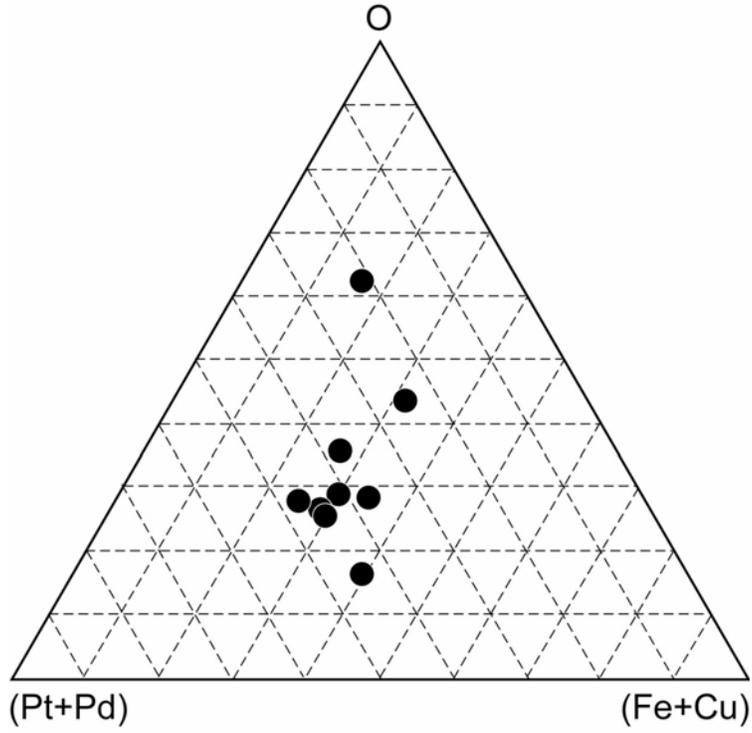


FIG. 7

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*Traore et al., 2007*

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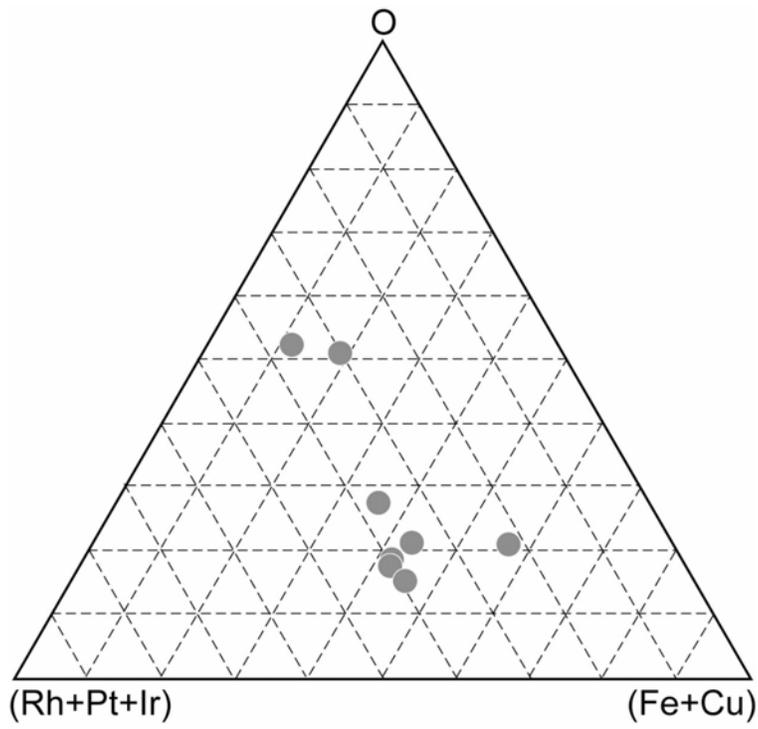


FIG. 8

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*Traore et al., 2007*

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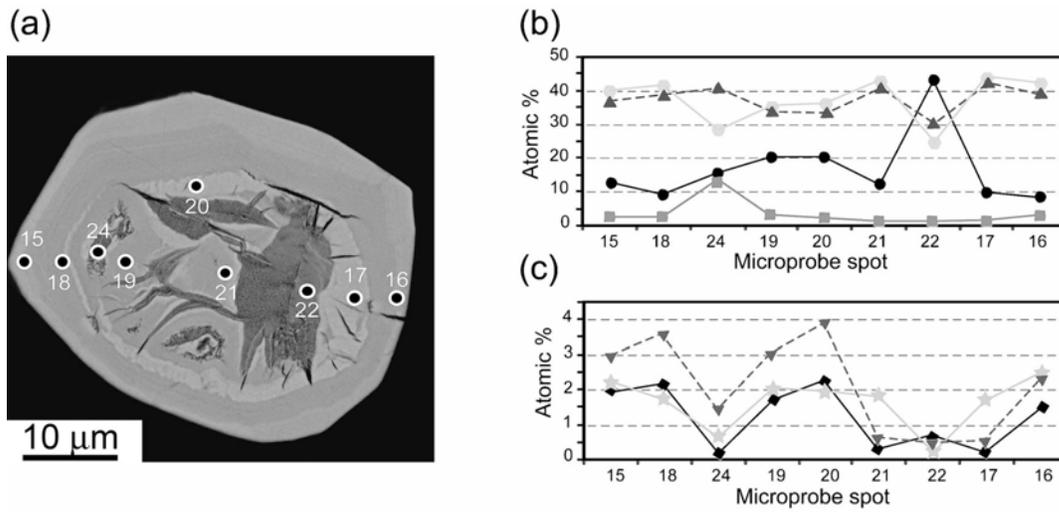


FIG. 9

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*Traore et al., 2007*

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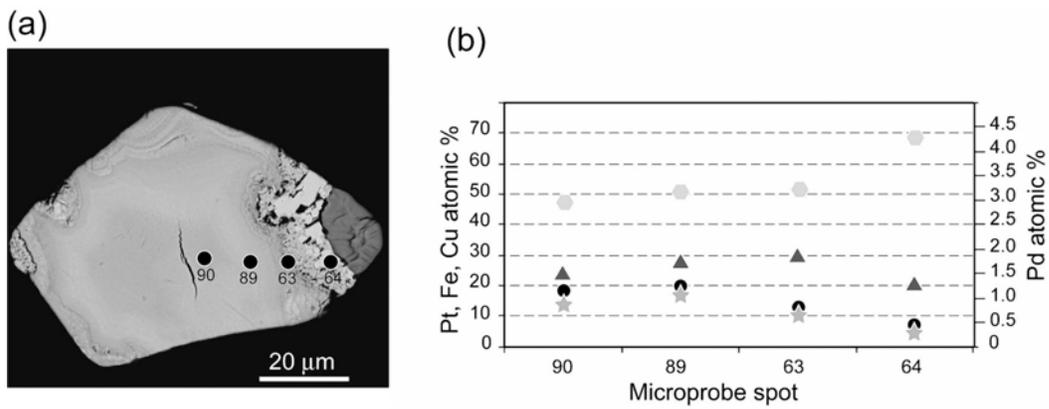


FIG. 10

*Traore et al., 2007*

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*Traore et al., 2007*

Isoferroplatinum Pt <sub>3</sub> Fe							Pt-Fe-(Cu) system												
							Tetraferroplatinum Pt-Fe					Tulameenite Pt-Fe-Cu							
Sample n°	PGB1_13	PGB1_16b	PGB7_8b	PGB7_8a	PGB7_13n	PGB6_19a	PGB1_5a	PGB1_16b	PGB7_13m	PGB5_1	PGB5_1	PGB1_6	PGB1_7a	PGB5_6	PGB5_6	PGB5_8	PGB7_7b	PGB5_8	
Atomic percent																			
Pt	65.45	65.26	69.43	58.26	64.29	65.97	44.31	47.02	37.99	39.27	38.88	41.71	38.10	38.88	40.33	42.85	50.60	47.00	
S	0.26	0.23	0.00	0.13	0.46	0.12	0.31	0.02	2.99	2.41	2.76	0.29	0.15	0.25	0.19	0.15	0.21	0.19	
Fe	25.08	24.91	22.92	26.47	21.51	21.39	41.66	40.21	50.61	48.09	48.03	27.94	24.76	26.78	27.82	26.52	27.27	20.32	
Pd	2.74	2.33	0.20	2.70	1.82	2.38	1.35	1.49	1.50	0.55	0.75	6.90	6.15	12.07	11.18	8.64	1.09	2.76	
As	0.00	0.08	0.00	0.00	0.05	0.18	0.00	0.23	0.00	0.00	0.00	0.18	0.10	0.00	0.20	0.05	0.00	0.07	
Ni	0.00	0.24	0.00	0.79	0.43	0.14	0.55	1.45	0.05	0.22	0.10	0.22	0.31	0.80	0.92	0.66	0.86	1.17	
Cu	0.22	0.18	0.72	3.69	4.04	0.75	0.64	1.63	0.06	0.00	0.13	12.60	14.86	20.23	17.74	20.48	19.06	26.23	
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.23	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	
Ir	0.11	0.00	0.37	0.09	0.18	0.22	0.40	0.11	0.00	0.22	0.01	0.12	0.18	0.05	0.00	0.00	0.10	0.03	
Cr	0.00	0.00	0.00	0.12	0.35	0.16	0.05	0.04	0.03	0.06	0.00	0.11	0.06	0.19	0.14	0.02	0.00	0.06	
Rh	0.39	0.43	1.19	0.32	0.46	0.75	0.28	0.30	0.38	0.31	0.20	0.76	0.28	0.15	0.02	0.51	0.48	0.42	
O	5.76	6.32	5.00	7.42	6.40	7.70	9.82	7.13	5.84	8.59	8.77	8.95	14.76	0.55	1.29	0.06	0.18	1.71	
Si	0.00	0.01	0.12	0.00	0.00	0.09	0.22	0.13	0.00	0.06	0.02	0.02	0.19	0.02	0.03	0.06	0.10	0.03	
Mg	0.00	0.00	0.00	0.00	0.00	0.09	0.32	0.02	0.54	0.23	0.35	0.13	0.10	0.02	0.03	0.00	0.00	0.00	
Mn	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.03	0.01	0.00	0.00	0.00	0.00	0.09	0.00	0.03	0.00	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

TABLE 1

*Traore et al., 2007*

Sample n°	(Pt-Pd)-Fe oxides						Pt-(Fe-Cu) oxides			(Rh-Ir-Pt)-(Fe-Cu) oxides							
	PGB1_8c	PGB1_9a	PGB1_16	PGB1_16e	PGB1_16a	PGB7_4h	PGB7_1	PGB4_1	PGB4_2a	PGB7_7b	PGB5_1	PGB6_8a	PGB5_8	PGB5_9	PGB6_19a	PGB6_19a	PGB1_9a
Atomic percent																	
Pt	38.57	31.74	38.78	37.90	20.94	24.50	46.47	35.29	41.86	18.45	7.14	14.65	0.25	0.43	0.37	0.47	0.13
S	0.07	0.18	0.25	0.18	0.03	0.54	0.01	0.17	0.32	0.50	2.46	0.87	0.39	0.42	1.00	0.06	1.35
Fe	28.95	26.46	29.38	28.16	16.67	29.98	17.59	27.55	28.49	11.65	53.61	18.47	35.12	32.19	41.97	39.76	32.77
Pd	5.39	5.64	1.41	6.73	0.64	0.26	0.44	0.86	1.26	0.00	0.09	0.03	5.74	9.58	0.23	0.88	0.03
As	0.00	0.00	0.15	0.00	0.05	0.00	0.00	0.00	0.06	0.04	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Ni	0.23	0.03	0.24	0.11	0.06	0.06	0.11	1.98	0.49	0.20	0.00	0.10	0.04	0.00	0.00	0.02	0.03
Cu	0.04	0.00	0.00	0.00	0.00	0.29	6.97	6.34	9.99	0.16	0.10	0.37	4.85	5.42	0.25	0.41	0.05
Co	0.01	0.00	0.14	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Ir	0.00	0.06	0.00	0.16	0.00	0.14	0.09	0.00	0.07	2.59	2.64	0.49	0.30	0.37	2.06	1.80	1.16
Cr	0.06	0.00	0.03	0.00	0.13	0.03	0.06	0.07	0.01	0.40	0.00	0.46	0.00	0.00	0.14	0.16	0.10
Rh	0.19	0.20	0.18	0.09	0.08	0.26	0.54	0.19	0.26	14.26	11.89	14.20	36.08	33.96	34.41	31.45	32.02
O	25.95	35.36	28.80	26.14	61.03	42.84	27.43	27.29	16.00	51.11	20.95	49.88	17.16	17.46	14.67	20.46	25.71
Si	0.48	0.06	0.63	0.32	0.31	0.59	0.16	0.26	0.15	0.23	0.44	0.15	0.02	0.04	1.96	1.84	2.41
Mg	0.06	0.03	0.00	0.00	0.00	0.42	0.08	0.00	0.16	0.22	0.61	0.23	0.03	0.11	2.95	2.70	4.20
Mn	0.00	0.26	0.00	0.20	0.04	0.04	0.00	0.00	0.85	0.18	0.05	0.11	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 2.

*Traore et al., 2007*