Early weathering of palladium gold under lateritic conditions, Maquíné Mine, Minas Gerais, Brazil

C.A.C. Varajão,*, F. Colin, P. Vieillard, A.J. Melfi, D. Nahon

DEGEO/Escola de Minas/Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, 35400, Ouro Preto, Brazil

UMR-CEREGE BP 80, 13545 Aix en Provence, France

HYDRASA, Faculté des Sciences, Université de Poitiers, 40 Avenue du Recteur Pineau, 86000, Poitiers Cedex 22, France

IAG, USP, Av. Miguel Stéfano, 4200, 01051-000, São Paulo, Brazil

CEREGE BP 80, 13545 Aix en Provence, France

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Abstract

Since the 80’s, studies have shown that Au is mobile in supergene lateritic surficial conditions. They are based either on petrological, thermodynamic studies, or experimental works. In contrast, few studies have been done on the mobility of the Pt group elements (PGE). Moreover, at the present time, no study has addressed the differential mobility of Au, Ag and Pd from natural alloys in the supergene environment. The aim of this study is to understand the supergene behavior, in lateritic conditions, of Au–Ag–Pd alloys of the Au ore locally called Jacutinga at the Maquina Mine, Iron Quadrangle, Minas Gerais state, Brazil.

The field work shows that the host rock is a “Lake Superior type” banded iron formation (BIF) and that the Au mineralization originates from sulfide-barren hydrothermal processes. Primary Ag–Pd-bearing Au has developed as xenomorphous particles between hematite and quartz grains. The petrological study indicates that the most weathered primary Au particles with rounded shapes and pitted surfaces were found, under the duricrust, within the upper friable saprolite. This layer, however, is not the most weathered part of the lateritic mantle, but it is where the quartz dissolution resulting porosity is the most developed. The distribution of Au contents in the weathered rocks are controlled by the initial hydrothermal primary pattern. No physical dispersion has been found. Most of the particles are residual and very weakly weathered. This characterizes early stages of Au particle weathering in agreement with the relatively low weathering gradient of the host itabiritic formations that leads essentially to the development of isostructural saprolite lateritic mantle. Limited dissolution of primary Au particles issued from the friable saprolite induces Pd–Ag depleted rims compared to primary Au particle Pd–Ag contents.

In addition, limited very short distance in situ dissolution/reprecipitation processes have been found at depth within the primary mineralization, as illustrated by tiny supergene, almost pure, Au particles. The supergene mobility order Pd > Ag > Au as reflecting early weathering stages of Au–Ag–Pd alloys under lateritic conditions is proposed. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Due to the increase of the Au price at the end of the seventies, research proposals were fully funded all over...
the world were Au occurrences were known from old surficial mining occurrences. Simultaneously to geological and geochemical surveys, fundamental research programs were carried out all over the tropical belt, at the request of both governmental and mining companies.

The supergene mobility of Au and Au particles (mostly Ag-bearing Au) has been demonstrated either chemically or mechanically with variable degrees, as a function of time, tectonic stability, climate, types of protores as well as host rocks, and chemical composition of Au (see Boyle, 1979; Mann, 1984; Webster and Mann, 1984; Butt and Zeegers, 1992; Colin, 1992; Bowell et al., 1993). The unique properties of Au particles, the very high specific gravity, the partial solubility and the high malleability led Colin et al. (1997) to propose Au as a tracer of the dynamics of laterites.

In most cases, surficial lateritic weathering implies a net mass loss of Au compared to parental fresh mineralizations (Colin et al., 1993a; Freyssinet, 1994). Au⁺ and/or Au⁴⁺ can be complexed by ligands present within the supergene environment. Hydroxy–chloride AuCl(OH)⁻ complexes and organo-metallic complexes have been proposed by Colin and Vieillard (1991), Krupp and Weiser (1992), Colin et al. (1993b) and Bowell et al. (1993), to explain the Au mobility in acid...
Fig. 2. Geological map of the Maquiné Mine area (Varajão, 1994).
highly oxidizing lateritic environments. These complexes are stable in diluted surficial lateritic waters and Benedetti and Boule`gue (1990) proposed their existence in the Congo River. Other complexes, such as \( \text{AuOH(H}_2\text{O)}^+ \) may also compete with the above mentioned ones, as proposed experimentally by Vlassopoulos and Wood (1990) and in natural conditions by Colin et al. (1993b). The Au chloride \( \text{AuCl}_4^- \) complex has been considered to explain lateritic Au mobility. Recent work, however, has shown that this natural complex is mostly susceptible to form in Western Australia where laterites are deeply drained by Cl-rich acid waters (Cl=10\(^{-1}\) mole/l) (Mann, 1984; Webster and Mann, 1984). These complexes are very unstable and Au precipitates to form saprolitic haloes in the very short scale neighborhood of the primary mineralization (Butt, 1987). Resulting tiny Au particles are very pure and have typical hexagonal or dentritic morphologies. Gold and Ag fractionate during such dissolution/reprecipitation processes.

The increasing chemical weathering induced morphological and chemical changes of primary Au particles. Partial dissolution produces microscopic pits at the surface of gold particles which leads to spongy aspects (Mann, 1984; Wilson, 1984; Giusti and Smith, 1984; Colin et al., 1989a; Colin et al., 1989b; Porto, 1991; Santosh and Omana, 1991; Oliveira and Campos, 1991; Colin and Vieillard, 1991; Costa, 1993; Sanfo et al., 1993).

The intensification of dissolution processes may induce the microdivision of the primary Au particles. The resulting particles, continuously subjected to chemical attack by supergene solutions, become smaller and smaller (up to their probable complete dissolution). The residual tiny rounded and pitted particles remaining at the surface of the lateritic mantle may be short scale translocated and constitute dispersion haloes (Colin and Lecomte, 1988; Freyssinet et al., 1989a; Colin et al., 1989a; Colin et al., 1989b, 1993a), easily detectable by regional Au surveys (Butt and Zeegers, 1992).

Silver-depleted domains develop centripetally both from the rims of the particles and from internal grain limits. As a consequence, most of the lateritic residual particles have a Ag-poor cortex compared to their core (Mann, 1984; Minko, 1988; Colin et al., 1989a; Colin et al., 1989b; Colin and Vieillard, 1991; Minko et al., 1992; Freyssinet et al., 1989a; Freyssinet et al., 1989b). This depletion is generally interpreted as a result of the preferential leaching of Ag compared to Au during weathering. Primary Au is easier dissolved as it is richer in Ag (Colin and Vieillard, 1991).

According to Bowles (1986, 1987), Au and PGE have similar chemical properties. As a consequence, the ligands able to complex Au, are expected to complex PGE in similar conditions. Theoretical work done by Wood et al. (1992) reported that thiosulphates and polysulphides should be the more efficient ligands to
complex the PGE in the sulfide oxidation zone and that organic acids may play a role in the complexation of noble metal colloids.

Weathering of Au–Ag–Pd gold particles in natural supergene lateritic systems is poorly documented. This paper address the behavior of such alloys found within itabirite-derived weathering mantle at the Maquiné Mine, located within the Iron Quadrangle (Minas Gerais, Brazil).

2. Geography, geology and mineralogy of the Maquiné mineralization

On the discovery of Au in the central part of the Minas Gerais state in 1698, the miners were in troubled due to the light yellow color of the Au nuggets. During the whole 18th century, until the identification of Pd by Chemvix (1803), palladium gold was named ‘white gold’ or ‘rotten gold’.

The Maquiné Mine is located SE of the Iron Quadrangle in the Minas Gerais State, next to the city of Mariana (Fig. 1). The climate is humid tropical with contrasted seasons with an annual mean rainfall of 1700 mm. The production extended up to 5 ton. of palladium gold between 1862 and 1896.

The regional geology was initially described by Harder and Chamberlin (1915), and then reviewed by Dorr (1969) and more recently, by Marshak and Alkmim (1989). Three geological units can be described: (1) the Metamorphic Complexes, which are Archean gneisses and migmatites with tonalite-granite composition; (2) the Rio das Velhas greenstone belt Supergroup; (3) the Minas Supergroup which consists of Early Proterozoic metasedimentary formations including BIFs, locally called itabirites.

These itabirites host the Maquiné Mine deposit (Fig. 2), an hydrothermal mineralization in which palladium gold in not associated with sulfides. Such deposits are called Jacutinga (Eschwege, 1833; Henwood, 1871;
Hussak, 1904; Dorr and Barbosa, 1963; Varajão, 1994Varajão, 1995; Cabral, 1996), and are associated with the last deformation event of the region (Guimarães, 1970; Galbiatti et al., 1997), the Brazilian–Pan–African Cycle (750–450 Ma). Boreholes were drilled during research works in 1986 to find the root of the Au mineralization and to make a feasibility study of the deposit (Fig. 3).

The so-called ‘Jacutinga ore’ from Maquine is quite similar to the ‘Jacutinga ores’ found elsewhere in Iron Quadrangle, Minas Gerais. It is essentially made up of narrow bodies (50 cm maximum) which are concordant with the schistosity or displayed in fractures. It is mainly composed of hematite (>90%) and quartz as major minerals and talc, kaolinite and goethite as accessory minerals.

Elsewhere, the Jacutinga ores may contain additional pyrolusite (Cabral, 1996), pyrolusite and tourmaline (Eschwege, 1833; Dorr and Barbosa, 1963; Polônia and Sousa, 1988), cassiterite (Henwood, 1871; Hussak, 1904) and monazite (Olivo et al., 1995) as accessory minerals.

Platinum group minerals (PGM) have also been described in association with the Jacutinga ore at the Itabira deposit: arsenopalladinite (Pd₄(As,Sb)₂), and isomorphicite ((Pd,Cu)₁₁Sb₂As₂) by Clark et al. (1974); atheneite ((Pd,Hg)₂As) by Clark et al. (1974) and Roese and Schuermann (1990); paladseite ((Pd, Cu, Hg)₁₇Se₁₅) by Olivo and Gauthier (1995) and Kwitko and Galbiatti (1998); and hongshiite (PtCu) by Kwitko and Galbiatti (1998).

At the Maquine Au Mine, Varajão (1994) identified a few particles of hydrothermal sperrylite (PtAs₂), stibiopalladinite (Pd₅₋₇Sb₂₋₇), and undefined Pd–Cu PGM phase (Pd₅(Cu, As)O₃) associated with unweathered primary Au particles.

As Dorr and Barbosa (1963) and Varajão (1995) stated, the term ‘Jacutinga’ corresponds to a deposit with an heterogeneous mineralogical composition, a palladium gold occurrence and a lack of sulfides.

3. Methodology

In the field, bulk samples of 20 kg of jacutinga ore were collected close to mineralized body outcrops in pits, trenches and along a quarry profile. Bulk samples of 0.5 kg were gathered from drillcore holes (Fig. 4). Then, each detected occurrences of Au within the various fresh mineralizations and weathered layers have been sampled. As a consequence, the results are representative of the global weathering lateritic system and primary orebody.

In addition, preserved structure samples were taken at the same locations for routine weathering pattern study. These samples were used for thin section study under a photo microscope, XRD examination, bulk ICP chemical analyses and density measurements. Bulk and mineral density measurements allowed the calculation of the total porosity of the rock samples.

The bulk samples were disaggregated under water and the heavy mineral fractions were obtained by gravity washing in a pan. Each resulting fraction per treated sample was then carefully examined under a binocular microscope, and about 300 Au particles were hand picked (Table 1).

One third of the total number of the extracted Au particles was investigated under a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), in order to study the morphology as well as potentially associated minerals (SEM Stereoscan 2000, ORSTOM, Bondy, France).

About 200 Au particles were epoxy impregnated, thin sectioned and polished for petrographical and chemical investigations. The chemical compositions of Au particles and associated minerals were determined by microprobe analyses using a SX 50 Cameca (15 kV, 20 nA and 1 μm size diameter focalization) at the Laboratory of Petrology of the Paris VI University. 1800 analyses were obtained for the following elements: Au, Ag, Pd, Pt, As, Cu with a detection limit of 100 ppm. In addition, microprobe analysis mappings of elements were completed for 10 representative Ag–Pd–Au particles with the SX 50 Cameca of BRGM Laboratory, Orleans, France.

4. Weathering patterns

4.1. The parent rock

Itabirites are BIFs formed of alternate dark and white mm to cm thick bands. The dark bands predominantly consist of hematite. Magnetite (<5%) and talc (<1%) may locally occur. The white bands are formed by quartz. This constitutes the main parent rock, i.e. the itabirite 1. The mean size of the crystals (150 μm) reveals that itabirites at Maquini Mine were
subjected to an amphibole-facies metamorphism. Magnetite crystals are partially transformed into martite, kenomagnetite or maghemite. Quartz crystals have corroded rims, which reflect an initial stage of weathering of the parent rock at depth (210 m). The porosity of this rock is approximately 15%. Hematites are not weathered at that level.

A second type of parent rock is also found as lenses at the Maquiné mine, that is the ‘hard hematite’ itabirite. It consists mainly of magnetites. These magnetites are also partially martitized and/or weathered in kenomagnetite or maghemite (Varajão et al., 1996).

4.2. Weathering layers

From field observations, it is clear that the parental schistosity of the itabirite 1 (the main concern) is preserved within the weathering mantle, except in the few centimeter thick top soil.

Although the schistosity is preserved all along the weathered cover, it is possible to distinguish 4 weathered layers from bottom to topsoil: the rough saprolite, the friable saprolite, the nodular saprolite and the duricrust locally called ‘canga’ (Fig. 5a,b).

Initial weathering stages seen at depth, develop progressively upward to the rough saprolite. All the quartz crystals are here partly affected by centripetal congruent dissolution. Subsequently, this process creates larger and larger voids and increases the total bulk porosity from 15 to 18% (Fig. 6). Within the friable saprolite, by increasing dissolution of both quartz and hematite, the bulk porosity may reach 48%. In addition, goethitic matrices are observed within some of the voids. Upward, through a clear textural discontinuity, the friable saprolite is overlain by a brownish duricrust. The pores, previously described from lower layers, are partially filled up by secondary goethitic/hematitic/gibbsitic matrices.

Where the ‘hard hematite’ (itabirite 2) lenses are present, a nodular layer develops upslope at the expense of the itabirite 1 derived duricrust. It consists of duricrust nodules embedded in a quartz-hematite-goethite-gibbsite-rich matrix. At the surface, duricrust transforms into a non-isostructural sandy soil.

As explained above, the weakly thick and punctual Au-mineralized bodies are concordant with the parent rock schistosity, parallel to the regional isoclinal fold axes. The spatial distribution of Au occurrences within the isostructural weathering mantle seems to obey the same structural law, which controls the distribution of the primary mineralization. As a consequence, in order to study the Au–Ag–Pd particles, 4 main sampling locations have been chosen, in relation to the previously described parent rock (Itabirite 1, from borehole samples) and derived weathering layers, i.e. the rough saprolite (from the quarry profiles), the friable saprolite (from trench profiles) and the nodular saprolite (from pit profiles). Neither duricrust or soils were not sampled for the Au study, because Au was fully extracted from those surficial easily accessible layers by miners during the last century.

5. The Au–Ag–Pd particles

5.1. The morphology of the particles

At depth Au contents are variable and can reach up to 1700 ppm. The Au alloy particles from these mineralizations in the drill core samples, have irregular shapes and their grains are essentially xenomorphic (Fig. 7). Their rough surfaces are marked by numerous imprints of associated minerals, mostly hematite (Fig. 8a,b), quartz and, in minor amount, sperrylite (PtAs₂), stibiopalladinite (Pd₃Sb) and isomertieite (Pd,Cu)$_₂$Sb$_₂$As$_₂$. A small amount of particles are partly covered by a goethitic matrix (Fig. 9). Rare larger particles have been found in the past such as a 20 cm nugget with a weight of 6.5 kg (Januzzi, 1986). However, the sizes of the collected particles range from a few microns to a few millimeters in length. Some of these particles have a few ‘blossom’ tiny particles on their surfaces.

The Au alloy particles extracted from the weathering layers have essentially similar morphologies (whatever the weathering layer they originated from) to those previously described within the mineralization at depth. However, a few other mineral-free Au particles collected at the top of the weathered itabirite 1 within the nodular and friable layers exhibit rounded shapes as well as very pitted surfaces (Fig. 10a,b). These dissolution features are more pronounced within the friable saprolite particles where pore sizes may reach 10 m in diameter.

5.2. The chemistry of the particles

The mean chemical composition of the collected Au particles within each weathering layer previously described as well as within the mineralization at depth (Fig. 11) of the Maquiné Mine shows the main global tendencies:

1. The Au particles collected near the surface (rough, friable and nodal saprolite) have higher mean Au-contents (92%) than those collected within the mineralization at depth (89%).
2. The Au particles collected near the surface (rough, friable and nodal saprolite) have poor mean Ag-contents (3.5%), whereas those collected within the mineralization at depth are Ag-richer (8.2%).
Fig. 5. (a) Geological map showing the distribution of the superficial formations of the pit area (as indicated in Fig. 4). (b) Geological Section AB (as indicated in (a)).
Fig. 5 (continued)
3. The Au particles collected near the surface (rough, friable and nodular saprolite) have higher mean Pd-contents (2.5%), than those collected within the mineralization at depth (1.5%).

4. The mean Cu-content distribution is similar to the mean Pd content one, and Cu is present in very small amount in all particles (<1.5%).

5. Pt is ubiquitous as traces in all the gold particles (<0.1%) and the Pt-contents have an irregular distribution.

6. The low standard deviations obtained for mean Au, Pd, Ag and Cu % of the Au particles inherited from mineralization at depth indicate the chemical homogeneity of this Au particle population, as opposed to the Au particles collected upwards next to the surface (rough, friable and nodular saprolite).

As the present concern is the Au–Pd–Ag alloy behavior, the chemical microprobe analyses of all the particles have been presented in Au–Ag–Pd ternary diagrams for each weathering layer and for the mineralization at depth (Fig. 12). The chemical homogeneity of the Au particles at depth is clearly shown, and only a few analyses close to the Au pole are separated from the rest of the whole population.

Within the weathering mantle, the chemistry of the alloys is variable and spreads out globally toward the Au pole, compared to the Au alloy particles at depth. At the very surface, within the nodular saprolite, the chemical analyses discriminate between two populations: the largest one is closer to the Au pole, while the other population of analyses is very similar to that found at depth.

The chemical composition of Au–Ag–Pd alloys within the weathered itabirite, independently of their size, are demonstrated to be variable. Thus large particles were identified close to the Pd–Au side as well as close to the Au pole. However, it is necessary to know about the degree of chemical homogeneity/heterogeneity within the Au alloy particles themselves. For each particle, the mean chemical composition was calculated with the relative standard deviation. Then for each
weathering layer the mean of the standard deviations as well as their own respective standard deviations have been calculated.

The results, i.e. the very low values of the standard deviations, demonstrate that the distributions of Pd and Ag within each particle are strongly homogeneous whatever the location of the particles. This can also be clearly proved by looking at Pd, and Ag-map obtained from 5 μm step by 5 μm step microprobe analyses done on the polished surface of the particles. As an example, the image of the distribution of Au, Pd, Ag from a nodular layer-derived particle is shown (Fig. 13). This result is representative of the whole assemblage of the collected particles.

The particles, extracted from the top of the weathered itabirite I within the nodular and friable saprolite layers, with rounded shapes and very pitted surfaces, show thin polished section with apparently external individualized small domains (Fig. 14). The microprobe analyses of these domains plotted in the Pd–Ag–Au diagrams (Fig. 12, TR, QP, PT) are very close to the Au pole. The Au contents of these domains range from 97 to 99 weight %, and their Ag and Pd contents do not exceed 1.5 and 0.1 weight %, respectively.

On the other hand, the ‘blossom’ tiny particles originated from the mineralization at depth, were found to be similar to the population placed very close to the Au-rich pole (Fig. 12, DH), with similar Ag and Pd chemistry.

Fig. 8. (a) SEM micrograph of a xenomorphic primary Au particle from trenches; (b) Detail of the unweathered areas related to hematite crystal imprints.

Fig. 9. SEM micrograph of the surface of a primary Au particle from trenches and covered by a goethitic matrix and residual hematite crystals.

Fig. 10. (a) SEM micrograph of a weathered residual primary Au particle from the friable saprolite with rounded shape and pitted surface. (b) Detail of the surface of the particle illustrating the dissolution pits.
6. Discussion

The Jacutinga Au ore is a very specific ore which is characterized by regional deposits with variable mineralogical composition, lack of sulfides and the presence of Au–Pd alloys. The mean Pd content of the Maquinê Mine materials is of the same order as most mined Au–Pd else-

Fig. 11. Mean Au, Ag, Pd, Cu, Pt chemical compositions (microprobe analyses) and standard deviations of Au particles extracted from the main sampling sites.
where in Brazil (See Table 2). Considering the worldwide palladium gold occurrences, it has to be noted that the sulfide-barren mineralization have only been found in Brazil.

The weathering patterns of the itabirite formations at the Maquiné Mine define 4 weathering layers from the parent rock to the topsoil, that are the rough saprolite, the friable saprolite, the nodular saprolite, and the duricrust. These layers clearly result from the in situ isostructural weathering of the itabiritic parent rock. However, the porosity pattern is demonstrated not to be controlled by increasing upward gradients. In fact, the more porous weathering layer is the friable saprolite, where congruent dissolution of quartz and hematite has led to an important porosity development. Above, within the upper surficial layers, the infilling of connected pores by secondary goethitic, hematitic, and gibbsitic matrices may reduce the microporosity.

However, this duricrust layer has to be considered of specific type. Its parent rock and the isostructural derived layers are Al poor. The Al content is less than 1%. As a consequence, the formation of kaolinite does not occur. Thus there is no gelaebular plasmic concentrations in the sense used by Nahon (1991). Kaolinite is however an indispensable mineral in the duricrust induration process development (Tardy, 1993). Then, in the isostructural duricrust which overlies the itabiritic parent rock, the Fe originated from the congruent dissolution of hematite and magnetite remains within the weathering mantle to precipitate as goethite. Therefore, itabirite duricrust ‘induration’ is mainly due to the high Fe₂O₃ content of the parent rock. Such content is considered to be at least 50 w%.

Within the isostructural weathered mantle, Au contents, mineral assemblages, and aleatory spatial distributions of the Au occurrences are similar to those of the parent rock mineralizations. In addition, within the weathered mantle, the Au alloy particles do not exhibit any surficial mechanical strains. These facts prove that

\[ (DH) \text{ drillholes; } (TR) \text{ trenches; } (QP) \text{ quarry profile; } (PT) \text{ pits.} \]
Fig. 13. Ag (a) Au (b) and Pd (c) microprobe mapping images illustrating the internal chemical homogeneity of the Au particles.

Fig. 14. Reflected natural light micrograph of a Au particle issued from the pits ( friable saprolite) showing external corroded domains which define the initial boundary of the Pd-rich Au primary parental particle.
Au distribution within the weathered mantle is only controlled chemically, that is by both initial hydrothermal patterns and superimposed in situ chemical weathering processes. Physical dispersion of particles has not taken place during isostructural weathering of the itabirite.

Table 2
Chemical composition of world-wide occurrences of palladium golda

<table>
<thead>
<tr>
<th>Origin</th>
<th>Au</th>
<th>Pd</th>
<th>Ag</th>
<th>Cu</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arraias–Goiás–Brazil</td>
<td>85.9</td>
<td>9.8</td>
<td>4.1</td>
<td>0.0</td>
<td>Berzelius, 1836</td>
</tr>
<tr>
<td>Gongo–Sóco–Minas Gerais–Brazil</td>
<td>88.2</td>
<td>3.8</td>
<td>5.8</td>
<td>1.9</td>
<td>Johnson, 1838a</td>
</tr>
<tr>
<td>Ouro Preto Minas Gerais–Brazil</td>
<td>92.3</td>
<td>5.2</td>
<td>0.0</td>
<td>2.2</td>
<td>da Silva et al., 1985</td>
</tr>
<tr>
<td>Sabará Minas Gerais–Brazil</td>
<td>0.0</td>
<td>5–8</td>
<td>0.0</td>
<td>nd</td>
<td>Seamon, 1882a</td>
</tr>
<tr>
<td>Stillwater–Montana–United States</td>
<td>91.3</td>
<td>6.6</td>
<td>1.1</td>
<td>nd</td>
<td>Cabri and Laflamme, 1974</td>
</tr>
<tr>
<td>Lac des Iles–Canada</td>
<td>93.1–94.1</td>
<td>2.8–4.1</td>
<td>3.5–5</td>
<td>nd</td>
<td>Cabri and Laflamme, 1979</td>
</tr>
<tr>
<td>Serra Pelada Pará–Brazil</td>
<td>97–98</td>
<td>1–2</td>
<td>1–8</td>
<td>.5</td>
<td>Meireles and da Silva, 1988</td>
</tr>
<tr>
<td></td>
<td>92–98</td>
<td>1–7</td>
<td>0.5</td>
<td>.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>89–91</td>
<td>9–10</td>
<td>25–50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morro da Mina–Amapá–Brazil</td>
<td>85.9</td>
<td>4.4</td>
<td>2.9</td>
<td>nd</td>
<td>Costa, 1993</td>
</tr>
<tr>
<td>Maquiné Minas Gerais–Brazil</td>
<td>88.3</td>
<td>1.4</td>
<td>8</td>
<td>0.3</td>
<td>Varajão, 1994</td>
</tr>
<tr>
<td></td>
<td>89–95</td>
<td>1.5–5</td>
<td>1–8</td>
<td>.8</td>
<td>Varajão, 1994</td>
</tr>
<tr>
<td>Itabira–Minas Gerais–Brazil</td>
<td>91.6</td>
<td>6.3</td>
<td>0.0</td>
<td>1.9</td>
<td>Roeser et al., 1991</td>
</tr>
<tr>
<td>Itabira–Minas Gerais–Brazil</td>
<td>88.5</td>
<td>11.5</td>
<td>tr</td>
<td>tr</td>
<td>Hussak, 1906</td>
</tr>
<tr>
<td>Itabira–Minas Gerais–Brazil</td>
<td>90.7</td>
<td>7.5</td>
<td>0.0</td>
<td>1.2</td>
<td>Olivo et al., 1994</td>
</tr>
<tr>
<td>Itabira–Minas Gerais–Brazil</td>
<td>94–96</td>
<td>4–6</td>
<td>&lt; 0.5</td>
<td>0.3–1.5</td>
<td>Varajão, 1994</td>
</tr>
</tbody>
</table>

The elements are given in weight %; nd = undetermined. * In Hussak, 1904.
Most of the Au particles, whatever their locations, have an homogeneous internal chemical composition. In addition, the Au–Pd–Ag contents vary from one particle to another. Only the Au particle population from the boreholes (fresh parent rock) has a more homogeneous chemical composition. However, within the weathering layers (rough, friable and nodular saprolites), the Au particle chemical compositions given in the Au–Ag–Pd triangular diagrams (Fig. 5), spread out globally close to the Au pole. It is also noticeable that large size particles are close to the Au-pole. These largest particles contain unweathered Pt group minerals (PGM) and are then demonstrated to be primary. Then the global chemical shift toward the Au pole could not be interpreted as resulting from the surficial dissolution of the parental particle. In fact, these tiny pure Au domains define, by their lined distribution, the initial boundary of the unweathered primary particles. Silver and Pd were preferentially leached during dissolution and these small particles as well as the rim of the coarsest particle show a high Au finesse. This depletion is illustrated by the microprobe Ag–Pd-mapping images (Fig. 15a,b).

Fig. 16. Reflected natural light micrograph of a primary Au particle issued from drillholes with tiny blossom supergene particles on its surface. Note the hexagonal habit of some of these tiny particles.

Pure Au micrometric particles, i.e. blossom particles found at depth are attached to biggest primary ones, from which they clearly differentiate (Fig. 16). Under the microscope, they show a strong yellow color. Some of these blossom particles exhibit hexagonal crystallographic habit. In addition, their distributions is not in spatial continuity with the primary neighboring particle. They are not related to corrosion fronts. Moreover, microprobe Ag–Pd-mapping images (Fig. 17a,b) illustrate clearly the very low Ag–Pd contents compared to the primary particle. In fact mean chemical composition is 97 to 99 Au wt %, and their Ag and Pd contents do not exceed 1.5 and 0.1 weight % respectively. It is then demonstrated that these tiny particles found at depth are of supergene origin.

It has to be noted that both precipitation of Au particles at depth, and surficial corrosion at the rim of primary Au particles within the friable saprolite lead to Ag–Pd-low contents. In the first case, this is due to fractionation of Au, and Ag,Pd during dissolution/precipitation processes. On the other hand this is due to preferential leaching of Ag and Pd during on going dissolution of primary Au. However, in both cases, this demonstrates the higher mobility of Ag and Pd in supergene lateritic environment compared to primary Au.

In addition, even the primary Au particles have higher Pd contents than Ag ones, the ratio \( \frac{Ag_{cores}}{Ag_{rims}} \) or \( \frac{Ag_{primary particle}}{Ag_{supergene particles}} \) are higher than the ratio \( \frac{Pd_{cores}}{Pd_{rims}} \) or \( \frac{Pd_{primary particle}}{Pd_{supergene particles}} \). This suggests that during weathering of Au–Ag–Pd particles, the mobility of these elements is Pd > Ag > Au.

 saprolite, where all quartz crystals have been affected by dissolution. Thus, the development of connected and open pores allowed the meteoric solutions to easily reach the Au particles themselves and the supergene solutions to be continuously recycled. The weathering of these Au particles is expressed as rounded shapes and surficial pits, similarly to the morphological features described elsewhere in laterites as reported above in the introduction. These particles have in their rims (Fig. 14) small domains apparently absent when observed in polished sections. Because this distribution is disrupted all along the present day primary particle limit, and with regard to the pitted surfaces, these domains are interpreted as resulting from the surficial dissolution of the parental particle. In fact, these tiny pure Au domains define, by their lined distribution, the initial boundary of the unweathered primary particles. Silver and Pd were preferentially leached during dissolution and these small particles as well as the rim of the coarsest particle show a high Au finesse. This depletion is illustrated by the microprobe Ag–Pd-mapping images (Fig. 15a,b).

Traces of surficial corrosion in deep Au particles were rarely observed. This agrees with the very beginning weathering state within the itabirite 1 parent rock. The more corroded Au particles originate from the trenches. The trenches were dug within the friable
7. Conclusions

The aim of the study was to understand the behavior of Au–Ag–Pd particles from the weathering lateritic mantle developed at the expenses of the Au ore locally called ‘Jacutinga’ hosted by itabiritic formations, at the Maquiné Mine, Iron Quadrangle, Minas Gerais state, Brazil.

The geological and petrological results allow us to draw the main following conclusions:

- The field work confirms that the host rock is a ‘Lake Superior type’ banded iron formation (BIF), and that the Au mineralization originates from sulfide-barren hydrothermal processes. This characterizes the so called ‘Jacutinga ore’, which consists of xenomorphic PGE-rich Au particles developed between hematite and quartz grains.
- The petrological study indicates that the weathering mantle is mostly isostructural with regards to the parent rock, and that the Ag–Pd bearing Au primary particles issued from the upper friable saprolite are the most weathered. This layer, however is not the most weathered part of the lateritic mantle, but it is where the quartz weathering derived porosity is the most developed.
- The distribution of Au contents in the weathered rocks is mainly controlled by the initial hydrothermal primary distribution. Most of the particles are residual and very weakly weathered. This characterizes early stages of Au particle weathering in agreement with the relatively low weathering gradient of the host itabiritic formations that leads essentially to the development of isostructural saprolite lateritic mantle. No physical dispersion of Au particles has been found.
- Limited dissolution of primary Au particles from the friable saprolite induces Pd–Ag depleted rims compared to primary Au particle Pd–Ag contents.
- Limited very short distance in situ dissolution/reprecipitation processes have been found at depth within the primary mineralization as illustrated by tiny supergene almost pure Au particles.
- The distribution of Pd and Ag within both depleted rims of surficial Au particles as well as supergene Au particles at depth suggests a supergene mobility order as Pd > Ag > Au as reflecting early weathering stages of Au–Ag–Pd alloys under lateritic conditions.

Further thermodynamic modeling will be done to explain the solubility of Au–Ag–Pd alloys under lateri-
tic conditions based on this petrological and mineralogical study (Vieillard et al., in prep.).

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