

ON THE ASSOCIATION OF PALLADIUM-BEARING GOLD, HEMATITE AND GYPSUM IN AN *OURO PRETO* NUGGET

ALEXANDRE RAPHAEL CABRAL[§] AND BERND LEHMANN

*Institut für Mineralogie und Mineralische Rohstoffe, Technische Universität Clausthal,
Adolph-Roemer-Str. 2A, D-38678 Clausthal-Zellerfeld, Germany*

ROGERIO KWITKO-RIBEIRO[§]

*Centro de Desenvolvimento Mineral, Companhia Vale do Rio Doce, Rodovia BR 262/km 296,
Caixa Postal 09, 33030-970 Santa Luzia – MG, Brazil*

RICHARD D. JONES

1636 East Skyline Drive, Tucson, Arizona 85178, U.S.A.

ORLANDO G. ROCHA FILHO

*Mina do Gongo Soco, Companhia Vale do Rio Doce, Fazenda Gongo Soco,
Caixa Postal 22, 35970-000 Barão de Cocais – MG, Brazil*

ABSTRACT

An *ouro preto* (black gold) nugget from Gongo Soco, Minas Gerais, Brazil, has a mineral assemblage of hematite and gypsum hosted by Pd-bearing gold. The hematite inclusion is microfractured and stretched. Scattered on the surface of the gold is a dark-colored material that consists partially of Pd–O with relics of palladium arsenide-antimonides, compositionally close to isomertieite and mertieite-II. The Pd–O coating has considerable amounts of Cu, Fe and Hg, and a variable metal:oxygen ratio, from O-deficient to oxide-like compounds. The existence of a hydrated Pd–O compound is suggested, and its dehydration or deoxygenation at low temperatures may account for the O-deficient Pd-rich species, interpreted as a transient phase toward native palladium. Although gypsum is a common mineral in the oxidized (supergene) zones of gold deposits, the hematite–gypsum-bearing palladian gold nugget was tectonically deformed under brittle conditions and appears to be of low-temperature hydrothermal origin.

Keywords: *ouro preto*, hematite–gypsum mineral assemblage, Pd-bearing gold, Pd–O coating, isomertieite, mertieite-II, Gongo Soco, Minas Gerais, Brazil.

SOMMAIRE

Une pépite de *ouro preto* (or noir) provenant de Gongo Soco, Minas Gerais, au Brésil, contient l'assemblage hématite + gypse dans un hôte d'or palladifère. L'hématite en inclusion est microfissurée et étirée. La surface de la pépite est recouverte d'un matériau foncé qui correspond en partie à une gaine de Pd–O avec des reliques d'arséniures et d'antimoniures de palladium dont la composition ressemble à celles de isomertieite et mertieite-II. Cette couche à Pd–O contient des quantités importantes de Cu, Fe et Hg, et montre un rapport variable de métal à oxygène, allant de matériau déficitaire en oxygène à des composés ressemblant à des oxydes. A notre avis, il y a des indications d'un composé Pd–O hydraté, et sa déshydratation ou sa perte en oxygène à faibles températures rendrait compte des variétés riches en Pd et appauvries en O, que nous interprétons comme phases transitoires dans une progression vers le palladium natif. Quoique le gypse est un minéral répandu dans la zone oxydée (supergène) des gisements d'or, la pépite d'or palladifère à hématite–gypse a été déformée tectoniquement sous conditions cassantes, et semble avoir une origine hydrothermale à faible température.

(Traduit par la Rédaction)

Mots-clés: *ouro preto*, assemblage à hématite–gypse, or palladifère, gaine riche en Pd–O, isomertieite, mertieite-II, Gongo Soco, Minas Gerais, Brésil.

[§] E-mail addresses: cabral@min.tu-clausthal.de, rogerio.kwitko@cvrd.com.br

INTRODUCTION

Recently, investigators have provided evidence for epigenetic, sulfide-poor, hydrothermal mineralization of palladium and platinum (e.g., Cabral *et al.* 2002a, Fleet *et al.* 2002, Grainger *et al.* 2002, Kwitko *et al.* 2002, Nickel 2002, Şener *et al.* 2002, Stanley *et al.* 2002, and references therein). However, the occurrence of Pd- and Pt-bearing minerals in highly oxidized mineral assemblages had already clearly been indicated in much earlier works (e.g., Johnson & Lampadius 1837, Henwood 1871, Hussak 1904, Ball & Shaler 1914, Knopf 1915, Wagner 1929). One of the most extraordinary cases described in the so-called “old literature” refers to the singular nuggets of *ouro preto* (black gold). *Ouro Preto* was so abundant in Villa Rica that the town was renamed Ouro Preto, the most sumptuous baroque village of the Brazilian Gold Cycle (ca. 1695–1785). Much of the *ouro preto* from the Ouro Preto area was presumedly recovered from itabirite-hosted, Pd-bearing gold mineralization, known as *jacutinga* (e.g., Hartt 1870, Scott 1902, Hussak 1904).

In the 19th century, Gongo Soco was the most important *jacutinga*-style gold deposit in Minas Gerais. The deposit is situated about 50 km north–northwest from Ouro Preto; Cabral *et al.* (2002b) provide a location map. Possibly, the first chemical investigation of *ouro preto* started there. In 1826, during his residence at Gongo Soco, Daniel Gardner (physician and mineralogist working for the Imperial Brazilian Mining Association) was not only capable of identifying palladium, but also of finding out that palladium was contained within Fe-rich oxide material: “... the remaining powder [crushed ore] ... produced a steel grey coloured amalgam weighing five grains, and one grain eight-tenths, after cupellation, of palladium, without gold, a circumstance altogether new, never having found it before but in combination with that metal. ... the greater part of the palladium remaining yet in the iron sand” (Gardner 1826, p. 117). This was probably the first indication that the Gongo Soco gold was associated with an Fe-rich Pd–O phase, a fact later confirmed by Johnson & Lampadius (1837) and Cabral *et al.* (2001). A review of the historical descriptions of *ouro preto* was given by Jedwab & Cassedanne (1998).

At present, Gongo Soco is an iron ore mine. The mine pit has recently exposed (at a depth of about 15 m) remains of old underground workings of the former gold mine, making it possible to recover *ouro preto* nuggets from cross-cutting, specular-hematite-rich auriferous veins hosted by itabirite (Cabral *et al.* 2002b). Results of chemical analyses by Percival Norton Johnson (reported in Henwood 1871 and Hussak 1904) indicated that the gold is alloyed with palladium. Electron-microprobe analyses confirmed the existence of palladian gold and demonstrated an inclusion assemblage of palladium arsenide–antimonides, compositionally close to mertieite-II and isomertieite (Cabral *et al.* 2002b). One

nugget of gold has been found with an inclusion assemblage of gypsum and hematite, partially coated by a dark Pd–O phase. This particular *ouro preto* nugget is described herein.

THE HEMATITE–GYPSUM-BEARING
OURO PRETO NUGGET

A nugget of gold, about 0.7 cm in length, was recovered in a Knelson concentrator at the iron ore plant. The nugget is partially coated by a black to reddish brown material, which gives the characteristic dark-colored appearance to the *ouro preto* (Fig. 1a). Microscopic investigation of a polished cross-section of the nugget shows inclusions of hematite and a gangue mineral, as well as a low-reflectance coating (Fig. 1b). The dark coating has relics of a higher-reflectance phase (Fig. 1c). Electron-microprobe analyses indicate that the gold is alloyed with about 6 wt.% Ag and 1 wt.% Pd, whereas the mineral relics in the dark coating are palladium arsenide–antimonides compositionally analogous to isomertieite and mertieite-II (Table 1).

The gangue mineral, approximately 160 µm in length, is euhedral (Fig. 2a) and has a homogeneous distribution of calcium and sulfur (Figs. 2b, c). During the reconnaissance energy-dispersion (ED) analysis, the incidence of the electron beam produced cavities, of about 5 µm in diameter (Fig. 2a), indicative of loss of H₂O from a hydrated calcium sulfate (gypsum). The euhedral crystal of hematite included in gold is microfractured and segmented (Fig. 3).

A relic of isomertieite in the dark coating is shown in Figure 4a. X-ray mapping shows that antimony is restricted to the relic (Fig. 4b), but that palladium and oxygen are dispersed throughout the matrix (Figs. 4c, d). Iron is concentrated in the lower half of the area (Fig. 4e), where the matrix has a “fibrous” microstructure (Fig. 4a). The iron-rich areas match those of higher oxygen content, which may correspond to a Pd-bearing Fe–O compound. Copper and, less abundantly, mercury are also present in the matrix (Figs. 4f, g). During the X-ray mapping, arrays of microcracks appeared in the upper part of the area (Fig. 4a), suggesting the presence of a hydrated Pd–O compound.

Quantitative electron-microprobe analyses of the dark coating of Pd–O are hampered by the irregular and poorly polished surface, formation of microcracks and, possibly, interference from gold. Furthermore, rather extreme analytical conditions for oxygen were used, compared to those reported in Augé & Legendre (1994). These are the reasons why the electron-microprobe data of Table 2 are not totally reliable and should be considered with caution. The data point to a variable metal:oxygen ratio, from oxygen-deficient compounds, approaching a Pd–Cu alloy (Table 2, column 2), to ratios close to 1:1 and 1:2, suggesting compounds similar to (Pd,Cu)O and (Fe,Pd)OOH, respectively (Table 2, columns 4 and 5).

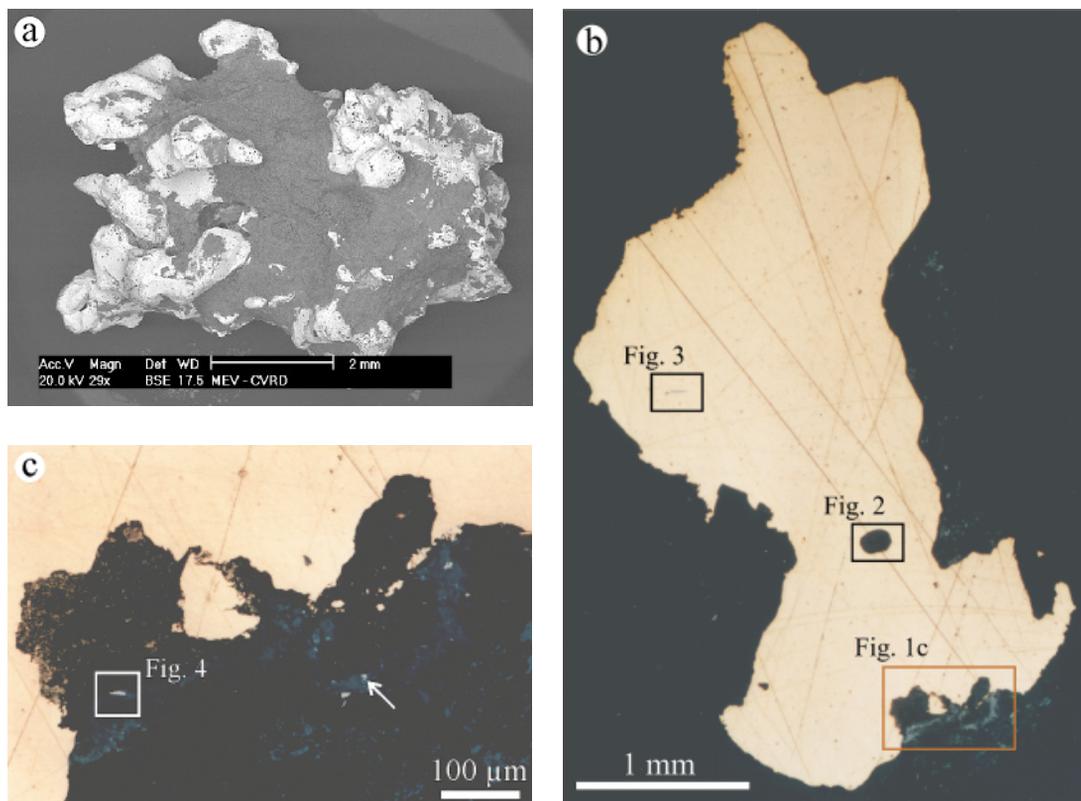


FIG. 1. a. Back-scattered electron (BSE) image of the gold nugget investigated in this study, with the dark appearance that characterizes *ouro preto*. b. Reflected-light photomicrograph (in air) of a polished cross-section of the nugget shown in (a). c. Reflected-light photomicrograph (in oil) of the area indicated in (b), in which a relic of isomertieite (white) is outlined. The arrow denotes a relic of mertieite-II (white). The dark matrix is composed of a goethite-like material with fine-grained crystals of platy hematite.

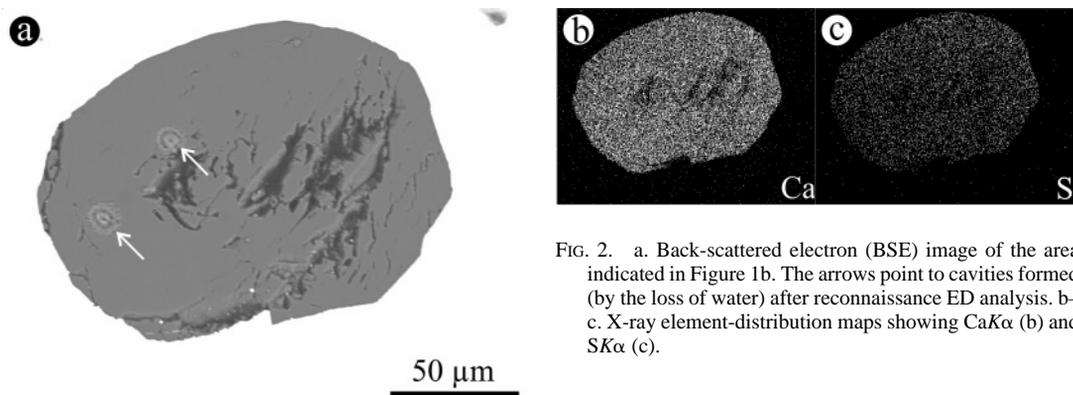


FIG. 2. a. Back-scattered electron (BSE) image of the area indicated in Figure 1b. The arrows point to cavities formed (by the loss of water) after reconnaissance ED analysis. b–c. X-ray element-distribution maps showing $\text{CaK}\alpha$ (b) and $\text{SK}\alpha$ (c).

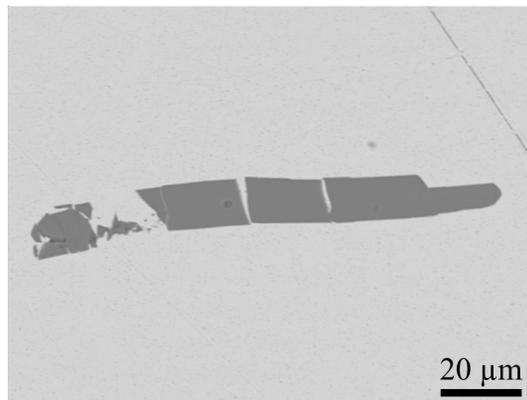


FIG. 3. BSE image of the hematite crystal indicated in Figure 1b. Note that the hematite is microfractured and stretched.

DISCUSSION AND CONCLUSIONS

The occurrence of gypsum as an inclusion in Pd-bearing gold has not, to the authors' knowledge, been previously reported. Gypsum is a common mineral in the oxidized zones of auriferous deposits (Boyle 1979). It is also well known that gypsum occurs as efflorescences ("desert roses") by evaporation in the dry season, and is found as a gangue mineral in gold-quartz deposits (Lindgren 1928, Boyle 1979). The temperature of breakdown of gypsum to anhydrite + H₂O in pure water is $49 \pm 2.5^\circ\text{C}$ (Innorta *et al.* 1980), and is considerably lowered by the presence of NaCl (Blount & Dickson 1973). Therefore, gypsum is expected to be encountered only in low-temperature hydrothermal deposits or in the supergene zone (Holland 1967). One may speculate that thiosulfate could have been involved in the transport of gold in order to form a gold-gypsum-hematite paragenesis (*e.g.*, Kucha *et al.* 1994). However, gypsum has hitherto been observed in only one nugget of gold from Gongo Soco, and sulfide minerals, the expected result of disproportionation of thiosulfate, are characteristically lacking. Whatever its origin, the presence of gypsum and hematite indicates highly oxidizing conditions of nugget formation at Gongo Soco.

The hematite crystal of Figure 3 is segmented. Other similar nuggets of gold in the suite, though lacking gypsum, have microfractured inclusions of isomertieite and mertieite-II, commonly with fissures healed by the host Pd-bearing gold (Cabral *et al.* 2002b). In some instances, coarse-grained palladian gold is cross-cut by veinlets of specular hematite, kaolinite and fine-grained palladian gold (Cabral & Lehmann 2003). These microstructures indicate that the gold nuggets were subjected to a late-stage tensile stress field under brittle conditions. Such a tectonic setting is more likely to have occurred

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF GOLD AND PALLADIUM ARSENIDE-ANTIMONIDES

	1	2	3	4	5
Au wt.%	92.63	92.94	92.91	3.71	0.95
Pd	0.96	0.84	0.91	72.31	73.10
Ag	6.13	6.27	6.11	<0.3	<0.3
Cu	0.19	0.11	0.11	1.15	0.48
Fe	<0.05	<0.05	<0.05	0.26	0.13
Sn	<0.03	<0.03	<0.03	0.05	0.09
Sb	<0.03	<0.03	<0.03	14.46	25.36
As	<0.15	<0.15	<0.15	9.87	2.08
Total	99.91	100.16	100.04	101.81	102.19

The electron-microprobe analyses were performed at 20 kV and 40 nA with a Cameca SX100 (TU Clausthal). The following X-ray lines and standards were used: pure metals (AgL β , AuL α , CuK α , PdL α and PtL α), HgTe (HgL α), Fe₂O₃ (FeK α), SnO₂ (SnL α), InSb (SbL α) and InAs (AsL α). Platinum and mercury were sought, but are below the detection limit, 0.3 wt.%. Column headings: 1–3: gold, 4: isomertieite, 5: mertieite-II.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE DARK COATING ON OURO PRETO

	1	2	3	4	5
Pd wt.%	73.74	78.18	79.17	41.47	65.86
As	0.29	0.44	<0.09	0.41	0.76
Cu	7.42	11.47	10.24	5.04	9.83
Fe	4.73	0.19	0.23	24.89	1.36
Mn	0.38	0.42	0.48	0.39	0.32
Hg	2.64	1.81	0.84	2.13	3.65
Au	1.55	3.39	6.65	1.04	2.84
O	3.85	1.58	2.47	29.13	12.06
Total	94.60	97.48	100.08	104.50	96.68
Pd <i>appfu</i>	1.19	1.39	1.34	0.42	0.77
As	0.01	0.01	–	0.01	0.01
Cu	0.20	0.34	0.29	0.09	0.19
Fe	0.15	0.01	0.01	0.48	0.03
Mn	0.01	0.01	0.02	0.01	0.01
Hg	0.02	0.02	0.01	0.01	0.02
Au	0.01	0.03	0.06	0.01	0.02
Σ metals	1.59	1.81	1.72	1.02	1.06
O	0.41	0.19	0.28	1.98	0.94
Σ <i>appfu</i>	2	2	2	3	2

Analytical conditions as in Table 1, with additional standards as follows: MnSiO₃ (MnK α), HgTe (HgL α) and Al₂O₃ (OK α). Antimony and platinum were sought, but are below the detection limit, 0.1 and 0.4 wt.%, respectively. See Figure 4a for the location of the points analyzed.

in hypogene conditions rather than as a result of weathering.

The dark Pd–O-bearing coating contains relics of isomertieite and mertieite-II and may have been derived, at least in part, by oxidation of these minerals. The oxidation process may have involved leaching of antimony and arsenic from the pre-existing palladium arsenide-antimonide, and incorporation of external metals, like iron and manganese, into Pd–O. The mercury in this assemblage was seemingly extraneous, as it was not detected in the relics.

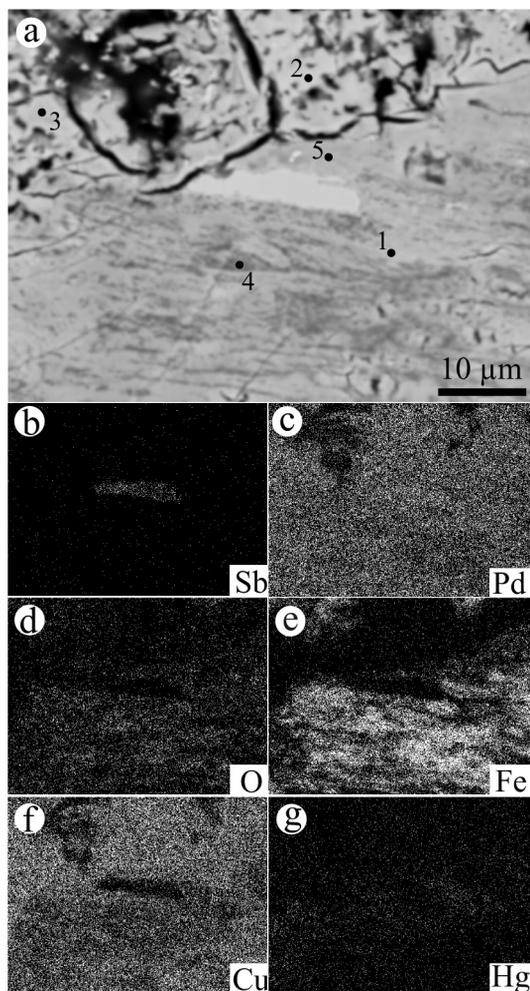


FIG. 4. a. BSE image of the area outlined in Figure 1c. Microcracks (upper part) were formed during the X-ray mapping. The numbers refer to column numbers in Table 2. The mineral phase at the center (white) has a composition close to isomertieite. b–g. X-ray element-distribution maps showing $SbL\alpha$ (b), $PdL\alpha$ (c), $OK\alpha$ (d), $FeK\alpha$ (e), $CuK\alpha$ (f) and $HgL\alpha$ (g).

Although the electron-microprobe data cannot be used for quantitative purposes (*i.e.*, evaluation of empirical stoichiometries), they provide evidence for a hydrated Pd–O compound. There is indication of a natural hydrated oxide of palladium in a dunite zone affected by the seasonal movement of groundwater near Lavatravo, Andriamena area, Madagascar (McDonald *et al.* 1999). Those authors suggested that a precursor Pd-rich mineral was leached and replaced by oxygen

and H_2O to form hydrated palladium oxide at the water-table interface. McDonald *et al.* (1999) also proposed that hydrated palladium oxide may repeatedly be heated during the tropical dry season, eventually dehydrating to native palladium. Not only could this dehydration–deoxygenation mechanism (*cf.* Cabral & Lehmann 2003) explain the formation of the native palladium found by Salpéteur *et al.* (1995), but also the oxygen-deficient Pd–Cu phase reported here (Table 2, column 2), which may represent an intermediate (metastable) phase between hydrated palladium oxide and native palladium.

The sample material (polished section) described in this contribution has been deposited at the mineral collection of the *Centro de Desenvolvimento Mineral, Companhia Vale do Rio Doce* (Rodovia BR 262/km 296, Caixa Postal 09, 33030–970 Santa Luzia – MG, Brazil), catalogued as QF/GS–Au–3b.

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