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ON THE ROSETTES OF "NATIVE PALLADIUM" FROM MINAS GERAIS, BRAZIL: EVIDENCE FROM GONGO SOCO

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Abstract

Minute rosette-like crystals (~1 μm) were found on the surface of a gold nugget from Gongo Soco, an iron ore deposit in Minas Gerais, Brazil. The rosettes consist essentially of palladium with some oxygen. The presence of oxygen and the occurrence of many of the rosettes on a coating of iron oxyhydroxide suggest that the rosettes crystallized from a Pd–O precursor that precipitated from aqueous solution, probably in the supergene environment, on the pre-existing gold nugget.

Keywords: rosettes, oxygen-bearing palladium, gold nugget, Gongo Soco, Minas Gerais, Brazil.

Sommaire

De très petits cristaux (~1 μm) en rosettes ont été déposés sur la surface d'une pépite d'or trouvée à Gongo Soco, gisement de fer à Minas Gerais, au Brésil. Ces rosettes contiennent essentiellement du palladium avec de l'oxygène. D'après la présence d'oxygène et la déposition de plusieurs de ces rosettes sur une couche d'oxyhydroxyde de fer, nous croyons que ces rosettes ont cristallisé à partir d'un précurseur de Pd–O déposé d'un solution aqueuse sur la pépite pré-existante, probablement dans un milieu supergène.

(Traduit par la Rédaction)

Mots-clés: rosettes, palladium avec oxygène, pépite d'or, Gongo Soco, Minas Gerais, Brésil.

Introduction

The remobilization of platinum-group elements (PGE) at low temperatures has been debated in the past decades. One of the questions refers to secondary growth of platinum-group minerals (PGM) in laterites (*e.g.*, Bowles 1986, 1995). The neoformation of PGM in the supergene environment has been advocated by some authors, whereas others have concluded that the PGM in placer deposits are of magmatic origin [*vide* Wood (2002) for a comprehensive list of references]. Recently, observations on detrital PGM from the Makwiro River, Zimbabwe, have pointed to a low-temperature origin for native platinum occurring as a coating on grains of sperrylite (Oberthür *et al.* 2003). In their opinion, grains of Pt–Fe alloy formed in the supergene environment from a pre-existing PGM (possibly by selective leaching) or as a result of precipitation from an aqueous solution. Precipitates from hydrothermal solutions, formed at a relatively low temperature, were recognized as the precursor of virtually Fe-free native platinum in the Waterberg district of South Africa (Wagner 1929, McDonald *et al.* 1999a).

The native palladium found in the state of Minas Gerais, Brazil, constitutes one of the most intriguing cases of PGM formed under low-temperature conditions. The occurrence of native palladium as a mineral species was noted for the first time in the early 1800s, when Wollaston (1809) investigated samples from gold mines in Brazil, possibly from Minas Gerais [*vide* Atencio (2000) for a discussion of the provenance of the samples]. Hussak (1904) detected grains of native

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palladium in residual concentrates from the gold washing at Itabira, later identified by electron-microprobe analysis (Olivo & Gauthier 1995). Also at Itabira, rosette-like crystals of native palladium were found on a crust of iron oxyhydroxide on Pd-bearing gold (Kwitko *et al.* 2002). Those authors, however, refrained from interpreting the origin of the rosettes. The same rose-shaped morphology has now been discovered at Gongo Soco, an iron ore deposit situated about 50 km southwest of Itabira, where Au–Pd-bearing specular hematite-rich veins, analogous to those at Itabira, occur. This remarkable rosette-like morphology of Pd-rich crystals is documented and discussed here.

Gongo Soco and Sample Material

Gongo Soco was a famous gold mine in the 19th century (Henwood 1871, Hussak 1904); now it is one of numerous iron ore mines of the Quadrilátero Ferrífero [*vide* Cabral *et al.* (2003b) for a geological map]. The Pd-bearing auriferous mineralization occurs as cross-cutting veins and veinlets (locally known as *jacutinga*) in soft hematite ore and in itabirite immediately adjacent to it. The term *itabirite* denotes a laminated, metamorphosed, iron-rich sedimentary rock (banded iron formation). Both the soft hematite and itabirite have a prominent foliation (S_1) defined by the planar arrangement of crystals of platy hematite (Cabral *et al.* 2003b). The S_1 foliation is generally attributed elsewhere in the Quadrilátero Ferrífero to the ~0.6 Ga Brasiliano Orogeny (*e.g.*, Alkmim & Marshak 1998, Hippertt & Davis 2000). The *jacutinga* veins are friable and consist predominantly of specular hematite and subordinate talc, kaolinite, quartz, goethite and manganese oxide (Hussak 1904). Gold, found as nuggets and aggregates intergrown with specular hematite, is typically alloyed with palladium (Henwood 1871, Hussak 1904) and commonly contains inclusions of arsenide–antimonides of palladium [compositionally close to mertieite-II and isomertieite (Cabral *et al.* 2002b)].

The sample material is a stick-shaped aggregate (nugget) of gold, about 1 cm long, recovered in a Knelson concentrator at the iron ore plant. The aggregate was investigated at Companhia Vale do Rio Doce (CVRD) with a Philips XL30 scanning electron microscope (SEM), equipped with an EDAX iDX4 Si(Li) super-ultrathin-window energy-dispersion spectrometer (EDS).

The Palladium-Rich Rosettes from Gongo Soco

The gold aggregate has some silver (~5 wt.%) and traces of palladium (<1 wt.%). It is sparsely covered by a coating of goethite-like iron oxyhydroxide. The ferruginous coating and the gold are partially covered by randomly spaced particles (Fig. 1a). Under higher magnification, the particles exhibit a rosette-like morphology, being thinly dispersed on the gold surface (Fig. 1b). An EDS spectrum of one of the rosettes resting on the gold surface, without any obvious association with iron oxyhydroxide, shows that the mineral is composed essentially of palladium, with minor amounts of oxygen, copper and iron (Fig. 1c). EDS spectra of rosettes on the goethite-like coating and on the gold surface are essentially the same (ignoring interference from the substrate). The Pd-rich rosettes also form aggregates (Figs. 1d, e). A single rosette consists of discs that intersect in apparently three orthogonal directions (Fig. 1f).

Discussion and Conclusions

The presence of oxygen in what initially appeared to be native palladium casts doubt on the rosettes of "native palladium" described by Kwitko *et al.* (2002) in sample material from Itabira. Oxygen was recognized in the rosettes from Itabira, but attributed to the subjacent iron oxyhydroxide.

At Gongo Soco, Cabral & Lehmann (2003) found native palladium derived from Pd–O masses that formed at the expense of a pre-existing arsenide–antimonide of palladium. The Pd-rich rosettes described here differ from that case because no relics of a primary Pd–Sb–As mineral were detected. Instead of a primary PGM, the rosettes seem to have crystallized as a Pd–O phase that precipitated directly from aqueous solution. An analogous case is the Pt–O precursor to the native platinum in the Waterberg district of South Africa (Wagner 1929, McDonald *et al.* 1999a). As suggested for the Waterberg district, deoxygenation and dewatering at low temperatures could be responsible for the crystallization of native palladium from Pd–O precipitates. In the Waterberg district, native platinum is intimately associated with specular hematite (Wagner 1929, McDonald *et al.* 1995), and the crystallization of native platinum from the Pt–O precipitate is interpreted to have occurred at temperatures of 100–200°C (McDonald *et al.* 1999a). Lower temperatures than those are envisaged for Gongo Soco and Itabira, since the Pd-rich rosettes are scattered over a goethite-like coating, which is possibly of supergene origin.

The Pd-rich rosettes precipitated not only on the coating of iron oxyhydroxide, but also directly on the surface of gold (Fig. 1b). In this connection, Gammons *et al.* (1993) emphasized that the steep decrease in solubility of palladium in the presence of gold-rich alloys could be an effective mechanism of precipitation. This mechanism may explain why palladium is apparently not dispersed in the weathered host-rock (itabirite), but restricted to the *jacutinga* veins.

Quantitative electron-microprobe analyses of the Gongo Soco rosettes are hampered by the small grain-size (<2 μm, Fig. 1f). However, electron-microprobe analyses of Pd–O alteration halos on arsenide–antimonide of palladium indicate the existence of an oxygen-deficient Pd–Cu phase (Cabral *et al.* 2003a) and a significant negative linear correlation between oxygen

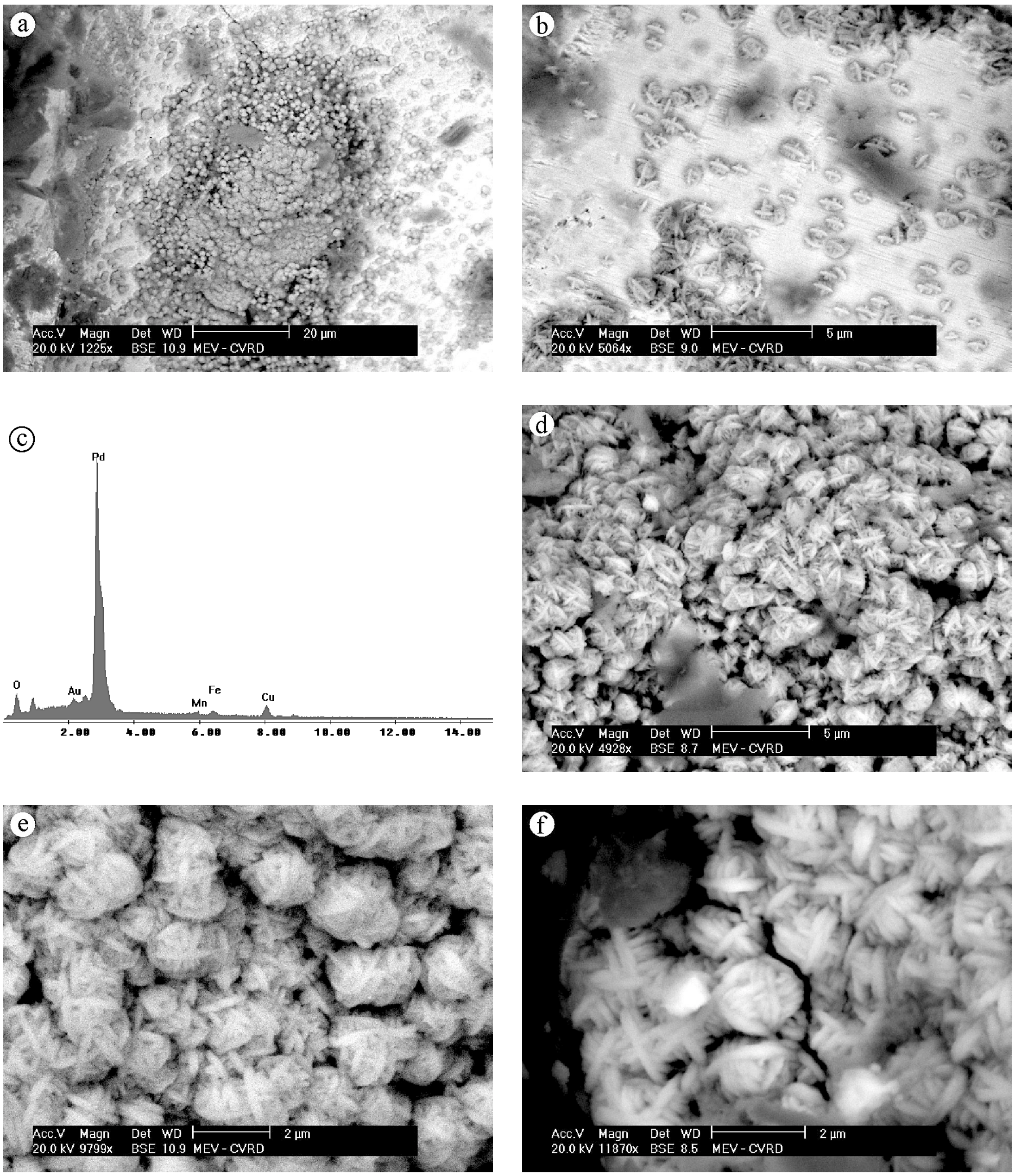

FIG. 1. Back-scattered electron (BSE) images and energy-dispersion spectrum (EDS) of Pd-rich rosettes from Gongo Soco. (a) Light grayish spots are scattered over iron oxyhydroxide (center, dark gray) and gold (white). (b) Under higher magnification, the spots exhibit a rosette-like morphology. They rest on gold (white). (c) Energy-dispersion spectrum of a rosette, consisting essentially of palladium, with subordinate amounts of oxygen, copper, iron and manganese. (d) Cluster of Pd-rich rosettes. (e) Close-up of an aggregate of rosettes. (f) Detail of a rosette (center), showing the intersecting discs apparently at three orthogonal directions (*cf.* Fig. 9d, Kwitko *et al.* 2002).

and palladium (Cabral & Lehmann 2003), suggesting a transitional range from an empirically derived PdO-like stoichiometry to native palladium, where native palladium would likely be the stable phase of palladium under supergene conditions (Cabral *et al.* 2004). Considering a hydrated palladium oxide, McDonald *et al.* (1999b) proposed that recurrent heating during the tropical dry season would eventually dehydrate it to native palladium. It is intriguing, but speculative, that the rosette-like morphology can be compared to those of efflorescences ("desert roses") formed by evaporation in a dry climate.

It was not possible to define whether the Pd-rich rosettes are true PdO (or a palladium hydroxide or hydrated compound) or an oxygen-deficient phase close to native palladium. Whatever the case, this study gives evidence for the neoformation of PGM at low temperatures. Possibly, the Pd-rich rosettes are supergene in origin, formed under oxidizing conditions (stability field of hematite). Palladium and platinum alloys that formed within the stability field of hematite at low temperatures are also known from other localities in Brazil. They are exemplified by the dendritic and botryoidal Pt and Pt–Pd alloys from Córrego Bom Sucesso, Minas Gerais (Cassedanne *et al.* 1996, Fleet *et al.* 2002, and references therein), and the Pd and veinlet Pt from the Serra Pelada area, Carajás mineral province, Pará (Cabral *et al.* 2002a).

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