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PLATINUM–PALLADIUM NUGGETS AND MERCURY-RICH PALLADIFEROUS PLATINUM FROM SERRO, MINAS GERAIS, BRAZIL

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Abstract

Arborescent, botryoidal and reniform grains of platinum and palladium from Córrego Bom Sucesso, Serro, Minas Gerais, Brazil, were investigated by scanning electron microscopy and electron-microprobe analysis. The nuggets reach a maximum length of 2.5 mm and exhibit core-to-rim compositional zoning in platinum, palladium and mercury contents. One grain is noteworthy for a marginal halo of mercury-rich palladiferous platinum and internal vermiform lamellae enriched in mercury and gold. The mercury-rich palladiferous platinum has 10–20 wt% Hg and an empirical stoichiometry close to $(Pt,Hg)_2Pd$. Hexagonal crystals occur in palladiferous platinum forming a peripheral zone of an arborescent grain. These crystals are compositionally analogous to stoichiometric PdPt and seem to represent an ordered phase distinct from either platinum or palladium. Most Pt–Pd grains have dissolution pits, suggesting that they are primary nuggets that have been weathered. Anatase, with or without intergrowth of gold, and Na–K–Cl-bearing aggregates postdate the Pt–Pd nuggets. Selenium is a minor alloying constituent (up to 0.3 wt%) in the Pt–Pd nuggets. The ratio S:Se is <1 and suggests fractionation of selenium from sulfur under low-temperature oxidizing conditions. Such oxidizing conditions are reflected in the Fe-poor bulk composition of the alloys. The Pt–Pd nuggets from Córrego Bom Sucesso are consistent with the observation that almost all economically important Brazilian Pd–Pt-bearing deposits associated with gold or hematite (or both) have a distinctive seleniferous signature.

Keywords: platinum, palladium, mercury-rich palladiferous platinum, PdPt, alluvial nuggets, Córrego Bom Sucesso, Serro, Minas Gerais, Brazil.

Sommaire

Des grains arborescents, botryoïdaux et réniformes de platine et de palladium provenant de Córrego Bom Sucesso, Serro, Minas Gerais, Brésil, ont fait l'objet d'analyses avec un microscope électronique à balayage et une microsonde électronique. Les pépites atteignent une longueur maximale de 2.5 mm et montrent une zonation du noyau à la bordure en Pt, Pd et Hg. Un grain est particulier pour son liseré de platine palladifère riche en mercure et des lamelles internes vermiformes enrichies en Hg et Au. Le liseré contient 10–20% de Hg par poids, et possède une stoechiométrie empirique proche de $(Pt,Hg)_2Pd$. Des cristaux hexagonaux de platine palladifère forment une zone périphérique d'un grain arborescent. Ces cristaux ont une composition analogue

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au PtPd stoechiométrique et semblent représenter une espèce ordonnée distincte à la fois du platine ou du palladium. La plupart des grains de Pt–Pd montrent des piqûres de dissolution, qui concorderaient avec l'hypothèse qu'ils sont des pépites primaires assujetties à un lessivage. L'anatase, avec ou sans intercroissance avec l'or, et des aggrégats riches en Na–K–Cl, sont venus par la suite. Le sélénium est présent en proportions mineures (jusqu'à 0.3% par poids) dans les pépites Pt–Pd. Le rapport S:Se est <1 et semble indiquer un fractionnement du Se à partir du S en milieu oxydant à faible température. De tels milieux oxydants expliqueraient les faibles teneurs en Fe des alliages. Les pépites Pt–Pd de Córrego Bom Sucesso concordent avec l'observation que la grande majorité des indices de Pd–Pt économiquement importants au Brésil associés avec l'or ou l'hématite (ou les deux) possèdent une signature sélénifère distinctive.

(Traduit par la Rédaction)

Mots-clés: platine, palladium, platine palladifère riche en mercure, PdPt, pépites alluvionnaires, Córrego Bom Sucesso, Serro, Minas Gerais, Brésil.

Introduction

What the hodiernal literature designates as "unconventional" deposits of platinum and palladium (*i.e.*, nonmagmatic, *e.g.*, Wilde *et al.* 2003) used to be quite conventional in Brazil. Sample material from Brazil, possibly from Minas Gerais, gave the first evidence of a natural gold–palladium alloy (Gehlen 1811). The characteristically lighter color of palladiferous gold was noticed by local miners at the dawn of the Gold Cycle in Minas Gerais (~1695–1785), when *ouro branco* (white gold) was recovered from specular-hematite-rich placers (Hussak 1904). Much of the *ouro preto* (black gold) then extracted from the Ouro Preto region originated from itabirite-hosted, palladiferous-gold-bearing lodes (*e.g.*, Eschwege 1818, Hartt 1870, Touzeau 1892, Ferrand 1894, Scott 1902, Hussak 1904, Jedwab & Cassedanne 1998, Cabral *et al.* 2003). A vein with Pt–Ag–Ir–Os-bearing gold associated with specular hematite from Minas Gerais was documented by Lampadius & Plattner (1833). Humboldt (1826) noted the occurrence of platinum and palladium in diamantiferous alluvia in the Serro area. The alluvia provided (i) the samples in which Wollaston (1809) identified native palladium for the first time (Hussak 1904, Atencio 2000), and probably (ii) the specimens from which the element palladium was discovered in 1803 (Cassedanne & Alves 1992, Cassedanne *et al.* 1996).

Alluvial platinum and palladium from the Serro region are noteworthy for the *sui generis* morphology of botryoidal, coralloidal and arborescent grains, as well as the low content of base metals, particularly iron (Hussak 1904, 1906, Guimarães 1959, Cassedanne & Cassedanne 1974, Cassedanne & Alves 1992, Cassedanne *et al.* 1996, Fleet *et al.* 2002). Such uniqueness led Hussak (1904, 1906) to propose a secondary (supergene) recrystallization of platinum after a primary platiniferous mineral. Recently, a low-temperature hydrothermal origin for the alluvial platinum and palladium from Córrego Bom Sucesso has been favored (Cassedanne *et al.* 1996, Fleet *et al.* 2002).

New observations on grains of platinum and palladium from Córrego Bom Sucesso, Serro, Minas Gerais, are presented here. In this study, we report for the first time a natural mercury-bearing alloy of palladiferous platinum, although platinum forms synthetic compounds with mercury (Berlincourt *et al.* 1981). We also document crystals of PdPt stoichiometry, as well as a significant enrichment in selenium of the Pt–Pd assemblage.

Sample Material and Córrego Bom Sucesso

Grains of platinum and palladium were purchased from a prospector, who recovered them by panning alluvium from a seasonal stream known as Corrégo Bom Sucesso, near the baroque village of Serro. A regional geological map and a location map of the historical Bom Sucesso prospect can be found elsewhere (Cassedanne *et al.* 1996, Fleet *et al.* 2002). The prospect has been worked manually for diamond, gold and platinum for more than two centuries. It consists of unsorted alluvium protected from erosion by boulders of quartzite (Cassedanne & Alves 1992). The source rock for the Pt–Pd nuggets is unknown.

The Bom Sucesso valley runs over a sequence of quartzite intercalated with schists, layers of massive hematite and lenses of diamantiferous metaconglomerate, cut by a mafic intrusion metamorphosed to amphibolite grade (Cassedanne *et al.* 1996). The quartzite sequence, previously attributed to the Paleoproterozoic Minas Supergroup (Cassedanne & Alves 1992, Fleet *et al.* 2002), possibly belongs to the Mesoproterozoic Espinhaço Supergroup because diamantiferous metaconglomerates are characteristic of the latter (*e.g.*, Chaves *et al.* 1998, Almeida-Abreu & Renger 1999). The Espinhaço Supergroup was deformed during the Brasiliano orogeny, at about 600 Ma (Trompette *et al.* 1992).

Analytical Techniques

Nuggets of platinum and palladium of up to 2.5 mm across were investigated by scanning electron microscopy (SEM) at Companhia Vale do Rio Doce (CVRD), Brazil, and at the Laboratoire de Microanalyse, Université Laval (UL), Canada. Some grains were mounted in resin and polished for electron-microprobe analysis with a Cameca SX100 at UL. Analytical conditions, standards and X-ray emission lines were as follows: 15 kV and 40 nA, a beam size 2 to 5 μm in diameter, and counting times of 20 s and 10 s on peak and background, respectively; we used PtFe and pure Pt (Pt*L*α), HgS (Hg*L*α), Au (Au*L*α), $CuFeS_2$ (Cu*K*α), PdS (Pd*L*α), FeS_2 (S*K*α), and pure Se (Se*L*α) as standards. X-ray-generated element-distribution images of 512 × 512 pixels were acquired using the same lines and spectrometers on a 256 × 256-μm square area with a counting time of 50 ms/pixel.

Morphology and Compositional Zoning

Grain morphologies are variable and delicate, and include arborescent (Fig. 1a), spongy (Fig. 1b) and botryoidal (Fig. 1c) types. Many of the botryoidal grains have a coating of titanium oxide (Fig. 1d). The Ti–O phase is considered to be anatase (Cassedanne *et al.* 1996). Anatase is not restricted to the surface of the grains, but is also found as veinlets and as infillings of cavities, where it is intergrown with nanometric gold (Fig. 1e). Remarkably, though rarely observed, K-bearing NaCl occurs on grain surfaces (Fig. 1f). It possibly consists of fine-grained crystals of halite and sylvite. Some nuggets display a coralloidal habit (Fig. 2a), which is composed of intricately reticulated, delicate threads of palladiferous platinum (Figs. 2b, c). This form is strikingly similar to that of Wollaston's original specimens, from which the element palladium was discovered (*vide* Fig. 3 of Cassedanne & Alves 1992).

Some grains show prominent cracking (Fig. 3a). Although botryoidal nuggets have a smooth appearance, closer inspection reveals that the surface is corrugated and pitted (Fig. 3b). One botryoidal nugget has a particularly complex internal microstructure, with rims of brighter (higher mean Z) material surrounding an irregular core with lower mean Z (Figs. 3c, 4a). The core contains vermiform lamellae of brighter material and gold (Figs. 3c, 4a). Platinum tends to be most enriched in the margin (Fig. 4b). This marginal halo is followed by a mercury-enriched zone toward the core (Fig. 4c), where relatively Pd–Pt-depleted (Figs. 4b, d), worm-shaped intergrowths are abundant (Fig. 4a). Gold occurs as Hg-bearing vermiform lamellae (Figs. 4c, e) and also as disseminated, patchy inclusions up to 30 μm in length (Fig. 3c). Selenium, though a trace component, exhibits a more homogeneous distribution (Fig. 4f).

Platinum, however, is not invariably concentrated at the margin of nuggets. One reniform grain of palladiferous platinum has internal areas of auriferous Pd–Hg alloy (potarite) surrounded by a concentric rim of almost pure platinum (Fig. 5a). Generally, palladium is more abundant in the internal areas of the nuggets (Figs. 5b, c, d), ranging from platiniferous palladium, with or without mercury, to auriferous, Hg-depleted potarite (Fig. 5e) (Cassedanne *et al.* 1996, Fleet *et al.* 2002). Hexagonal crystals of approximate $Pd_{50}Pt_{50}$ composition (Fig. 5f) occur in the marginal zone of an arborescent grain.

Mineral Chemistry

Representative electron-microprobe analyses of Córrego Bom Sucesso nuggets indicate that platinum, palladium and mercury are the major elements (Table 1, Fig. 6). Five compositional fields (Fig. 6) were distinguished for the Córrego Bom Sucesso nuggets by Fleet *et al.* (2002): (1) pure platinum (>90 at.% Pt), (2) palladiferous platinum, (3) platinum–palladium alloy (~PtPd), (4) platiniferous palladium, (5) auriferous, Hg-depleted potarite. A compilation of previous information and our new data suggest that an almost complete Pt–Pd solid solution exists in nature and, therefore, that fields (2), (3) and (4) of Fleet *et al.* (2002) are not discrete. We have identified two new compositional fields: (6) mercury-enriched platiniferous palladium, and (7) mercury-enriched palladiferous platinum. Field (6) may be fortuitous, since it is represented by only one data point. Field (7) comprises compositions close to $(Pt,Hg)_2Pd$, with up to 20 wt% Hg. Figure 3c demonstrates that the micro-analyses were made in clearly resolved areas that display different mean Z. The analytical points cannot represent intricate mixtures of potarite and palladiferous platinum because the composition of adjacent mercury-enriched palladiferous platinum and host Pt–Pd alloy are linked by tie-lines at a high angle to hypothetical mixing lines between potarite and various Pt–Pd alloy compositions (Fig. 6). This $(Pt,Hg)_2Pd$ phase displays a negative correlation between levels of mercury and platinum (Fig. 7), which suggests substitution of platinum for mercury.

The alloy close to the stoichiometry PdPt not only occurs in core areas of botryoidal nuggets (Fig. 3c), as also observed by Fleet *et al.* (2002), but also as hexagonal crystals (Fig. 5f). Such discrete crystals suggest an ordered $Pd_{50}Pt_{50}$ phase. Bimetallic PdPt clusters produced by laser vaporization have well-formed hexagonal faces (Rousset *et al.* 1995), which are analogous to those of Figure 5f.

Selenium is present as a minor element, possibly in solid solution in the alloy (Fig. 4f). Its concentration ranges from below the detection limit, 0.03 wt% to 0.29 wt% Se (Table 1). Sulfur was occasionally detected (up to 0.06 wt% S), but was mostly below the detection limit, 0.01 wt% S. It is thus reasonable to affirm that the grains of platinum and palladium have S:Se less than 1.

Discussion

The Pd–Pt nuggets at Córrego Bom Sucesso are characterized by: (i) delicate shapes, (ii) the absence of mineral inclusions other than gold (Figs. 3c, 4a, e) and PdPt (Fig. 5f), (iii) open spaces between the limbs

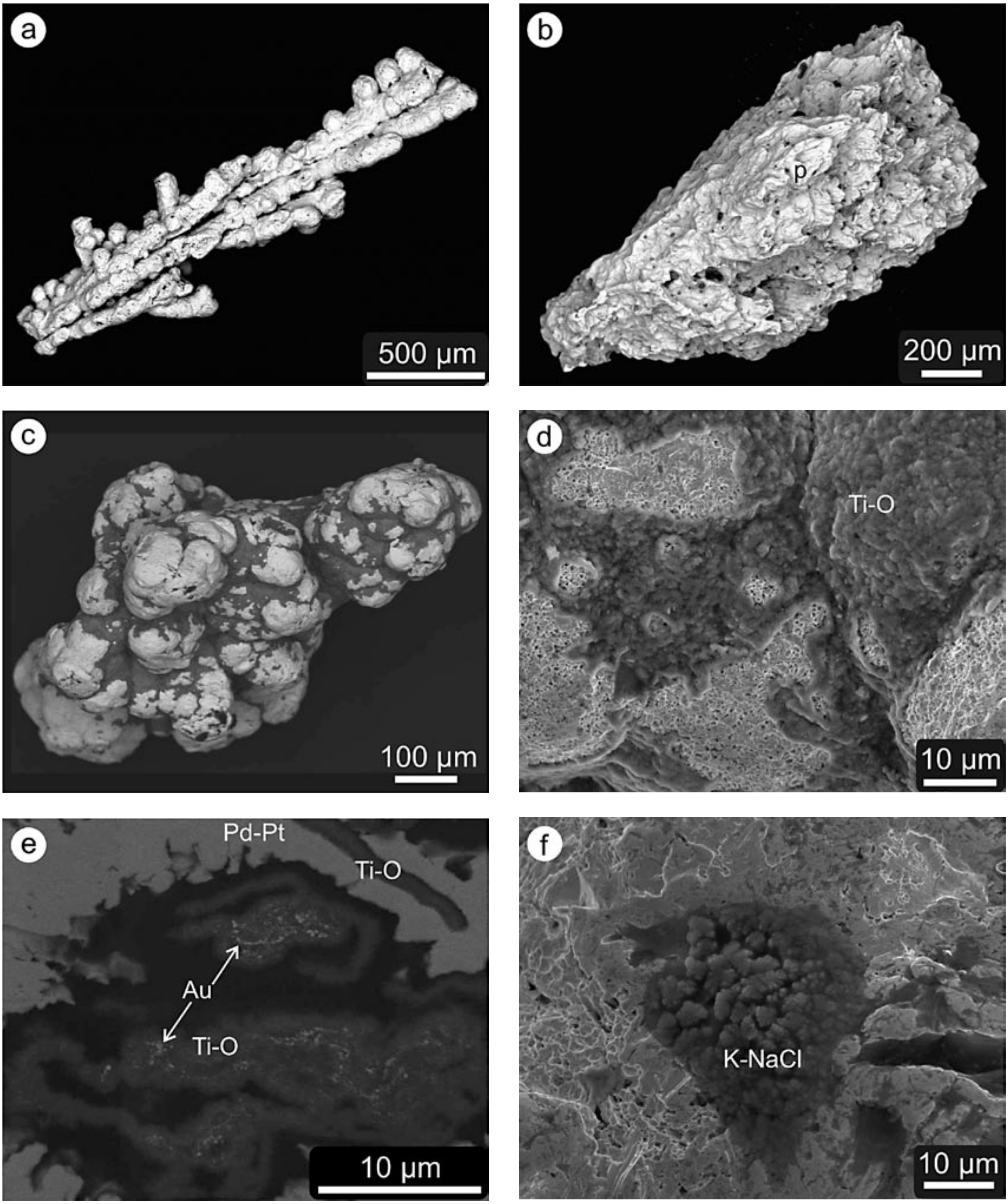


FIG. 1. Back-scattered electron (BSE, a, b, c and e) and secondary electron (SE, d and f) images of alluvial Pt–Pd–Hg nuggets from Córrego Bom Sucesso. (a) Arborescent Pt–Pd grain. (b) Grain of potarite (p, ideally PdHg). (c) Botryoidal Pt–Pd nugget (white) partially coated with aggregates of titanium oxide. (d) Detail of the coating of titanium oxide (Ti–O, possibly anatase) on the pitted surface of the grain in c. (e) Submicrometric gold associated with anatase (Ti–O) that fills part of a cavity in the Pt–Pd nugget (*vide* Fig. 5b). (f) Aggregate of K-bearing sodium chloride (K–NaCl) on the pitted surface of a Pt–Pd grain.

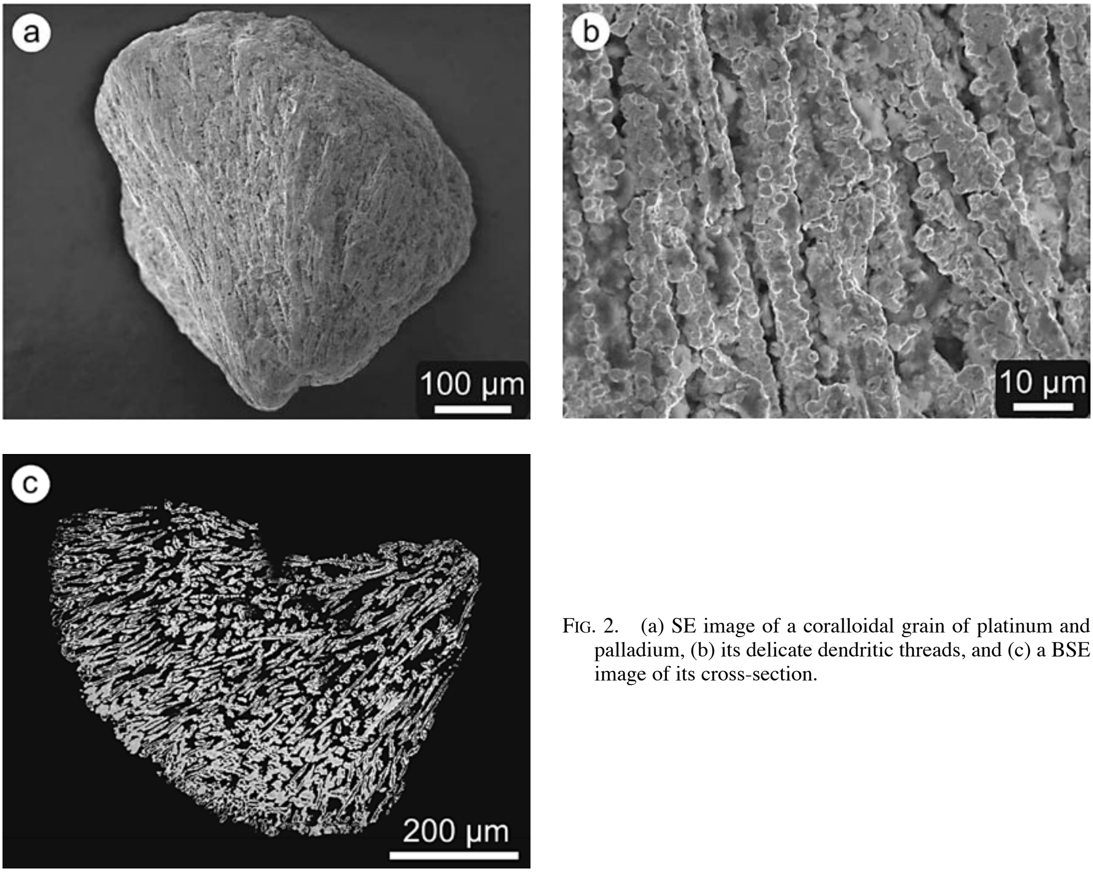


FIG. 2. (a) SE image of a coralloidal grain of platinum and palladium, (b) its delicate dendritic threads, and (c) a BSE image of its cross-section.

of arborescent grains, (iv) intragranular microfractures, and (v) very unusual compositions, without base metals. Preliminary results of quantitative micro-analyses indicate that iron is generally below the detection limit, 0.05 wt% Fe. Copper does not exceed 0.3 wt% (Table 1). In this respect, our findings, like those of Fleet *et al.* (2002), do not corroborate the SEM investigation of Cassedanne *et al.* (1996), who found "cuproplatinum" in Córrego Bom Sucesso.

Dissolution pits on the surface of grains have morphological characteristics analogous to those formed during tropical weathering of residual (primary) gold (Colin *et al.* 1997, Varajão *et al.* 2000). Consequently, the Córrego Bom Sucesso nuggets were derived from a primary source that was weathered, *i.e.*, they are not supergene in origin as proposed by Hussak (1904) and Cassedanne & Alves (1992). The occurrence of anatase (Fig. 1d) and Na–K–Cl-bearing aggregates (Fig. 1f) on pitted surfaces supports the interpretation that a late fluid circulated through the Mesoproterozoic quartzite sequence and dissolved chlorine from apatite and titanium from rutile (and other titaniferous minerals) in quartzite to precipitate salt and anatase on, and within, the nuggets, as suggested by Cassedanne *et al.* (1996). Gold precipitated as nanometric particles within anatase (Fig. 1e). Therefore, the Na–K–Cl-bearing aggregates, anatase and its associated gold are most likely of supergene origin and postdate the nuggets of platinum and palladium. These supergene saline fluids could have originated by evaporation of groundwater during dry seasons.

Mercury-enriched palladiferous platinum

Mercury-enriched palladiferous platinum, a $(Pt,Hg)_2Pd$-like alloy, occurs as continuous, clearly resolved areas in Figures 3c and 5d. The mineral's composition therefore represents a discrete phase and not an intimate mixture of palladiferous platinum ($Pt_{80}Pd_{20}$) and potarite (Fig. 6). The mercurian palladiferous platinum coexists with PtPd alloy ($Pt_{50}Pd_{50}$), not with $Pt_{80}Pd_{20}$ (Figs. 3c, 6, Table 1). The tie-lines at a high angle with the hypothetical mixing line thus indicate that the $(Pt,Hg)_2Pd$ alloy cannot be an intricate

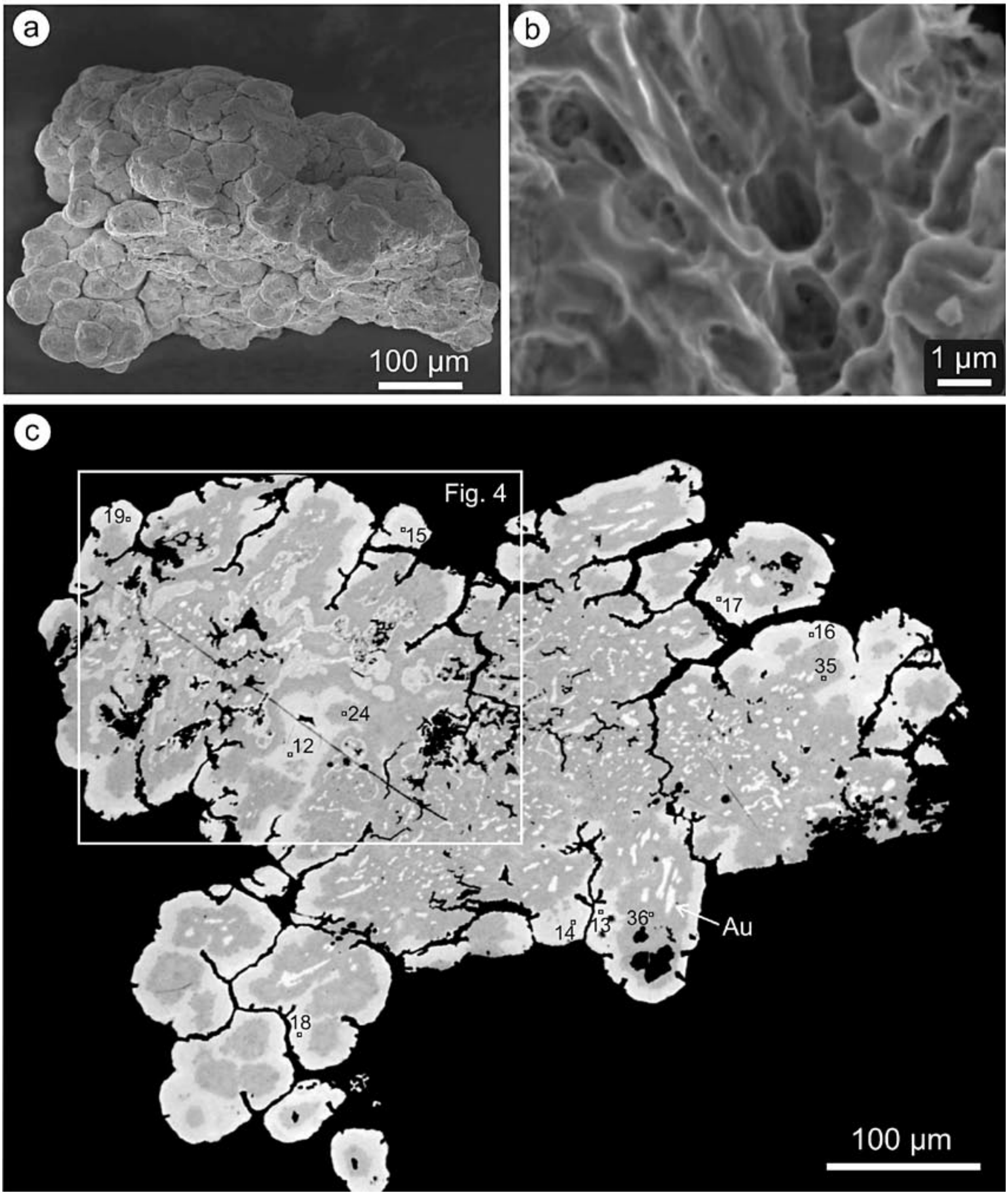


FIG. 3. SE images of (a) a botryoidal nugget and (b) its surface, showing dissolution pits. (c) BSE image of a cross-section indicating the core-to-rim compositional zoning with vermiform lamellae of relatively high mean Z. Bright white patches are gold (arrow). The outlined area is presented in Figure 4; numbers correspond to sites of micro-analyses, with results recorded in Table 1.

TABLE 1. ELECTRON-MICROPROBE DATA ON NUGGETS OF PLATINUM AND PALLADIUM, CÓRREGO BOM SUCESSO, BRAZIL

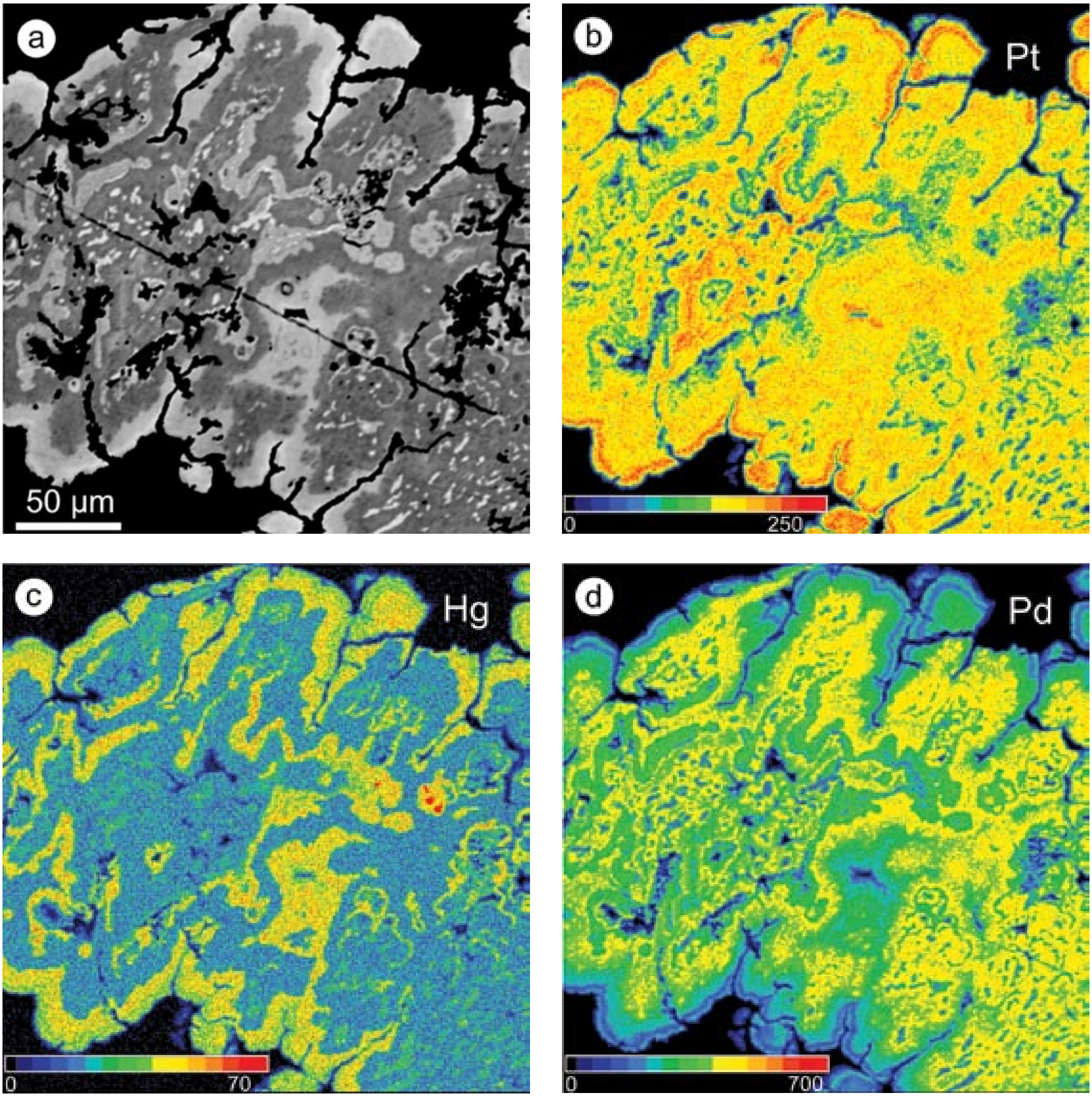
No.	Pt	Pd	Hg	Au	Cu	S	Se	Total	Pt	Pd	Hg	Au	Cu	S	Se	Σ
1	98.50	0.32	1.46	<0.4	0.23	<0.01	0.05	100.56	0.972	0.006	0.014		0.007		0.001	1
2	94.09	0.33	3.60	1.61	0.33	<0.01	0.03	99.99	0.933	0.006	0.035	0.016	0.010		0.001	1
3	94.00	1.00	3.67	1.76	0.27	<0.01	0.03	100.72	0.921	0.018	0.035	0.017	0.008		0.001	1
4*	88.63	11.36	0.55	<0.4	<0.04	0.06	0.03	100.62	0.803	0.189	0.005			0.003	0.001	1
5*	81.16	17.79	0.44	<0.4	<0.04	0.06	0.06	99.51	0.707	0.284	0.004			0.003	0.001	1
6	78.21	17.17	3.63	0.93	0.11	<0.01	0.07	100.12	0.682	0.274	0.031	0.008	0.003		0.002	1
7	77.43	19.62	2.25	0.88	0.09	<0.01	0.15	100.43	0.661	0.307	0.019	0.007	0.002		0.003	1
8	76.42	22.74	<0.6	<0.4	<0.04	<0.01	0.09	99.24	0.646	0.352					0.002	1
9	74.18	23.70	1.85	<0.4	0.08	<0.01	0.10	99.92	0.619	0.362	0.015		0.002		0.002	1
10*	69.84	29.76	1.09	<0.4	<0.04	0.04	0.10	100.84	0.554	0.433	0.008			0.002	0.002	1
11*	67.23	31.37	1.02	<0.4	<0.04	0.03	0.22	99.88	0.532	0.455	0.008			0.001	0.004	1
12	57.35	24.96	18.29	<0.4	<0.04	<0.01	0.03	100.63	1.422	1.135	0.441				0.002	3
13	60.90	21.41	17.63	0.52	0.12	<0.01	0.03	100.61	1.545	0.996	0.435	0.013	0.009		0.002	3
14	55.74	24.03	20.09	<0.4	0.10	<0.01	0.03	100.00	1.397	1.104	0.490		0.007		0.002	3
15	55.71	25.69	18.42	<0.4	0.06	<0.01	0.03	99.90	1.382	1.168	0.444		0.004		0.002	3
16	58.84	24.20	16.59	<0.4	<0.04	<0.01	<0.03	99.63	1.479	1.115	0.406					3
17	60.23	23.06	16.57	<0.4	<0.04	<0.01	<0.03	99.85	1.524	1.069	0.408					3
18	62.22	21.19	15.92	<0.4	<0.04	<0.01	<0.03	99.33	1.602	1.000	0.399					3
19	61.31	23.16	16.00	<0.4	<0.04	<0.01	<0.03	100.47	1.541	1.067	0.391					3
20	67.08	21.83	10.36	<0.4	<0.04	<0.01	0.03	99.31	1.716	1.024	0.258				0.002	3
21	63.97	22.93	12.94	<0.4	<0.04	<0.01	0.04	99.88	1.617	1.062	0.318				0.003	3
22	40.05	42.07	17.71	<0.4	<0.04	<0.01	0.05	99.88	0.298	0.573	0.128				0.001	1
23	63.94	34.63	1.46	<0.4	0.06	<0.01	0.08	100.17	0.990	0.983	0.022		0.003		0.003	2
24	61.98	36.63	1.34	<0.4	0.04	<0.01	0.05	100.04	0.949	1.028	0.020		0.002		0.002	2
25	64.27	34.84	1.26	<0.4	0.04	<0.01	0.03	100.43	0.992	0.986	0.019		0.002		0.001	2
26	66.35	32.93	1.34	<0.4	0.05	<0.01	<0.03	100.66	1.035	0.942	0.020		0.002			2
27	50.65	46.02	2.09	<0.4	<0.04	<0.01	0.29	99.05	0.368	0.612	0.015				0.005	1
28	54.91	44.59	<0.6	<0.4	<0.04	<0.01	0.03	99.52	0.402	0.598					0.000	1
29	54.21	43.87	1.79	<0.4	<0.04	<0.01	0.19	100.06	0.396	0.588	0.013				0.003	1
30	55.30	43.33	1.56	<0.4	<0.04	<0.01	0.17	100.36	0.405	0.581	0.011				0.003	1
31	56.88	42.08	<0.6	<0.4	<0.04	<0.01	0.04	99.01	0.424	0.575					0.001	1
32	54.88	41.41	2.80	<0.4	<0.04	<0.01	0.04	99.13	0.411	0.568	0.020				0.001	1
33	57.39	40.63	0.82	<0.4	<0.04	<0.01	0.24	99.08	0.431	0.559	0.006				0.004	1
34	56.74	40.18	2.54	<0.4	0.04	<0.01	0.08	99.57	0.426	0.553	0.019		0.001		0.002	1
35	61.29	37.89	<0.6	<0.4	<0.04	<0.01	0.03	99.21	0.469	0.531					0.001	1
36	58.96	37.88	3.60	<0.4	<0.04	<0.01	0.06	100.50	0.447	0.526	0.026				0.001	1
37	<0.6	42.42	50.70	6.57	<0.04	<0.01	<0.03	99.70		1.164	0.738	0.097				2

Compositions are first reported in wt%, then recast as atoms per formula unit (*apfu*) according to the total number of atoms Σ in the formula. Sample numbers: 1–3: pure platinum, 4–11: palladiferous platinum, 12–21: Hg-bearing palladiferous platinum, ~$(Pt,Hg)_2Pd$, 22: Hg-bearing platiniferous palladium, 23–26: ~PtPd, 27–36: platiniferous palladium, 37: auriferous potarite.
* Micro-analyses made using PtFe as standard for platinum (*vide* text).

mixture of $Pt_{50}Pd_{50}$ and auriferous potarite. If it were so, the mercury-enriched palladiferous platinum should lie along a hypothetical $Pt_{50}Pd_{50}$ – auriferous potarite mixing line (Fig. 6). This is consistent with the negative correlation between mercury and platinum (Fig. 7). If this mineral phase were a mixture of potarite and Pt–Pd alloy phases, one would expect no correlation between mercury and platinum.

The S:Se ratio

Differences in the geochemical behavior of selenium and sulfur result in distinct ratios of S:Se that can assist in understanding the origin of rocks and ores (*e.g.*, Goldschmidt & Hefter 1933, Stanton 1972). Most clastic sedimentary rocks, evaporites and seawater have S:Se in excess of 10^5 (Hattori *et al.* 2004). Electron-microprobe analyses indicate that the Córrego Bom Sucesso nuggets have S:Se less than 1. This extreme fractionation of selenium from sulfur is expected to occur where reduced selenium predominates over reduced sulfur in hydrothermal fluids at conditions within the stability field of hematite (Simon *et al.* 1997, Xiong 2003). However, values of the ratio S:Se less than 1 are also known from supergene iron sulfoselenides formed by bacterial activity in a stagnant body of water over the Zapadno–Ozernoe copper–zinc massive sulfide deposit, South Urals (Belogub *et al.* 2003, Yakovleva *et al.* 2003). Such a stagnant fluid regime, if applied to Córrego Bom Sucesso, could not account for the zoning



of platinum, palladium and mercury, which likely represents episodic fluctuation in the supply of metals during growth of the nuggets (Fleet *et al.* 2002).

The possibility that the S:Se ratio in the Pt–Pd alloys was not acquired during precipitation should be taken into account. The S:Se ratio would thus bear no relation to the fluid from which the alloys precipitated. As an alternative, its ratio may be a product of weathering, *i.e.*, leaching of selenium and sulfur from the Pt–Pd nuggets by supergene fluids. There is, however, no evidence for change in the distribution of selenium in the alloys that could be related to weathering (Fig. 4f). On the contrary, selenium is homogeneously distributed (Fig. 4f). For a weathering-derived S:Se ratio to be viable, one must assume that some sulfur-bearing phase formed contemporaneously with the Pt–Pd alloys so that sulfur was partitioned into the original sulfur-bearing phase, which was later dissolved selectively. There is no evidence for the former existence of a S-bearing mineral intimately intergrown with the alloys (Fleet *et al.* 2002).

Origin of metals

The origin of the alluvial Pt–Pd nuggets from Córrego Bom Sucesso is controversial. Cassedanne *et al.* (1996) and Fleet *et al.* (2002) considered a low-temperature hydrothermal origin more likely than the diagenetic hypothesis of Hussak (1904). Within the

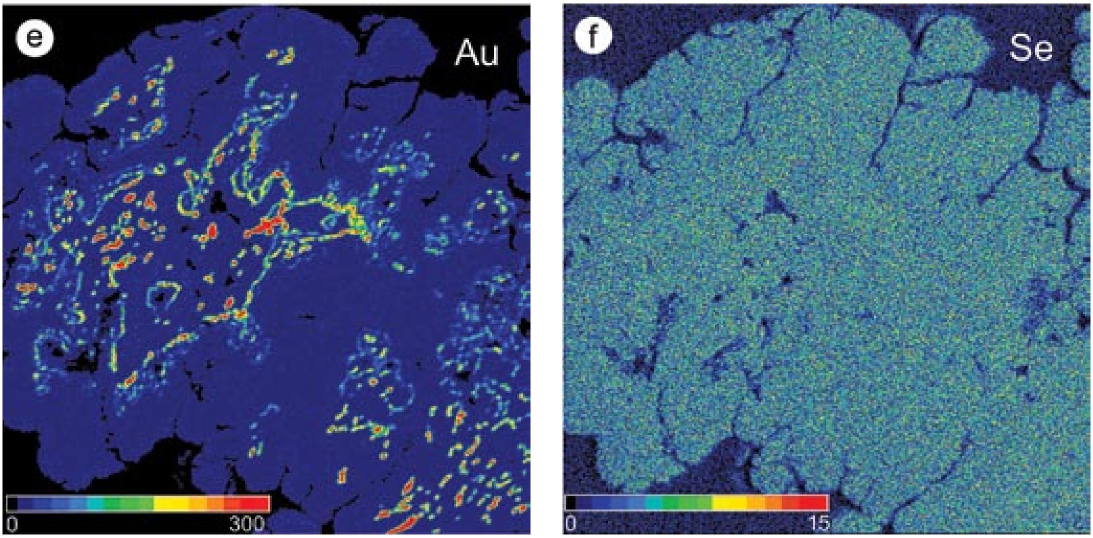


FIG. 4. Detail of the grain shown in Figure 3, with (a) BSE image depicting the internal fabric and X-ray element-distribution maps for (b) platinum, (c) mercury, (d) palladium, (e) gold, and (f) selenium.

drainage basin, the most probable source-rocks for the precious metals in the nuggets are the amphibolitized mafic intrusive rocks that cut the quartzite sequence (Cassedanne *et al.* 1996). Fleet *et al.* (2002) suggested that hydrothermally remobilized platinum and palladium precipitated in open spaces in the host quartzite. However, mafic–ultramafic rocks are unlikely sources for mercury, and it is conceivable that mercury may have been leached from the surrounding metasediments (*cf.* Arai *et al.* 1999).

Since mercury is an element closely related to near-surface hydrothermal systems (Barnes & Seward 1997) and since the arborescent and botryoidal shapes of nuggets are suggestive of open-space-filling, shallow-level circulation of hydrothermal fluid through the quartzite sequence and the amphibolite lenses is favored (Cassedanne *et al.* 1996, Fleet *et al.* 2002). Significantly, there is some Hg-bearing overprint by manganiferous veinlets, with and without hematite, that cross-cut Brasiliano fabrics in the Paleoproterozoic banded iron formations (Cauê Formation) of the Quadrilátero Ferrífero (Cabral *et al.* 2002d, Cabral 2006), in the southern extension of the Brasiliano belt, ~200 km south–southwest of Serro. This late- to post-Brasiliano enrichment in mercury probably led to the Hg-bearing Pt–Pd alloys sporadically associated with Pd–O-like species after Pd–Sb–As phases in palladiferous gold (Cabral *et al.* 2002c, Cabral & Lehmann 2003). We thus suggest that the Pt–Pd–Hg nuggets from Córrego Bom Sucesso (Serro) are late- to post-Brasiliano in age.

Comparison with other (Au)–Pd–Pt deposits

The high oxidation state of the ore fluid from which the Córrego Bom Sucesso Pt–Pd alloys precipitated is indicated by the low S:Se ratio. This high oxidation state is reflected in the bulk composition of the Pt–Pd alloys, which lack significant iron and resemble the Fe-free Pt–Pd alloy from hematite-rich veins of the Waterberg deposit, South Africa (Wagner 1929, McDonald *et al.* 1999). A veinlet of Fe-poor Pt–Pd alloy, enveloped by an iron oxide halo, is also known from the Elefante prospect, Serra Pelada area, northern Brazil (Cabral *et al.* 2002b). All these occurrences of Pt–Pd alloys, which are characterized by low contents of iron, corroborate experimental evidence that under low fugacity of sulfur and low-temperature conditions, platinum alloys are poor in iron (Evstigneeva & Tarkian 1996).

The occurrence of some selenium in solid solution in the Córrego Bom Sucesso Pt–Pd alloys is noteworthy. All known instances of economically important palladiferous gold mineralization in Brazil, comprising the world-class Serra Pelada Au–Pd–Pt deposit (Moroni *et al.* 2001, Şener *et al.* 2002, Cabral *et al.* 2002a, b) and the *ouro preto*-bearing hematite deposits of Minas Gerais (Hussak 1904, 1906, Olivo & Gauthier 1995, Cabral 2006), have a seleniferous signature. This signature results from oxidizing conditions under which sulfur is in the form of sulfate and accentuates the sulfide-poor character of all these deposits. The recognition of this fact is relevant because prospecting for platinum- and palladium-bearing mineralization in Brazil has traditionally focused on sulfide-rich systems.

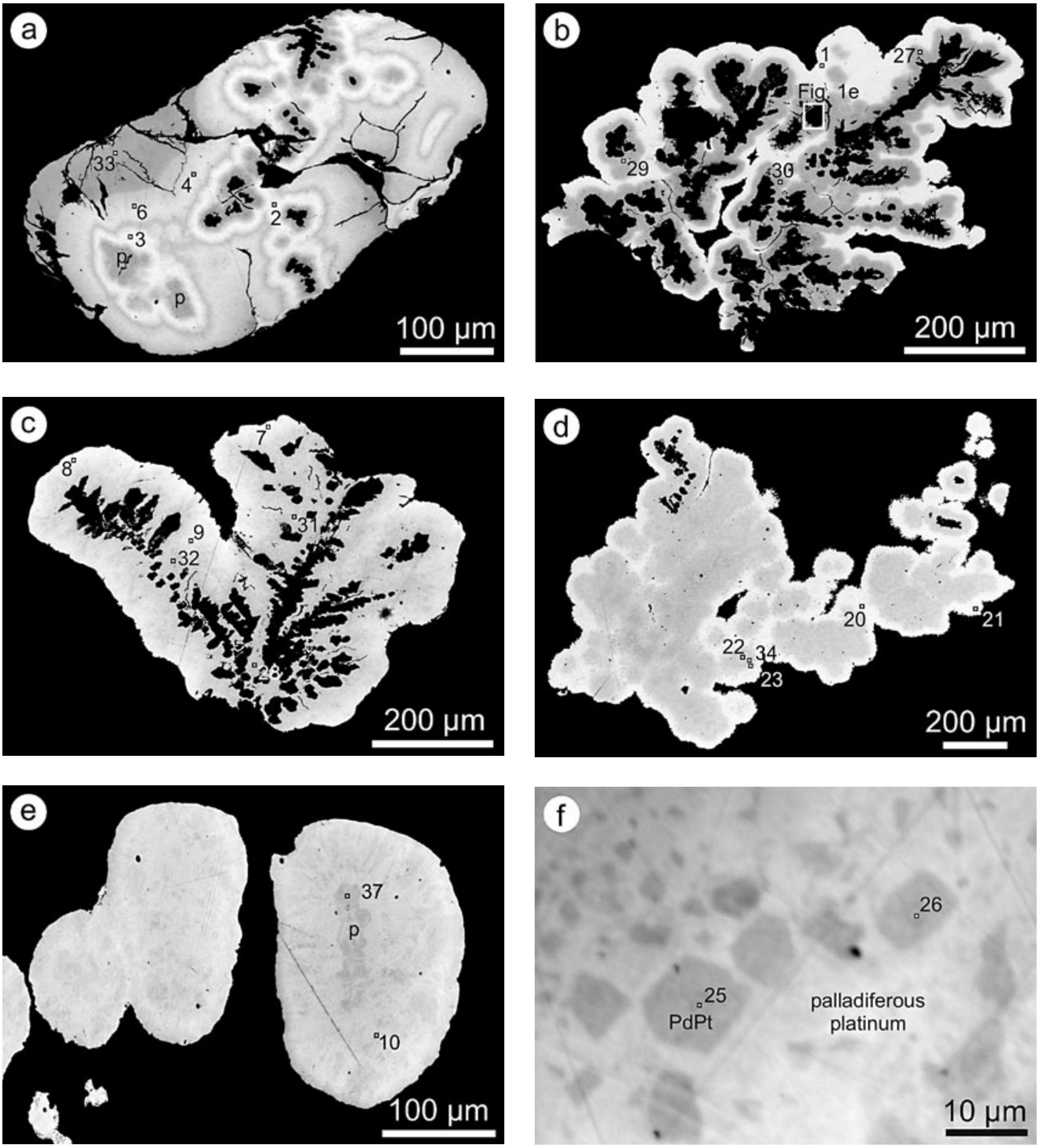


FIG. 5. BSE images illustrating a core-to-rim pattern of compositional zoning. Numbers correspond to sites of micro-analyses being reported in Table 1. (a) Auriferous potarite, p, surrounded by a rim of platinum (white) within palladiferous platinum (medium grey), which is partially coated by platiniferous palladium (dark grey). (b) Arborescent grain of platiniferous palladium core (dark grey) and platinum rim (white). (c) Dendritic grain of platiniferous palladium core (dark grey) and palladiferous platinum rim (medium grey). (d) Botryoidal grain consisting of a core varying in composition from mercury-bearing platiniferous palladium (medium grey) to platiniferous palladium (darker grey tints). (e) Botryoidal cluster of palladiferous platinum (medium grey), with a core of auriferous potarite, p. (f) Hexagon-shaped crystals of PdPt stoichiometry in palladiferous platinum from a marginal zone of an arborescent grain.

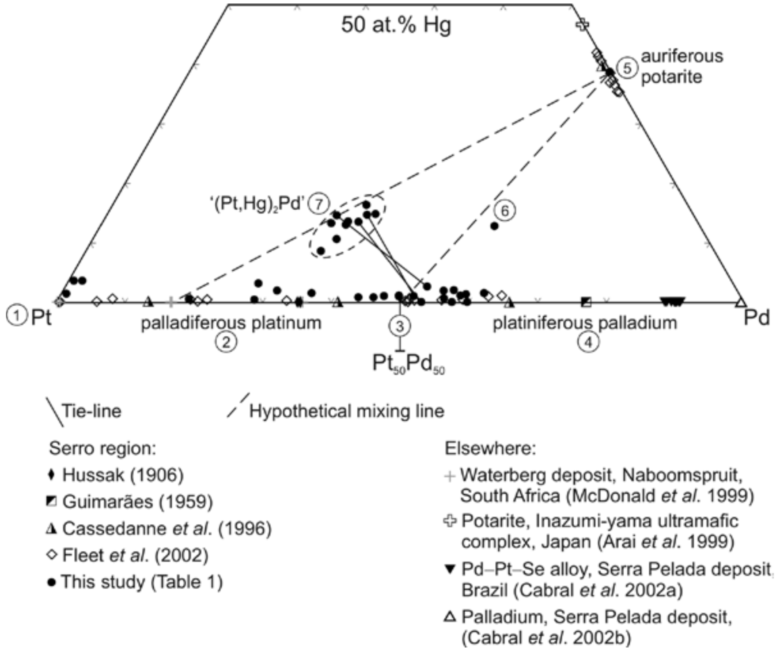


FIG. 6. Compositional variation of platinum and palladium nuggets from Córrego Bom Sucesso (Table 1) and other localities. Areas numbered 1 to 5 are compositional fields from Fleet *et al*. (2002): (1) platinum (>90 at.% Pt), (2) palladiferous platinum, (3) platinum–palladium alloy (~PtPd), (4) platiniferous palladium, (5) auriferous, Hg-depleted potarite. Continuous lines link mercury-rich palladiferous platinum compositions with nearby host platiniferous palladium (Fig. 4, Table 1). Dashed lines are hypothetical mixing lines between $Pt_{80}Pd_{20}$ or $Pt_{50}Pd_{50}$ and potarite.

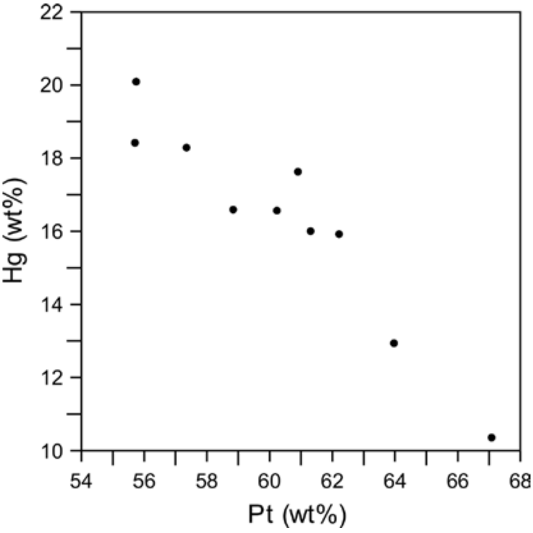


FIG. 7. Compositional variation of mercury-rich palladiferous platinum from Córrego Bom Sucesso (Table 1, Fig. 4) in terms of mercury *versus* platinum.

CONCLUSION

In summary, we provide the first evidence of a natural Hg-bearing Pt–Pd alloy, with an empirical composition close to $(Pt,Hg)_2Pd$, as well as evidence for PdPt crystals. We also show that (i) the peculiar nuggets of platinum and palladium from Córrego Bom Sucesso have been subjected to weathering (*i.e.*, residual primary grains), and that (ii) they formed under oxidizing conditions. The high oxidation state of the ore fluid, where sulfur is mainly in the form of sulfate, is indicated by the seleniferous signature and the Fe-poor composition of the Pt–Pd alloys.

The historical Pd–Pt-bearing deposits of economic importance in Brazil are hosted by metasedimentary rocks and were formed in an oxidizing environment that favored fractionation of selenium from sulfur. The nuggets of platinum and palladium from Córrego Bom Sucesso corroborate this observation. It should be noted that one century after its publication, Hussak's work on palladium and platinum remains stimulating and inspiring.

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REFERENCES

ALMEIDA-ABREU, P.A. & RENGER, F.E. (1999): Discussão – Sobre a polêmica da origem do diamante na Serra do Espinhaço (Minas Gerais): um enfoque mineralógico. *Rev. Bras. Geoc.* **29**, 669-672.

ARAI, S., PRICHARD, H.M., MATSUMOTO, I. & FISHER, P.C. (1999): Potarite (Pd–Hg) in thermally metamorphosed dunite from the Inazumi-yama ultramafic complex, southwestern Japan: an implication for the behaviour of mercury in PGE mineralization in peridotite. *Mineral. Mag.* **63**, 369-377.

ATENCIO, D. (2000): *Type Mineralogy of Brazil*. Instituto de Geociências, Universidade de São Paulo, São Paulo, Brazil.

BARNES, H.L. & SEWARD, T.M. (1997): Geothermal systems and mercury deposits. *In* Geochemistry of Hydrothermal Ore Deposits (H.L. Barnes, ed.). John Wiley & Sons, New York, N.Y. (699-736).

BELOGUB, E.V., NOVOSELOV, C.A., SPIRO, B. & YAKOVLEVA, B.A. (2003): Mineralogical and S isotopic features of the supergene profile of the Zapadno–Ozernoe massive sulphide and Au-bearing gossan deposit, South Urals. *Mineral. Mag.* **67**, 339-354.

BERLINCOURT, L.E., HUMMEL, H.H. & SKINNER, B.J. (1981): Phases and phase relations of the platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 233-250.

CABRAL, A.R. (2006): *Palladiferous Gold Mineralisation (Ouro Preto) in Brazil: Gongo Soco, Itabira and Serra Pelada*. Sonderhefte Reihe D – Geol. Jahrb. **8**. Schweizerbart'sche, Stuttgart, Germany (in press).

CABRAL, A.R. & LEHMANN, B. (2003): A two-stage process of native palladium formation at low temperatures: evidence from a palladian gold nugget (Gongo Soco iron ore mine, Minas Gerais, Brazil). *Mineral. Mag.* **67**, 453-463.

CABRAL, A.R., LEHMANN, B., KWITKO, R. & CRAVO COSTA, C.H. (2002a): The Serra Pelada Au–Pd–Pt deposit, Carajás mineral province, northern Brazil: reconnaissance mineralogy and chemistry of very high grade palladian gold mineralization. *Econ. Geol.* **97**, 1127-1138.

CABRAL, A.R., LEHMANN, B., KWITKO, R. & CRAVO COSTA, C.H. (2002b): Palladium and platinum minerals from the Serra Pelada Au–Pd–Pt deposit, Carajás mineral province, northern Brazil. *Can. Mineral.* **40**, 1451-1463.

CABRAL, A.R., LEHMANN, B., KWITKO, R. & JONES, R.D. (2002c): Palladian gold and palladium arsenide–antimonide minerals from Gongo Soco iron ore mine, Quadrilátero Ferrífero, Minas Gerais, Brazil. *Appl. Earth Sci.* (*Trans. Inst. Mining. Metall. B*) **111**, 74-80.

CABRAL, A.R., LEHMANN, B., KWITKO-RIBEIRO, R., JONES, R.D. & ROCHA FILHO, O.G. (2003): On the association of palladium-bearing gold, hematite and gypsum in an *ouro preto* nugget. *Can. Mineral.* **41**, 473-478.

CABRAL, A.R., LEHMANN, B., SATTLER, C.D., PIRES, F.R.M. & KANEKO, K. (2002d): Hg–Tl-bearing manganese oxide from Conta História manganese deposit, Quadrilátero Ferrífero, Minas Gerais, Brazil. *Appl. Earth Sci.* (*Trans. Inst. Mining Metall. B*) **111**, 123-127.

CASSEDANNE, J.P. & ALVES, J.N. (1992): Palladium and platinum from Córrego Bom Sucesso, Minas Gerais, Brazil. *Mineral. Rec.* **23**, 471-474.

CASSEDANNE, J.P. & CASSEDANNE, J.O. (1974): As aluviões platiníferas de Serro (Minas Gerais). *Anais XXVIII Congresso Brasileiro de Geologia* (*Porto Alegre*) **6**, 33-47.

CASSEDANNE, J.P., JEDWAB, J. & ALVES, J.N. (1996): Apport d'une prospection systématique à l'étude de l'origine de l'or et du platine alluviaux du Córrego Bom Sucesso (Serro – Minas Gerais). *Anais da Academia Brasileira de Ciências* **68**, 569-582.

CHAVES, M.L.S.C., KARFUNKEL, J. & SVISERO, D.P. (1998): Sobre a polêmica da origem do diamante na Serra do Espinhaço (Minas Gerais): um enfoque mineralógico. *Rev. Bras. Geoc.* **28**, 285-294.

COLIN, F., SANFO, Z., BROWN, E., BOURLÈS, D. & MINKO, A.E. (1997): Gold: a tracer of the dynamics of tropical laterites. *Geology* **25**, 81-84.

ESCHWEGE, W.L.V. (1818): Physikalische und bergmännische Nachrichten aus Brasilien. *Annalen der Physik* **59**, 117-139.

EVSTIGNEEVA, T. & TARKIAN, M. (1996): Synthesis of platinum-group minerals under hydrothermal conditions. *Eur. J. Mineral.* **8**, 549-564.

FERRAND, M.P. (1894): *L'or a Minas Geraes* (*Brésil*) II(1). Imprensa Official do Estado de Minas Geraes, Ouro Preto, Brasil.

FLEET, M.E., DE ALMEIDA, C.M. & ANGELI, N. (2002): Botryoidal platinum, palladium and potarite from the Bom Sucesso stream, Minas Gerais, Brazil: compositional zoning and origin. *Can. Mineral.* **40**, 341-355.

GEHLEN, A.F. (1811): Platin und Palladium in Brasilien und St. Domingo gefunden. *Journal für Chemie und Physik* **1**, 362-373.

GOLDSCHMIDT, V.M. & HEFTER, O. (1933): Zur Geochemie des Selens. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse*, 245-252.

GUIMARÃES, D. (1959): Notas à margem de "o paládio e a platina no Brasil", de E. Hussak. *Departamento Nacional da Produção Mineral, Divisão de Fomento da Produção Mineral, Rio de Janeiro, Boletim* **106**, 81-98.

HARTT, C.F. (1870): *Geology and Physical Geography of Brazil*. Fields, Osgood, and Co., Boston, Massachusetts.

HATTORI, K.H., CABRI, L.J., JOHANSON, B. & ZIENTEK, M.L. (2004): Origin of placer laurite from Borneo: Se and As contents, and S isotopic compositions. *Mineral. Mag.* **68**, 353-368.

HUMBOLDT, A.V. (1826): Ueber die Lagerung des Platins. *Annalen der Physik* **83**, 515-520.

HUSSAK, E. (1904): Über das Vorkommen von Palladium und Platin in Brasilien. *Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der Kaiserlichen Akademie der Wissenschaften* **113**, 379-466.

HUSSAK, E. (1906): Über das Vorkommen von Palladium und Platin in Brasilien. *Z. prakt. Geol.* **14**, 284-293.

JEDWAB, J. & CASSEDANNE, J. (1998): Historical observations on oxygen-bearing compounds of platinum and palladium in Minas Gerais, Brazil. *Can. Mineral.* **36**, 887-893.

LAMPADIUS, W.A. & PLATTNER, G.P. (1833): Ueber das gemeinschaftliche Vorkommen des Platinerzes und des gediegenen Silbergoldes in einem Gangfossile aus Brasilien. *Journal für Technische und Ökonomische Chemie* **18**, 353-365.

MCDONALD, I., OHNENSTETTER, D., ROWE, J.P., TREDOUX, M., PATTRICK, R.A.D. & VAUGHAN, D.J. (1999): Platinum precipitation in the Waterberg deposit, Naboomspruit, South Africa. *S. Afr. J. Geol.* **102**, 184-191.

MORONI, M., GIRARDI, V.A.V. & FERRARIO, A. (2001): The Serra Pelada Au–PGE deposit, Serra dos Carajás (Pará State, Brazil): geological and geochemical indications for a composite mineralizing process. *Mineral. Deposita* **36**, 768-785.

OLIVO, G.R. & GAUTHIER, M. (1995): Palladium minerals from the Cauê iron mine, Itabira district, Minas Gerais, Brazil. *Mineral. Mag.* **59**, 455-463.

ROUSSET, J.L., CADROT, A.M., CADETE SANTOS AIRES, F.J., RENOUPREZ, A., MÉLINON, P., PEREZ, A., PELLARIN, M., VIALLE, J.L. & BROYER, M. (1995): Study of bimetallic Pd–Pt clusters in both free and supported phases. *J. Chem. Phys.* **102**, 8574-8585.

SCOTT, H.K. (1902): The gold field of the state of Minas Geraes, Brazil. *Trans. Am. Inst. Mining Eng.* **33**, 406-444.

ŞENER, A.K., GRAINGER, C.J. & GROVES, D.I. (2002): Epigenetic gold – platinum-group element deposits: examples from Brazil and Australia. *Appl. Earth Sci.* (*Trans. Inst. Mining Metall. B*) **111**, 65-73.

SIMON, G., KESLER, S.E. & ESSENE, E.J. (1997): Phase relations among selenides, sulfides, tellurides, and oxides. II. Applications to selenide-bearing ore deposits. *Econ. Geol.* **92**, 468-484.

STANTON, R.L. (1972): *Ore Petrology*. McGraw-Hill Book Company, New York, N.Y.

TOUZEAU, E.M. (1892): Gold-mining in Brazil. *Trans. Fed. Inst. Min. Eng.* **4**, 219-232.

TROMPETTE, R., UHLEIN, A., DA SILVA, M.E. & KARMANN, I. (1992): The Brasiliano São Francisco craton revisited (central Brazil). *J. S. Am. Earth Sci.* **6**, 49-57.

VARAJÃO, C.A.C., COLIN, F., VIEILLARD P., MELFI A.J. & NAHON D. (2000): Early weathering of palladium gold under lateritic conditions, Maquiné mine, Minas Gerais, Brazil. *Appl. Geochem.* **15**, 245-263.

WAGNER, P.A. (1929): *The Platinum Deposits and Mines of South Africa*. Oliver and Boyd, Edinburgh, U.K.

WILDE, A., EDWARDS, A. & YAKUBCHUK, A. (2003): Unconventional deposits of Pt and Pd: a review with implications for exploration. *Soc. Econ. Geol. Newslett.* **52**(1), 10-18.

WOLLASTON, W.H. (1809): On platina and native palladium from Brazil. *Philos. Trans.* **99**, 189-194.

XIONG, Y. (2003): Predicted equilibrium constants for solid and aqueous selenium species to 300°C: applications to selenium-rich mineral deposits. *Ore Geol. Rev.* **23**, 259-276.

YAKOVLEVA, V.A., BELOGUB, E.V. & NOVOSELOV, K.A. (2003): Supergene iron sulpho-selenides from the Zapadno–Ozernoe copper–zinc massive sulphide deposit, South Urals, Russia: a new solid-solution between pyrite FeS_2 and dzharkenite $FeSe_2$. *Mineral. Mag.* **67**, 355-361.

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