BOTRYOIDAL PLATINUM, PALLADIUM AND POTARITE FROM THE BOM SUCESSO STREAM, MINAS GERAIS, BRAZIL: COMPOSITIONAL ZONING AND ORIGIN

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Abstract

Platinum–Pd nuggets from the Bom Sucesso stream alluvium, Minas Gerais, Brazil, have been investigated by electron-probe microanalysis. The nuggets attain 1 mm in maximum dimension and have a botryoidal habit, with pronounced compositional core-to-margin zoning of internal structures. Although there is a wide variation in internal morphology and individual zones vary markedly in thickness (<1–100 μ m), a typical composite arborescent nugget comprises a broad irregular core region of massive auriferous Pd–Hg alloy (potarite; δ -PdHg) or cavity space + relict potarite enclosed by a narrow zone of platiniferous palladium or alloy of near Pt₅₀Pd₅₀ composition, and is progressively oscillatory zoned by palladian platinum, with growth eventually enveloping the whole botryoidal "colony", to a narrow rim of palladian platinum or pure platinum. Other nuggets comprise an arborescent to dendritic core of auriferous potarite, a broad internal zone of either pure platinum or palladian platinum, and a narrow rim of platinum. The mineral palladium contains up to about 65 at.% Pd; this is the first detailed modern confirmation of palladium in its type locality. Auriferous potarite ranges in composition from ~Pd₃Hg₂ to near Pd(Hg,Au). The origin of these nuggets remains unclear, but their mineralogy is broadly equivalent to that of palladian gold, potarite and platinum in alluvial sediments and overburden from Devon, England, which are considered to be detrital, and their platinum-group-element geochemistry is consistent with precipitation from hydrothermal fluids. We suggest that the Bom Sucesso nuggets resulted from high-level episodic hydrothermal alteration of mafic and ultramafic rocks within the drainage basin, with the remobilized Pt and Pd precipitated in open spaces in the enclosing metaquartzites.

Keywords: platinum, palladium, potarite, botryoidal nuggets, alluvium, Bom Sucesso, Brazil.

SOMMAIRE

Nous avons caractérisé des pépites alluvionnaires de platine et de palladium provenant du ruisseau Bom Sucesso, dans l'état de Minas Gerais, au Brésil, par analyses à la microsonde électronique. Ces pépites atteignent 1 mm et possèdent un aspect botryoïdal, avec une zonation compositionnelle prononcée des structures internes allant du coeur vers la bordure. Quoiqu'il y a une variation importante de la morphologie interne et que les zones individuelles varient de facon importante en épaisseur (<1-100 µm), une pépite arborescente composite typique contient un noyau large et irrégulier fait d'un alliage Pd-Hg aurifère massif (potarite; δ-PdHg) ou d'un espace vide avec des reliques de potarite, qu'entoure une zone étroite de palladium platinifère ou d'un alliage ayant une composition proche de $Pt_{50}Pd_{50}$. Cette zone centrale est enveloppée progressivement par des zones oscillatoires de platine palladifère, avec une croissance éventuelle enveloppant toute la "colonie", menant à un liséré externe de platine pur ou légèrement palladifère. Dans d'autres cas, les pépites contiennent un noyau de potarite aurifère arborescent ou dendritique, une zone interne relativement large composé de platine pur ou légèrement palladifère, et un liséré étroit de platine. Le minéral palladium contient jusqu'à 65% de Pd (proportion atomique); nous confirmons ainsi pour la première fois avec des méthodes analytiques modernes la présence de cette espèce dans sa localité-type. La potarite aurifère varie en composition de ~Pd₃Hg₂ à environ Pd(Hg,Au). L'origine de ces pépites n'est pas très évidente, mais leur minéralogie est à peu près équivalente à l'association d'or palladifère, de potarite et de platine dans des sédiments alluvionnaires et des graviers à Devon, en Angleterre. Cette suite de minéraux serait détritique, et les aspects géochimiques des éléments du groupe du platine semblent indiquer une origine à partir de fluides hydrothermaux. A notre avis, les pépites de Bom Sucesso se sont formées par altération hydrothermale épisodique de roches mafiques et ultramafiques près de la surface dans un bassin de drainage, le Pt et le Pd remobilisés ayant été précipités dans des vacuoles dans les métaquartzites encaissantes.

(Traduit par la Rédaction)

Mots-clés: platine, palladium, potarite, pépites botryoïdales, alluvions, Bom Sucesso, Brésil.

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INTRODUCTION

Information on the occurrence and paragenetic position of the mineral palladium is sparse (e.g., Ramdohr 1969, Cabri 1981). It occurs uncommonly in placer deposits in Minas Gerais (Brazil), Choco (Colombia), and Guyana in South America, and in the Urals (Russia). The type material for this species was found in placer deposits in Brazil (Wollaston 1805, 1809), and probably included the Pt-rich nuggets from the Bom Sucesso stream alluvium (Cassedanne & Alves 1992), the topic of our investigation. In contrast, platinum alloys are the most commonly occurring platinum-group minerals (PGM) in placer deposits, and the mineral platinum is quite common also [e.g., Cabri et al. (1996) reported platinum from placers in Canada and Russia]. The bulk Pd contents of the Pt-Pd nuggets from Bom Sucesso were reported to range from 11.7 to 29.3 wt% (Cassedanne & Alves 1992). Preliminary study of the mineralogical distribution of Pd in these nuggets was made using scanning electron microscopy (SEM) in Cassedanne et al. (1996). However, they have not been investigated systematically by modern analytical methods. This is a significant omission, because solid solution along the Pt-Pd binary join is extensive, as it is in many Pt-Pd compounds (e.g., Shelton et al. 1981). The highest recorded content of Pd in the mineral platinum listed in the recent review of Daltry & Wilson (1997) is 37.1 wt%. We are not aware that palladium has been established as a primary mineral of in situ platinumgroup element (PGE) deposits, although small amounts of Pd alloy minerals are routinely reported (cf. Kinloch 1982, Mostert et al. 1982). Palladium does occur in association with Uralian-type ultramafic bodies and the Merensky Reef, but in the Bushveld Complex it is associated with surface exposure of the PGE deposits, where it originates from oxidation of Pd-bearing sulfides and of stibiopalladinite (Ramdohr 1969).

In this paper, we investigate the growth habit and compositional zoning of Pt–Pd alloys from the Bom Sucesso occurrence, support the presence of palladium in its historical type-locality, and speculate on the origin of these unusual nuggets. It is very appropriate to dedicate this paper to Louis J. Cabri in light of his seminal contributions to our understanding of the PGM, and particularly to the PGM in placer deposits.

REVIEW OF THE LITERATURE

In placer deposits, and stream sediments in general, platinum-group minerals originate dominantly from the erosion of *in situ* high-temperature (magmatic) deposits (Cabri *et al.* 1996); their provenance is clearly indicated by their characteristic compositions. In particular, they tend to have significant contents of a broad spectrum of the platinum-group elements (PGE; Os, Ir, Ru, Rh, Pt, and Pd), as well as inclusions of early-magmatic minerals (e.g., olivine, chromite and chromian spinel). Cabri et al. (1996) disputed the suggested supergene and authigenic origins of Pt nuggets in laterites and Witwatersrand paleoplacers (Augustithis 1965, Bowles 1986, 1988. Cousins 1973, Cousins & Kinloch 1976), and cited only two likely exceptions where Pt nuggets may have formed in the surficial environment: (1) palladian gold, potarite (PdHg) and platinum in alluvial sediments and overburden from Devon, England (Leake et al. 1991), and (2) the Pt-Pd nuggets from the Bom Sucesso stream alluvium (Cassedanne & Alves 1992). Leake et al. (1991) concluded that the Au-Pd-Pt grains from south Devon are detrital vein-type minerals that had grown from oxidizing saline fluids at about 100°C, noting mineralogical similarities to palladium and gold minerals from carbonate veins cutting Middle Devonian limestones, of possible Permo-Triassic age (Clark & Criddle 1982, Stanley et al. 1990). Cassedanne & Alves (1992) reported that Pt-Pd nuggets from the Bom Sucesso stream sediments were too delicate to withstand significant alluvial transport, and supported the diagenetic hypothesis of Hussak (1906). However, this hypothesis was abandoned in Cassedanne et al. (1996) in light of the complex mineralogical nature of the nuggets, which have an inner core of potarite (δ -PdHg), and the presence of Pt and Au nuggets in soil on top of quartzite cliffs high above the stream alluvium. They suggested instead that the Pt-Pd-Hg nuggets formed by very-low-temperature hydrothermal processes, with the precious metals originating from mafic and ultramafic rocks within the watershed, but they recognized that biogeochemical processes may have been active also.

Certainly, the crystallization of PGM is not limited to magmatic processes. There is now abundant evidence from mineral paragenesis, geochemistry, laboratory experiments, and theoretical calculations for significant mobility and deposition of PGE in high-temperature dry fluids (e.g., Wood 1987, Fleet & Wu 1993), low-temperature hydrothermal fluids (e.g., McCallum et al. 1976, Gammons et al. 1992, Olivo et al. 1994), and epithermal-type hydrothermal fluids (Clark & Criddle 1982, Stanley et al. 1990, Leake et al. 1991, Wood et al. 1994). There is also a growing literature on the association of Pt with organic matter. Significant developments here include: (1) Pt is enriched by a factor of 18 in some bituminous coals (Chyi 1982), (2) the "solubility" of Pt in aqueous solution at room temperature is enhanced in the presence of dissolved organic acids (Wood 1990), (3) a new type of Pt deposit hosted by low-rank coal and black shale has been discovered in the Voronezk geological province of Russia (Chernyshov & Korobkina 1995), and (4) chemisorption onto maturing organic matter lowers the solubility of Pt in hydrothermal fluids by up to two orders of magnitude (Plyusnina et al. 2000), the chemisorption being significantly greater at 400°C than at 200°C.

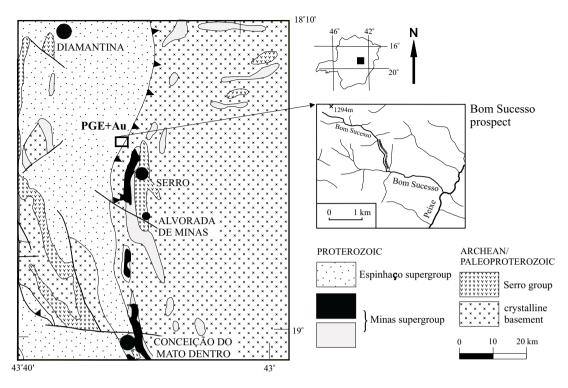


FIG. 1. Geological map for the Serro area, Minas Gerais, Brazil, with detail of the Bom Sucesso stream prospect on the southern flank of Mount Condado. The Espinhaço Supergroup in the region comprises quartzites, metaconglomerates and phyllites, with local intercalations of metamafic rocks and banded iron formation. The Minas Supergroup comprises itabirites (metamorphosed banded iron-formation; black) and mixed lithologies of quartzites with pyritiferous metaconglomerates and phyllites and mafic–ultramafic rocks (light shade). The Serro Supergroup comprises muscovite schists, quartzites, phyllites, banded iron-formation, mafic schists, and serpentinites with chromitite bands. The crystalline basement consists of gneisses and migmatites with intercalations of amphibolites, and granitic rocks [after Dossin (1985), Cassedanne *et al.* (1996)].

SAMPLES AND ELECTRON-PROBE MICROANALYSIS

A small sample (~0.5 g) of heavy minerals was purchased from a prospector who had obtained it by panning sediment from the Bom Sucesso stream about 10 km north of the historical town of Serro, Minas Gerais, Brazil (Fig. 1). The sample location was downstream from the historical prospect discussed in Cassedanne & Alves (1992). We also collected four dark rocks from the drainage basin, to evaluate their potential as source rocks for Pt and Pd.

Samples were studied by thin and polished section petrography. Electron imaging (secondary and back-scattered electrons) and X-ray microanalyses were performed using a JXA 8600 electron microprobe at the University of Western Ontario. Secondary electron images of Pt–Pd nuggets (Fig. 2) were made on unpolished Au₆₀Pd₄₀-coated samples with the electron microprobe operated at an accelerating voltage of 15 kV. Back-scattered electron images and X-ray microanalyses were made on carbon-coated polished specimens. X-ray mi

croanalyses were obtained by wavelength-dispersion spectrometry with an accelerating voltage of 20 kV, a probe current of 35 nA (measured on a Faraday cup), a fully focused beam, and counting times of 20 seconds on peak and background. The characteristic X-ray lines used were $L\alpha$ for Pt, Hg, and Au, and $L\beta$ for Pd. We used cinnabar (HgS) and synthetic pure elements as standards. No major efforts were made to characterize the trace components. Nevertheless, preliminary results indicate that Os and Ir are below 0.15 wt%, and Ru and Rh, below 0.05 wt%. Also, based on qualitative energydispersion spectrometry, Fe, Ni, Cu, Sn pnictides and S are not present. The compositions of silicates, oxides, and sulfides were also determined by wavelength-dispersion spectrometry. For the silicates and oxides, the instrument was operated with an accelerating voltage of 15 kV and a probe current of 15 nA, whereas the sulfides were analyzed at 25 kV and 25 nA. The Ka characteristic X-ray line was used for all elements except As $(L\alpha)$. Calibration was done with synthetic and natural standard materials. In all cases, matrix effects were

No.

Pt Pd Hg Au

terozoic Minas Supergroup. The historical prospect is a north-northeast-trending section at an elevation of about 1000 m, where high white quartzite cliffs mark the eastern side of the valley (Cassedanne & Alves 1992, Cassedanne et al. 1996). The Minas quartzites on Mount Condado have local intercalations of rusty metasediments, banded iron-formation, and metamafic and meta-ultramafic rocks.

The region has been prospected for placer Pt, Au and diamonds since historical times, and there has been active debate on the origin of these commodities. There are a number of occurrences of PGE and PGM along a 90-km tract between the towns of Serro and Morro do Pilar, which is south of the map area of Figure 1. These are mostly small alluvial placer deposits, yielding about 2-3 g/tonne PGE, but occasionally they have a close spatial association with quartzites (Hussak 1906, de Erichsen 1949, Guimarães & Belezkiy 1959, Cassedane & Alves 1992). These mineralized zones are sheared. and the quartzites are locally cemented with carbonate. At the Salvador Farm near Conceição do Mato Dentro (Fig. 1), metaquartzites are cut by veins of quartz with

TABLE 1. COMPOSITION OF PGM IN NUGGETS, BOM SUCESSO

total

Pt Pd Ηg Au

at %

0

0

0.08

0.15

0.23

0.05

0.07

0.02

0

0

0

0.07

0.08

0.05

0.07

0.06

at.% wt% wt% wt% wt% at % at % olatinum 100.01 0.13 0 100.53 0 99 76 0.24 0 1 0.43 0 2 99 31 0.24 0 0 99.71 99 57 palladian platinum 4.41 0.08 100.46 91.59 7,77 3 95,36 0.6 0.56 4 86.07 13.03 0.46 0.16 99 72 77.84 21.61 0.41 87.6 5 11.44 0.47 0.26 99.76 80.16 19.19 0.41 0.06 99.8 66.37 33.34 0.23 6 78.07 21.39 0.28 7 96.64 3.2 0.09 0.07 100 94 13 5 72 0.08 8 0.15 0.02 100.33 79.46 20.4 0.13 87.86 12.3 platiniferous palladium near PtsePdse 9 63.71 36.39 0.05 0 100 16 48.82 51.13 0.04 10 0.49 0.09 99.75 48,46 51,11 0.37 36.21 62.95 47 77 51 95 0.28 11 62 33 36 97 0.37 0 99.66 35.74 0.24 0 99.58 49.16 50.66 0.18 12 63.6 platiniferous palladium 13 48 5 49.13 1 56 0.11 99 29 34 59 64 25 1.08 14 50.93 47.34 1.32 0.07 99.67 36.62 62.41 0.93 15 54.58 43.16 0.57 0.1 98.4 40.62 58.9 0.41 58.04 40.45 0.45 0.08 99.02 43.73 55.88 0.33 16 Pd-Hg alloy (auriferous potarite)

17	0.48	40.2	53.93	6.32	100.93	0.36	55.46	39.47	4.71
18	0.75	47.48	49.61	2.06	99.91	0.55	63.04	34.94	1.48
19	0.28	42.77	48.35	8.05	99.45	0.21	58.65	35.17	5.96
20	0	37.48	44.44	18.04	99.97	0	52.94	33.3	13.76
21	0.38	36.73	47.7	15.31	100.12	0.3	52.09	35.88	11.73
22	0.32	36.96	50,82	12.15	100.25	0.24	52.31	38.15	9.29
23	0.48	43.3	47.42	8.29	99.5	0.36	59,16	34.36	6.12
24	1.17	45,09	50.57	3.59	100.41	0.85	60.53	36.01	2.6
25	0.33	43.03	44.6	11.61	99.56	0.25	58.83	32.35	8.57

FIG. 2. Secondary electron images of (a) botryoidal and (b) stick-shaped Pt-Pd nuggets from Bom Sucesso stream sediment. The width of (a) is 150 μ m; the length of (b) is 240 µm.

corrected using the Heinrich - Duncumb-Reed correction model (CITZAF) provided with the dQant program of Geller MicroAnalytical Laboratory. Representative back-scattered electron (BSE) images of the Pt-Pd nuggets are given in Figure 3, and results of representative electron-probe microanalyses (EPMA), in Table 1. In addition, a single Pt-Pd nugget was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), following NiS fire-assay fusion, by Lakefield Geosol Ltda of Belo Horizonte, Minas Gerais.

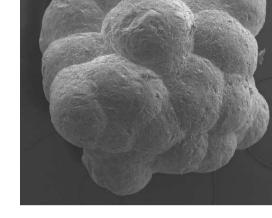
GEOLOGY AND PETROGRAPHY

The Bom Sucesso is a seasonal stream that drains the southern flank of Mount Condado (Fig. 1). The stream valley is incised into quartzite of the Middle Pro-



а

b



pyrite and chalcopyrite and minor garnet and magnetite. Interestingly, these veins have yielded anomalous contents of Pt and Pd, but the host minerals for the precious metals have not been identified. The Mata-Cavalo volcanic-sedimentary sequence at the Limeira Farm near Morro do Pilar was investigated for source minerals for the Pt placers (Neves 1998), but without success. In this area, the alluvial placers of the Limeira stream and Picão River yielded anomalous PGE contents as well as nuggets of PGM and gold.

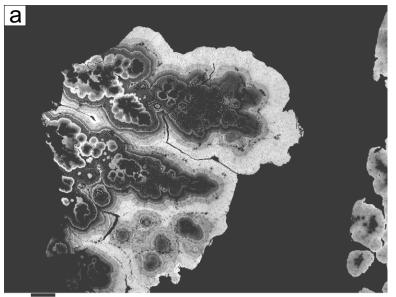
Angeli & de Carvalho (1996) were unable to correlate the occurrence of PGM in the Bom Sucesso stream alluvium with the chromite deposits in the nearby district of Serro. Cassedanne et al. (1996) extensively investigated quartzites, mafic and ultramafic rocks, rusty rocks and weathered rock surfaces at elevations above the Bom Sucesso for source rocks for the Pt-Pd nuggets. One sample of mafic-ultramafic rock ("roche verte" #MG3) had high, and possibly anomalous, contents of Pt and Pd (108 and 28 ppb, respectively). In situ PGM were not identified, although a sample of soil from on top of the prominent quartzite cliffs yielded two grains of Pt and three of gold. These grains of precious metals were assumed to be equivalent to the nuggets in the stream alluvium, but evidence for this was not presented. Banded iron-formation on Mount Condado is also a possible source for the PGE, particularly since an anomalous content of Pd occurs with gold mineralization in Lake-Superior-type iron ore deposits in the Iron Quadrangle (Gandarela Formation, Itabira District; Olivo et al. 1994).

The four samples of dark rock collected in this study were all from laterally extensive (>200 m width) intercalations; three samples believed to be iron formation were from lenses 0.5-1.0 m thick, and a metabasite lens that yielded sample DBSU was 0.3-0.5 m thick. Two "ferruginous" samples were from near Mount Condado: BSU-02 is a hematite-rich rock with scattered euhedral porphyroblasts of spessartine (Ca_{0.20}Mn_{2.45}Fe*_{0.35}Cr_{0.01} $Al_{1,93}Si_{3}O_{12}$) and minor inclusions of quartz + ferruginous muscovite + goethite + an unidentified hydrous Ba-Al-P-bearing phase and talc + gibbsite (or diaspore), and sample BSU-04 is a pyrolusite $(Mn_{0.994} Fe_{0.005}O_2) + quartz rock, with the manganese$ oxide replacing mosaic grains of quartz. The two other samples are from about 300 m below the peak of Mount Condado; these consist of banded ironformation (DCSJ; muscovite, magnetite, ilmenite, and carbonates) and an ultramafic amphibolite {DBSU; actinolite [K_{0.01}Na_{0.07} Ca_{2.03}Mn_{0.04}Mg_{3.32}Fe*_{1.41} $Al_{0.39}Si_{7.92}O_{22} (OH)_2 + chlorite [K_{0.01}Ca_{0.01}Mn_{0.03}]$ $Mg_{2.69}Fe_{1.87}^*Al_{2.55}Si_{2.84}O_{10}(OH)_8$ with epidote, titanite, ilmenite, zircon, dispersed chalcopyrite and pyrrhotite (Fe_{0.857}Co_{0.001}Ni_{0.012} S_{1.000}), and rare pyrite and sphalerite }.

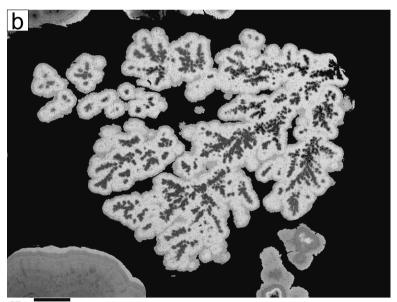
The alluvium beds in the Bom Sucesso valley are thin (1.2–1.5 m), poorly sorted, and transected by the

modern stream. The alluvium has been worked for gold, platinum, palladium and diamonds since the eighteenth century. As described in Cassedanne & Alves (1992) and Cassedanne et al. (1996), the historical prospect consists of unsorted alluvium protected from erosion by blocky metaquartzite rubble. Large nuggets of precious metal were removed by sieving, and additional particles of gold and platinum were recovered by sluicing and panning. Heavy minerals recovered from the coarse fraction (1-5 mm) included: anatase and rutile, xenotime, zircon, kyanite, cassiterite, crichtonite, hematite, ilmenite, magnetite, gold and platinum nuggets and small crystals of diamond. Additional minerals found only in the fine-grained fraction include: monazite, tourmaline, tremolite, baddelevite, corundum, epidote, garnet, lazulite, perovskite, ferrocolumbite, and topaz. The Pt–Pd nuggets attain 1.5 cm in size and display a range of habit (reniform, mammillary, coralloidal, dendritic, and arborescent). Some broken nuggets have a hollow core region. The nuggets show no marks of abrasion, and rounded grains are very rare.

The present placer sample is medium to fine grained (<1.0 mm) and consists of about 80 grains of Pt-Pd, 35 grains of gold, one rounded grain of ferrocolumbite, one euhedral grain of wodginite, six rounded grains of pink zircon, and 19 pellets of lead. Viewed in SEM and BSE images (Figs. 2-3), the Pt-Pd nuggets have a botryoidal habit with pronounced core-to-margin compositional zoning. One sectioned nugget is reticulate, and three others are stick-shaped. There is a marked variation in interior morphology, particularly in respect to complexity of zoning and porosity, from nugget to nugget. An additional complication for nuggets with a pronounced botryoidal or arborescent habit is the variation in their appearance in polished section with change in orientation and level of sectioning. In general, complex arborescent nuggets tend to comprise a core of dendritic (or branching) auriferous Pd-Hg alloy (potarite) immediately surrounded by a narrow (~10 µm) zone of platiniferous palladium and alloy of near Pt50Pd50 composition, then a broad interior of oscillatorily zoned platinum and Pt-Pd alloy, with the thickness of individual zones varying from ~1 to ~100 µm, and a narrow rim of either pure platinum or palladian platinum. Other nuggets or parts of nuggets have a core region of open space and relict auriferous potarite, again immediately surrounded by platiniferous palladium and alloy of near Pt50Pd50 composition. This core material has the appearance of being poorly consolidated, to the extent that some of the open-space areas may have represented friable core material lost during polishing. However, much of the cavity space was filled with epoxy, confirming that inner core regions are commonly hollow, as observed by Cassedanne & Alves (1992). In our opinion, dendritic auriferous potarite tended to be present in the interior of limbs and protuberances of the nuggets, whereas the core region at the base (or point of attach-

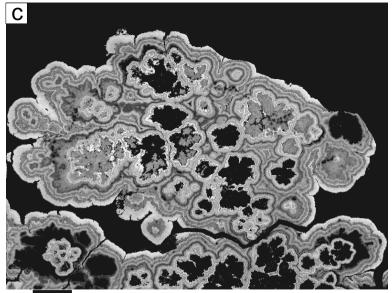


SE 100µm

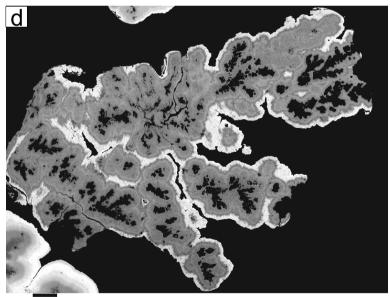


SE 100µm

FIG. 3. Back-scattered electron images of composite compositionally zoned botryoidal Pt–Pd nuggets from Bom Sucesso stream sediment (bright zones are enriched in Pt relative to Pd). (a) Complex nugget, oscillatory zoning from core to margin, with a broad outer margin of palladian platinum; EPMA results are plotted in Figure 4a; note fractures indicative of brittle failure. (b) Arborescent nugget with a core of dendritic auriferous potarite, a broad interior zone of nearly pure platinum, and a narrow (20 μm) rim of palladian platinum; EPMA results are included in Figure 4b. (c) Transverse section of a complex arborescent nugget; broad irregular core region of individual limbs is



SE 100µm



SE 100µm

of massive auriferous potarite \pm cavity space (black) enclosed by a narrow zone of platiniferous palladium or alloy of near $Pt_{50}Pd_{50}$ composition. Fine-scale oscillatory zoning in palladian platinum completes individual limbs and encloses the colony, and grades to a bright margin; EPMA results are plotted in Figure 4c. (d) Oblique section through arborescent grain; broad core regions are composed variably of massive auriferous potarite or cavity space (black), with relict potarite enclosed by a narrow zone of platiniferous palladium or alloy of near $Pt_{50}Pd_{50}$ composition, zoned to a narrow (20 μ m) rim of palladian platinum. Note the absence of gangue minerals between limbs; EPMA results are plotted in Figure 4d.

ment in the crystal-growth environment) of the nuggets tended to be cavernous. A few examples will illustrate the variation in morphology of these composite Pt–Pd nuggets:

1. Complex oscillatory zoning from core to margin, with a broad outer margin of palladian platinum (Fig. 3a).

2. Core of dendritic auriferous Pd–Hg alloy (potarite), a broad ($100 \ \mu m$) interior zone of pure platinum; oscillatory zoning in margin, with a rim of palladian platinum.

3. Cavernous core, with palladian platinum interior and outer margin showing multiple oscillatory zones, with Pd content generally decreasing outward.

 Stick-shaped grain: cavernous core, surrounded by auriferous potarite, then platiniferous palladium, grading to palladian platinum.

5. Core of dendritic auriferous potarite, a broad interior of nearly pure platinum, and a narrow (20 μ m) rim of palladian platinum (Fig. 3b).

6. Transverse section of a complex arborescent nugget (Fig. 3c). Broad core region of individual limbs consists of massive auriferous potarite \pm cavity space immediately surrounded by a narrow zone of platiniferous palladium and alloy of near Pt₅₀Pd₅₀ composition. Fine-scale oscillatory zoning in palladian platinum completes individual limbs and encloses the "colony", and grades to a bright margin.

7. Cavernous core surrounded by a broad interior of platiniferous palladium, grading to an inner margin of palladian platinum and minor auriferous potarite, and a narrow (5 μ m) bright margin.

8. Oblique section through an arborescent grain (Fig. 3d). Broad core regions are composed variably of massive auriferous potarite or cavity space with relict potarite enclosed by a narrow zone of platiniferous paladium and alloy of near $Pt_{50}Pd_{50}$ composition and then zoned to a narrow (20 µm) rim of palladian platinum. This type of nugget is similar to that illustrated in Cassedanne *et al.* (1996), which has a branching inner core of potarite (Pd_{59.5}Pt_{0.7}Hg_{39.8}), surrounded by platiniferous palladium (Pd_{66.0}Pt_{34.0}), and a broad margin of palladian platinum that was subdivided into an inner zone of Pt_{59.0}Pd_{40.9}Hg_{0.1} and outer zone of Pt_{86.6}Pd_{13.2}Hg_{0.2}.

9. Transverse section of a deformed fine-scale reticulate nugget. Individual limbs comprise a cavernous core region surrounded by a narrow (25 μ m) zone of pure platinum, followed by a narrow (10 μ m) zone of palladian platinum, and a narrow (25 μ m) rim of pure platinum.

In general, the nuggets have few abrasion marks and display little evidence of rounding due to abrasion. However, one nugget seems to be an agglomeration of deformed and rounded fragments. Also, compressional flattening or marginal "flow" of compositionally zoned platinum in some nuggets evidently represents malleable deformation during transport and deposition. Fractures (Fig. 3a) are common and consistent with dessication cracks and brittle failure during transport and deposition. One nugget has a large pocket filled with several grains of detrital zircon, which were only loosely bound and, therefore, are interpreted to have been entrained during deposition. Otherwise inclusions are conspicuously absent and, significantly, the open-space areas between limbs of arborescent grains (Figs. 3b, d) and cavities are devoid of relict fragments of gangue minerals. Thus, there is no evidence that other minerals had crystallized with or after the alloy phases. Compositional details of the Pt–Pd nuggets are discussed below.

Grains of Ag-bearing gold have a Ag-depleted margin, which is typical of Ag-bearing gold grains from placer deposits (e.g., Fig. 290E of Ramdohr 1969). The content of Cu in gold nuggets is sporadic (0.0 to 0.09) wt%); all other elements are below minimum detectionlimit by EPMA. Cassedanne et al. (1996) reported up to 2.0 wt% Pt and Pd in gold nuggets and as well as enrichment of Cu (up to 0.6 wt%) in the rims of these nuggets, but these features are not substantiated in this study. The lead pellets appear to be single-crystal fragments, as evidenced by etch (or solution) patterns displaying cubic symmetry and limited study with a single-crystal precession camera. They are embayed or encrusted to a variable thickness with a mixture of PbO (massicot), PbO₂ (plattnerite) and an unidentified hydrous Pb⁴⁺ alteration product. Gaines et al. (1997) noted that lead recorded as pellets in alluvium is probably artificial. An anthropogenic origin for the Bom Sucesso lead pellets is confirmed by the presence of Sb in several grains. One grain in particular has a cellular microstructure, with cell walls formed by myriad platelets of a Sb-rich alloy. This evidently represented precipitation of Sb during quenching of liquid Pb-Sb alloy. Antimony is widely used as an alloying agent to increase the hardness and mechanical strength of lead.

CHEMICAL COMPOSITION OF NUGGETS

Representative results of EPMA spot analyses for the Bom Sucesso nuggets are given in Table 1; all data are plotted in Figure 4. We presently recognize five distinct compositional fields along the Pt-Pd and Pd-Hg joins: (1) essentially pure platinum, (2) palladian platinum, (3) platinum-palladium (with ~50 at.% Pd; ~50 at.% Pt), (4) platiniferous palladium to a maximum Pd content of about 65 at.%, and (5) auriferous potarite with up to 14 at.% Au. With the exception of the distinction between platinum (<50 at.% Pd) and palladium (<50 at.% Pt), the composition fields along the Pt-Pd join are arbitrary and entirely for the convenience of description. The ternary Pt-Pd-Hg compositions are likely to represent contamination from adjacent phases, because the compositions of clearly resolved phases plot very close to the binary joins (Figs. 4c, d). The alloy of near Pt50Pd50 composition and platiniferous palladium

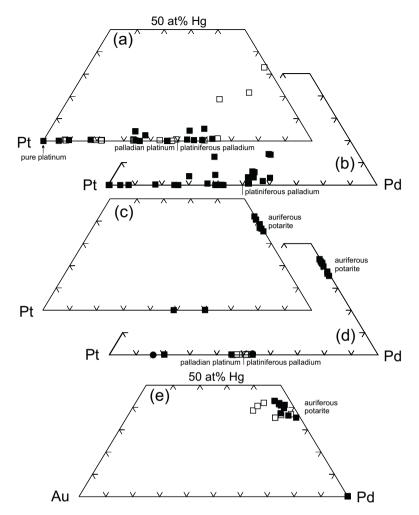


FIG. 4. EPMA compositions of composite Pt–Pd nuggets. (a) Nugget of Figure 3a (full squares) and a second nugget of similar internal structure (open squares). (b) Data for fifteen nuggets, including all results from the nugget of Figure 3b. (c) Data on nugget of Figure 3c; auriferous potarite plots are from inner core area. (d) Data on nugget of Figure 3d; auriferous potarite plots are from inner core area and plots of alloy of near Pt₅₀Pd₅₀ composition are from narrow lighter grey zone immediately surrounding it. (e) Auriferous potarite of nugget of Figure 3d (full squares) and Figure 3c (open squares). (a)–(d) are plots of Pt–Pd–Hg, whereas (e) is a plot of Au–Pd–Hg.

compositions are from porous core areas of the botryoidal nuggets (*e.g.*, Figs. 3b, d). It is conceivable that these binary compositions near 50 at.% Pd represent an ordered phase (*e.g.*, primitive PdPt), but we have not attempted to confirm this by X-ray or electron diffraction. Binary Pt–Pd alloys do not exhibit ordering in phase-equilibria studies (Predel 1998), although bimetallic Pd–Pt atomic clusters of close to 1:1 stoichiometry are formed by molecular beam and laservaporization-source methods (Taylor *et al.* 1990, Rousset *et al.* 1995). Palladium in the Bom Sucesso nuggets is Pt-rich and has a maximum Pd content of about 65 at.%. The EPMA spot compositions of the auriferous potarite near the binary join approximate to Pd₃Hg₂ (*cf.* Yang & Seccombe 1993), but our Au-rich Pd–Hg alloy compositions (Table 1, Fig. 4e) are more consistent with the ideal composition of potarite (PdHg) when reorganized to Pd(Hg,Au). Note that significant amounts of Au are not associated with platinum and palladium coexisting with the potarite. Osmium, Ir, Ru,

and Rh are not present beyond minimum detection-limits of the EPMA method in the essential minerals of the Bom Sucesso nuggets. We did not detect Cu either in the rim or on the external surface of the Pt–Pd nuggets and, thus, are not able to substantiate the SEM study of Cassedanne *et al.* (1996).

The single nugget investigated by ICP-MS analysis vielded a bulk composition of 77.62 wt% Pt, 19.96 Pd, 2.23 Hg, 1.61 Ir, 1.32 Ru, 1.05 Au, and 99.79 wt% total, in good agreement with the wet-chemical results for Bom Sucesso Pt-Pd nuggets summarized in Cassedanne & Alves (1992). Interestingly, although we did not detect Os, Ir, Ru, and Rh in our EPMA study, the Ir-subgroup metals are consistently present in whole-nugget analyses; for example, Hussak (1906) reported 0.08-0.88 wt% Ir and 3.14-3.92 Os, and Cassedanne & Cassedanne (1974) reported 1.2-2.1 wt% Ir. The low levels of the Ir-subgroup metals in the Pt-subgroup phases platinum, palladium and Pd-Hg alloy (PPGM; Yang & Seccombe 1993) are readily understood by the separate behavior of individual PGE at low temperature. The Ir-subgroup do not form extensive solid-solutions with the PPGM at low temperature. If the Bom Sucesso nuggets formed by precipitation from hydrothermal fluids, the Ir-subgroup would tend to segregate as Ir-subgroup-rich minerals (IPGM; Yang & Seccombe 1993). The IPGM may have been present as either very finegrained particles intergranular to the PPGM or, perhaps, within the blackish precipitate in the interior of some nuggets (Cassedanne & Alves 1992). Sporadically distributed coarser grains of IPGM are unlikely, since we investigated about 60 nuggets and nugget fragments by EPMA.

DISCUSSION

Palladium

This study demonstrates unequivocally that the mineral palladium occurs in the Bom Sucesso nuggets, as Pd–Pt solid solution with up to 65 at.% Pd (Table 1, Fig. 4). Palladium occurs in the interior of the nuggets and may have formed by alteration of earlier dendritic auriferous potarite (*e.g.*, Figs. 3c, d). The more common product of alteration is an alloy of composition near Pt₅₀Pd₅₀, whose status as a phase distinct from either platinum or palladium is dubious. The broad interior areas and oscillatorily zoned margins (Fig. 3) of these nuggets consist of palladian platinum, with narrow zones of nearly pure platinum. The narrow rim (and, therefore, the exterior surface) of the pristine nuggets is commonly of pure platinum as well.

As Cassedanne & Alves (1992) reported, it is very likely that the sample of Brazilian nuggets investigated by Wollaston (1809) included material from the Bom Sucesso stream alluvium. Wollaston (1809) reported that the nugget grains "seem to be small fragments of a spongy substance" and "their surface consists of small spherical protuberances closely coherent to each other". Two Pd-rich grains were recognized by Wollaston based on their rapid reaction and deep red color with a nitric– hydrochloric acid solution (presumed to be aqua regia), and adroitly removed for further study. The larger grain was determined to be Pd-rich based on the color of the resulting chloride precipitate, which was red compared to yellow for his typical platinum chloride precipitate. Wollaston's (1809) description of his material is consistent with that of nuggets from Bom Sucesso. The two nuggets presumed to be of native palladium examined by Wollaston were likely to be composite. However, no fragments of this material nor of other nuggets identified by Wollaston as being similar in appearance to them were preserved.

Potarite and Pd-Hg alloys

Potarite (δ -PdHg) is the only Pd–Hg alloy mineral. It is poorly characterized and, like palladium, information on its occurrence and paragenetic position is sparse (Ramdohr 1969, Cabri 1981). Potarite occurs in placers as small nuggets associated with platinum and palladium. The type locality is the Potaro River of Guyana (Harrison & Bourne 1925, Spencer 1928, Peacock 1945), where it occurs in the neighborhood of the gorge below Kaieteur Falls. Potarite also occurs in placer deposits at Morro de Pilar, Minas Gerais (Cabri 1981) and Serro (Cassedanne et al. 1996), and auriferous potarite is found in drainage and overburden derived from Lower Devonian sediments in south Devon, England (Leake et al. 1991). The Potaro River nuggets have a fibrous structure and are Au-bearing (Peacock 1945). On the basis of weight loss on heating, two of four samples analyzed by Harrison & Bourne (1925) and Spencer (1928) were found to be stoichiometric and two were found to be Pd-rich, corresponding to Pd₃Hg₂. The sample analyzed by Peacock (1945) is stoichiometric. Potarite occurs in situ, usually in trace amounts, in the UG2 Chromitite reef of the Bushveld Complex (Cousins & Kinloch 1976, Kinloch 1982), chromitite pods and banded chromitite (both near PdHg composition) from the Great Serpentinite Belt of New South Wales, Australia (Yang & Seccombe 1993), chromite from the Cliff locality in the Shetland ophiolite complex (Prichard et al. 1986; single grain only), chromite from the Bragança massif, northern Portugal (Bridges et al. 1993), thermally metamorphosed dunite from the Inazumi-yama ultramafic complex, southwestern Japan (Arai et al. 1999), where it has a composition of Pd1.1-1.2Hg and is the most abundant PGM, the hydrothermally altered part of the Zabargad peridotite in the Red Sea (Jedwab 1992), and the Kupferschiefer shales of Poland (Kucha 1982, Grange 1996). The list of unidentified PGM in Daltry & Wilson (1997) includes four Pd–Hg phases; Pd₃Hg₂, Pd₂Hg₃ and two of unspecified composition. The Pd₃Hg₂ phase is Cu- and Fe-bearing, with a probable formula of (Pd,Cu,Fe)₃Hg₂, and it is associated with hydrothermal PGM assemblages in banded chromitite (Yang & Seccombe 1993). Most descriptions of potarite in the literature either state or imply a hydrothermal origin. Significantly, perhaps, potarite was not encountered in the recent study of the weathered zone of the UG2 Chromitite reef (Hey 1999), where there is geochemical and mineralogical evidence for the supergene mobility of Pd. In the Inazumi-yama ultramafic complex, potarite is invariably associated with pentlandite–heazlewoodite intergrown with antigorite. Thus, Arai *et al.* (1999) concluded that it formed by contact metamorphism at about 500°C, with Pd remobilized in the dunite by hydrothermal fluids from a crystallizing granitic pluton and Hg possibly originating in the surrounding sediments.

Potarite is readily synthesized at room temperature by reaction of mercury with palladium nitrate solution, or by dry reaction of the elements at 400°C (Terada & Cagle 1960). The alloy phases in the Pd–Hg binary system down to room temperature and at 1 bar are PdHg, Pd₂Hg₅ and PdHg₄ (Predel 1997). A Pd₃Hg₂ phase is not present, and there is no field of solid solution at PdHg above 0°C. Terada & Cagle (1960) noted that the rate of penetration of Pd powder into mercury (amalgamation of Pd) at low temperatures is slight.

In the Bom Sucesso stream sediments, the Pd-Hg alloy phase contains more Pd (52.1 to 60.5 at.%) than ideal potarite, and it is auriferous (1.5-13.8 at.% Au; Table 1). This phase is distinct from cuprian Pd_3Hg_2 in the banded chromitite of the Great Serpentine Belt of New South Wales (Yang & Seccombe 1993), where Cu appears to substitute for Pd. Instead, our Au-rich compositions suggest the formula Pd(Hg,Au), which is consistent with that of auriferous potarite from south Devon, England. There is a rudimentary correlation between the Pd content of Pd-Hg alloys and the composition of coexisting Pt-Pd alloy. Auriferous potarite from south Devon, England occurs with platinum and palladian gold, and potarite from the podiform chromitite of the Great Serpentine Belt is part of a Pt-rich PGM assemblage, whereas potarite of composition Pd_{1,1-1,2}Hg occurs in a Pd-rich assemblage in the Inazumi-yama ultramafic complex, southwestern Japan (Arai et al. 1999), and ~Pd₃Hg₂ occurs with a more Pd-rich PGM assemblage in the banded chromitite of the Great Serpentine Belt. Although Pd-rich, the composition of the auriferous Pd–Hg alloy in the Bom Sucesso nuggets is still within the composition range of the type-locality potarite (Harrison & Bourne 1925, Spencer 1928), and natural material described as potarite ranges from PdHg or Pd(Hg,Au) to Pd₃Hg₂. X-ray powder patterns of potarite are also quite variable in terms of breadth of diffraction lines and presence of weak lines (Terada & Cagle 1960), and possibly reflect a low-temperature defect solid-solution that is not evident in laboratory phase-equilibrium studies. We therefore follow Cassedanne et al. (1996) in referring to the Pd-Hg alloy in the Bom Sucesso nuggets as "potarite". Regardless of the precise mineralogical nature of the Pd–Hg alloy, it is clear that the auriferous potarite + platinum + palladian gold assemblage of south Devon, England is broadly equivalent to the auriferous potarite + platinum + palladium assemblage of Bom Sucesso.

Platinum – palladium – potarite assemblages

The mineral palladium is associated with placer deposits, surficial or near-surface mineralizing environments, including supergene alteration of PGE deposits (Ramdohr 1969) and, possibly, very low-temperature carbonate veins (Leake et al. 1991), and hydrothermal (greenschist-facies) alteration. Potarite and other Pd-Hg alloys appear to have a similar paragenesis. We anticipate that the platinum - palladium - potarite assemblage in the Potaro River of Guyana is broadly analogous to that presently described for the Bom Sucesso stream, but the writings of Spencer (1929) and Peacock (1945) are not helpful in this respect. Similarly, we have no information on the occurrences of potarite in Morro de Pilar (Cabri 1981) and UG2 chromitite (Cousins & Kinloch 1976, Kinloch 1982). The Au-Pd-Pt grains in drainage and overburden in south Devon, England represent four main stages of development (Leake et al. 1991). The first stage produced dendritic and zoned grains of gold enriched in Pd (≤10 wt%), gold-potarite (with 16 wt% Pd) or Au-bearing potarite (with 34 wt% Pd). The second phase was represented by argentian gold (8 wt% Ag) in thin, intergranular films and crack fillings. The third phase produced argentian gold as an overgrowth of the second phase, and the fourth phase is represented by a thin rim of the mineral platinum showing oscillatory zoning, and containing varying amounts of Hg, Pd, Au, Ag, and Cu. Also present are minute grains of selenides (Bi-, Pb-, Hg-, Cu- and more complex Pb-bearing varieties). The dendritic gold is similar to that in carbonate veins at Hope's Nose, Torquay, Devon (Clark & Criddle 1982) and, together with the high levels of Pd and trace selenides, does point to the carbonate veins as likely source rocks for these minerals in the alluvium and overburden. However, we note that potarite and the platinum rims have not been observed in the in situ assemblage, and these absences may be significant. Potarite is not associated directly with Pt-Pd alloy in the chromitite from the Great Serpentine Belt, but it does appear to be of hydrothermal origin. Yang & Seccombe (1993) concluded that the IPGM occur as sulfides, sulfarsenides and alloys in podiform chromitite, and represent primary magmatic phases. On the other hand, the Pd-subgroup PGM (PPGM) occur as alloys with Hg, Sb and Cu in the banded chromitites and likely formed by hydrothermal alteration of primary minerals during the pervasive serpentinization.

Notwithstanding the accumulating evidence for involvement of organic matter in the transport and deposition of Pt at very low temperatures (*e.g.*, Chyi 1982, Wood 1990, Chernyshov & Korobkina 1995, Plyusnina et al. 2000) and biogeochemical cycling of gold (Dyer et al. 1994, Southam 1998), the available evidence favoring an authigenic origin for the Bom Sucesso Pt-Pd nuggets is not overwhelming. Cassedanne & Alves (1992) reported that Pt-Pd nuggets in sediments from the Bom Sucesso stream are too delicate to withstand significant alluvial transport, and supported the diagenetic hypothesis of Hussak (1906). However, this hypothesis was deemed to be untenable in Cassedanne et al. (1996). Moreover, the diagenesis hypothesis is contradicted by the absence of relict primary PGM grains required as a source for the remobilized PGE and the absence of correlation between the compositional banding of nuggets from the same body of alluvium. Assuming that the oscillatory zoning of Pt and Pd represents episodic fluctuation in the supply of metals to the growing nuggets, adjacent nuggets should have similar patterns of compositional zones, as is observed in arsenian pyrite showing oscillatory zoning (Fleet et al. 1988). The present sample was obtained from the stream sediment and, therefore, could have represented nuggets and nugget fragments eroded from bodies of alluvium further upstream. This sample history would explain the lack of correlation of compositional banding among nuggets (Fig. 3), but negates the evidence that the morphology of the nuggets was too delicate to withstand significant alluvial transport. In this regard, we note that platinum is significantly harder than gold (Mohs hardness is 4-41/2 for Pt, 41/2-5 for Pd, and 21/2-3 for Au), and the hardness of Pt is increased by alloying. The nuggets do show some evidence of mechanical alteration (flattening deformation of compositional banding, brittle fractures, etc.), and if they were derived by erosion of the white quartzite cliffs, or the mafic and ultramafic rocks above these cliffs, their preservation would not be too remarkable.

Nevertheless, formation of the nuggets in a surficial or supergene environment is not entirely discounted. The precious metals could have been removed from surficial waters by electroplating onto a nucleating substance, but the direct evidence for this is lacking. Also, the two grains of Pt of eluvial or colluvial origin recovered by Cassedanne *et al.* (1996) might represent relict primary grains from the PGM source if they are indeed distinct from the botryoidal Pt–Pd nuggets. Finally, we emphasize that there is no direct evidence for a detrital origin of the Bom Sucesso Pt–Pd nuggets in the form of comparable *in situ* material from the drainage basin of the Bom Sucesso or from any other locality.

However, following Cassedanne *et al.* (1996), we suggest that these nuggets are most likely the products of rock–fluid alteration of mafic–ultramafic lenses in the drainage basin, based on the established paragenesis of the PGM, PGE geochemistry, and the absence of compelling evidence for an authigenic origin. The rock–fluid alteration was most likely to be hydrothermal, but supergene and even subaerial alteration are not excluded. However, the absence of relict gangue minerals in the

cavity space and of crenulations of the nuggets suggests that they formed as open-space fillings. A high-level, very-low-temperature ($\sim 100^{\circ}$ C) carbonate vein system, such as that postulated as the source for the palladian gold, auriferous potarite and platinum in alluvial sediments and overburden from Devon, England (Leake *et al.* 1991), is a distinct possibility, as is supergene alteration of magmatic sulfides in mafic rocks.

The PGE geochemistry is consistent with hydrothermal alteration of mafic rocks, but precludes the involvement of unevolved peridotite (*i.e.*, lherzolite or komatiite). Although the absolute abundance of PGE decreases with magmatic evolution of mafic and ultramafic rocks, the abundance of Pt, Pd and Au relative to that of Ir and Os increases progressively, as indicated schematically in Figure 5. Ruthenium and, particularly, Rh exhibit intermediate behavior as a result of fractionation, such that the progressively evolving pattern due to fractionation has a positive slope. In contrast, PGE fractionation patterns resulting from hydrothermal transport and deposition have peaks at Pt and Pd, with low to intermediate Au and low to very low Os, Ir, Ru, and Rh. In the New Rambler deposit, Wyoming, the proportions Pd:Pt:(Os,Ir,Ru,Rh) are estimated to be 1800:100:1 (McCallum et al. 1976). Although the Cu sulfide ore

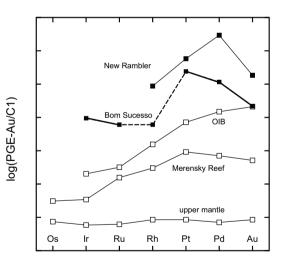


FIG. 5. PGE fractionation pattern for Bom Sucesso Pt–Pd nuggets, compared with upper mantle peridotite (Chou 1978), Merensky Reef (typical ore represented by SARM 7; SA Bureau of Standards, Private Bag X191, Pretoria 0001, Republic of South Africa), ocean-island basalt (OIB; Greenough & Fryer 1990), and gossan associated with hydrothermal Cu–Pt–Pd mineralization at the New Rambler mine, Wyoming (McCallum *et al.* 1976). Results for Ir, Ru, Pt, Pd and Au for Bom Sucesso are based on ICP–MS analysis of a single nugget, Os is taken from Hussak (1906), and Rh is set equal to Ru. All data have been normalized with respect to average values for C1 chondrite (Naldrett 1989), and the vertical scale is arbitrary.

there is Pd-rich, the proportion of metals in gossan approaches that of the Bom Sucesso nuggets (Fig. 5). We suggest that if these Pt–Pd nuggets were authigenic, the fractionation of Pt and Pd from Os, Ir, Ru, and Rh would have been far more extreme.

Furthermore, McCallum et al. (1976) demonstrated that Pd was far more mobile than Pt in the supergene and subaerial environments at the New Rambler mine. Palladium is also more mobile than Pt in supergene alteration of the UG2 Chromitite reef (Hey 1999), and the ratio Pd:Pt is 9:1 in the thermally metamorphosed dunite in the Inazumi-yama ultramafic complex (Arai et al. 1999). Therefore, when fluid transport and depositional environments are spatially removed from mafic and ultramafic source-rocks, the precious metals deposited are likely to be just Pd and Au. Thus, only Pd of the PGE occurs with Au in both carbonate veins cutting Middle Devonian limestones (Clark & Criddle 1982, Stanley et al. 1990) and Lake-Superior-type iron ore deposits in the Iron Quadrangle, Itabira District (Olivo et al. 1994). From the foregoing discussion, it is apparent that, in agreement with Cassedanne et al. (1996), the only likely source-rocks within the drainage basin for the metals in the Bom Sucesso nuggets are the mafic-ultramafic lenses. The ultramafic amphibolite (DBSU) is of the appropriate bulk-composition to yield (Pt,Pd) >> (Os,Ir,Ru,Rh), and high-level episodic hydrothermal alteration of it could have remobilized Pt and Pd and, perhaps, precipitated the precious metals in open spaces in the enclosing metaquartzites.

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