Mineralogical Magazine, February 2006, Vol. 70(1), pp. 123–130

Kalungaite, PdAsSe, a new platinum-group mineral from the Buraco do Ouro gold mine, Cavalcante, Goiás State, Brazil

N. F. Botelho[1],*, M. A. Moura[1], R. C. Peterson[2], C. J. Stanley[3] and D. V. G. Silva[1]

[1] Instituto de Geociências, Universidade de Brasília, DF, 70910-900 Brazil
[2] Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6
[3] The Natural History Museum, Cromwell Road, London SW7 5BD, UK

ABSTRACT

Kalungaite, PdAsSe, is a new mineral discovered in the Buraco do Ouro gold mine, Cavalcante town, Goiás State, Brazil. It occurs in a quartz-muscovite mylonite, related to a peraluminous granite, in platy anhedral aggregates along foliation planes. Associated ore minerals are gold, chalcopyrite, bohdanowiczite, an unnamed Pb-Bi-Se-S mineral, clausthalite, guanajuatite, stibiopalladinite, sperrylite and padmaite. Gangue minerals are muscovite, quartz and rare tourmaline and magnetite. Kalungaite is lead-grey, has a metallic lustre, a black streak and is brittle with uneven fracture. No cleavage was observed. The mineral has a micro-indentation hardness of $VHN_{25} = 438$ (range of 429−455 kg/mm^2 from five indentations). Under reflected light, kalungaite is cream, or creamy grey adjacent to gold grains, has no internal reflections and is isotropic. Reflectance values in air (and in oil) are: 47.5 (33.3) at 470 nm, 46.9 (32.6) at 546 nm, 46.8 (32.6) at 589 nm and 48.0 (34.0) at 650 nm. The average of eight electron-microprobe analyses gives: Pd 41.32, As 27.49, Bi 0.35, Sb 1.59, Se 27.67 and S 1.22, total 99.64 wt. %, corresponding to $Pd_{1.006}(As_{0.950}Sb_{0.034}Bi_{0.004})_{\Sigma 0.988}(Se_{0.908}S_{0.099})_{\Sigma 1.007}$. Kalungaite is cubic, space group $Pa\bar{3}$, $a = 6.089(4)$ Å, $V = 225.78$ Å^3, $Z = 4$. D_{calc} is 7.59 g/cm^3. The strongest seven X-ray powder-diffraction lines [d in Å(I)(hkl)] are: 3.027(75)(002), 1.838(100)(113), 1.172(95)(115, 333), 1.077(80)(044, 144, 334), 0.988(70)(116, 235, 253), 0.929(90)(335) and 0.918(70)(226). Kalungaite is interpreted as having formed from hydrothermal fluids of granitic origin, during syn-emplacement shearing and alteration, producing an unusual gold-platinum-group element deposit.

Keywords: Kalungaite, PdAsSe, new mineral species, Brazil, Buraco do Ouro, gold deposit.

Introduction

Kalungaite, PdAsSe, is a new mineral discovered in ore samples from Buraco do Ouro gold mine (S13º47′45″; W47º27′35″), Cavalcante town, Goiás State, central Brazil (Fig. 1). The name is for the Kalunga people, a community of descendants of African slaves living outside Cavalcante and other nearby towns. Both the mineral and its name were approved by the Commission on New Minerals and Mineral Names of IMA (2004-047). A cotype sample (polished section CAV1B) is deposited at The Natural History Museum in London (BM2004,35).

Platinum-group minerals (PGM) were identified for the first time in the Cavalcante gold mine by Marchetto *et al.* (1993), who described selenides and arsenides closely associated with gold in a strongly sheared, hydrothermally altered, quartz-rich rock, including an unknown Pd-As-Se phase that was reported based on semi-quantitative EDS analysis. Recent investigations on the granite-related gold mineralizations in the Cavalcante region (Botelho and Silva, 2004) have allowed a detailed study and characterization of the platinum-group element-bearing paragenesis as well as this complete characterization of the Pd-As-Se phase.

* E-mail: nilsonfb@unb.br
DOI: 10.1180/0026461067010318

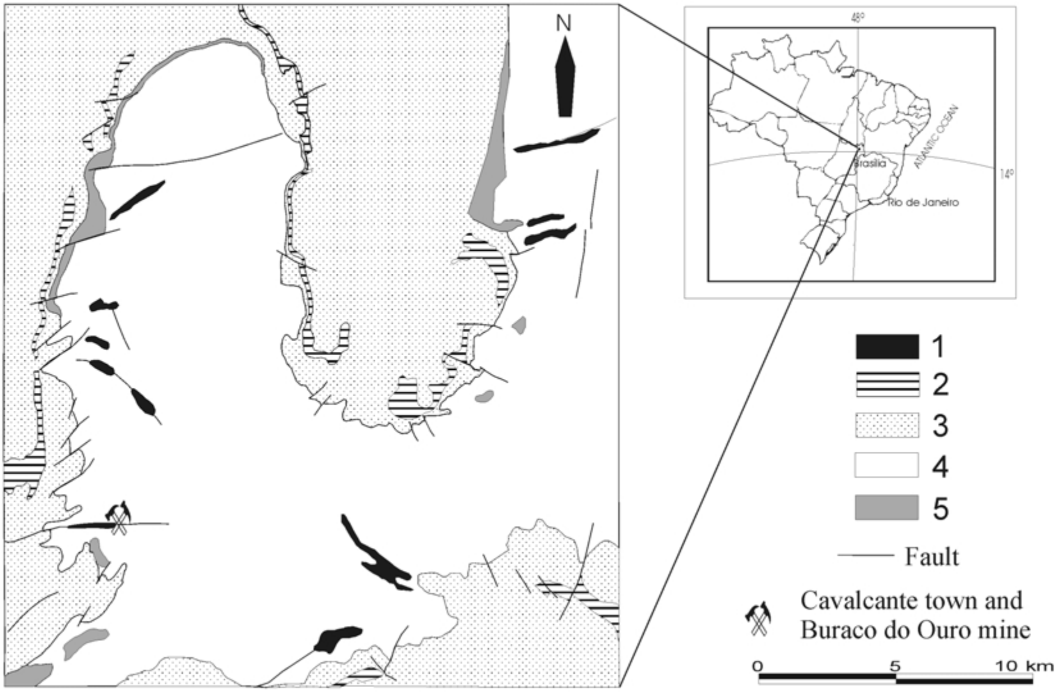

FIG. 1. Geological sketch map of the Cavalcante region showing the location of the Buraco do Ouro gold mine. (1) Shear zone with quartz veins and quartz-muscovite mylonite; (2) metavolcanic rocks of the 1.7 Ga Araí rift; (3) metasedimentary rocks of the Araí rift; (4) 2.1 Ga peraluminous syn-collisional granites (Aurumina suite); (5) graphite-bearing schist and paragneiss (Ticunzal Formation).

Occurrence and paragenesis

The Buraco do Ouro gold mine has been producing gold since 1750. However, in the 1970s, with the improvement of underground operations, PGM mineralization became better known and commercially attractive.

The area of study is located in the basement of the Neoproterozoic Brasília Fold Belt (Pimentel *et al.*, 2000), which comprises in the Cavalcante region: Archaean to Palaeoproterozoic graphite-bearing metasedimentary rocks (Ticunzal Formation), comprising paragneiss and mica schist; 2.2–2.1 Ga peraluminous, syn-collisional granites (Aurumina suite), locally containing xenoliths of the Ticunzal Formation; and volcano-sedimentary rocks of the ~1.77 Ga rift sequence (Araí Group).

The gold deposit is hosted by a quartz-muscovite mylonite, related to an E–W-trending shear zone in a 2.15 Ga peraluminous granite from the Aurumina Suite, that intrudes graphite-bearing metasedimentary rocks of the Ticunzal Formation (Fig. 1). This granite is part of a widespread syn-tectonic granitic suite distributed in the northeastern part of Goiás State, containing several gold occurrences with minor PGE anomalies (Botelho and Moura, 1998; Botelho and Silva, 2004). Ar-Ar geochronology on muscovite porphyroclasts within the mylonite body (Massucatto, 2003), interpreted as relicts of granite phenocrysts, indicates an age of 2.1 Ga, which is near the age of the host granite.

The hydrothermal alteration in the 500 m long Cavalcante shear zone (Fig. 1) includes mainly sericitization and silicification, forming a small deposit (4 tonnes of Au), in which the orebody is an amalgamation of four lenses displaying sigmoidal geometry (D'El-Rey Silva and Senna, 1998).

Kalungaite and associated minerals generally occur as 0.1–0.5 mm platy anhedral aggregates controlled by the mylonitic foliation plane with major concentrations occurring in greyish green muscovite-rich zones. Associated ore minerals are gold, chalcopyrite, bohdanowiczite ($AgBiSe_2$), clausthalite (PbSe), guanajuatite

(Bi_2Se_3), an unnamed Pb-Bi-Se-S mineral, padmaite (PdBiSe), sperrylite ($PtAs_2$) and stibiopalladinite (Pd_5Sb_2). Gangue minerals are muscovite, quartz, rare tourmaline and magnetite. In the type material (Fig. 2*a*), kalungaite is the most abundant PGM. It occurs as composite grains with fine intergrowth between bohdanowiczite and an unnamed Pb-Bi-Se-S mineral, the most abundant ore minerals, after gold. Kalungaite is also found associated with guanajuatite, which contains inclusions of clausthalite (Fig. 2*b*), and with gold and stibiopalladinite (Fig. 2*c*,*d*). In all these associations, the typical texture is represented by kalungaite grains located at the margins of the composite grains. Kalungaite does not occur as isolated grains, and usually contains fine inclusions of gold, stibiopalladinite, sperrylite and padmaite.

Physical and optical properties

Kalungaite occurs as anhedral crystals, reaching a maximum size of 0.3 mm, in composite grains with gold and other PGM and ore minerals. The small size and the similarity with other companion selenides preclude a positive identification of the mineral in hand specimens. Separated grains show a lead-grey colour, metallic lustre, and black streak. The mineral has a micro-indentation hardness of VHN_{25} = 438 (range of 429–455 kg/mm^2 from five indentations), which corresponds to a Mohs hardness of 4 to 5. Kalungaite is brittle with an uneven fracture and no cleavage was observed. Density could not be measured due to the small grain size and aggregate impurities. The calculated density is 7.59 g/cm^3, based on the empirical formula and unit-cell parameters acquired from X-ray powder diffraction data.

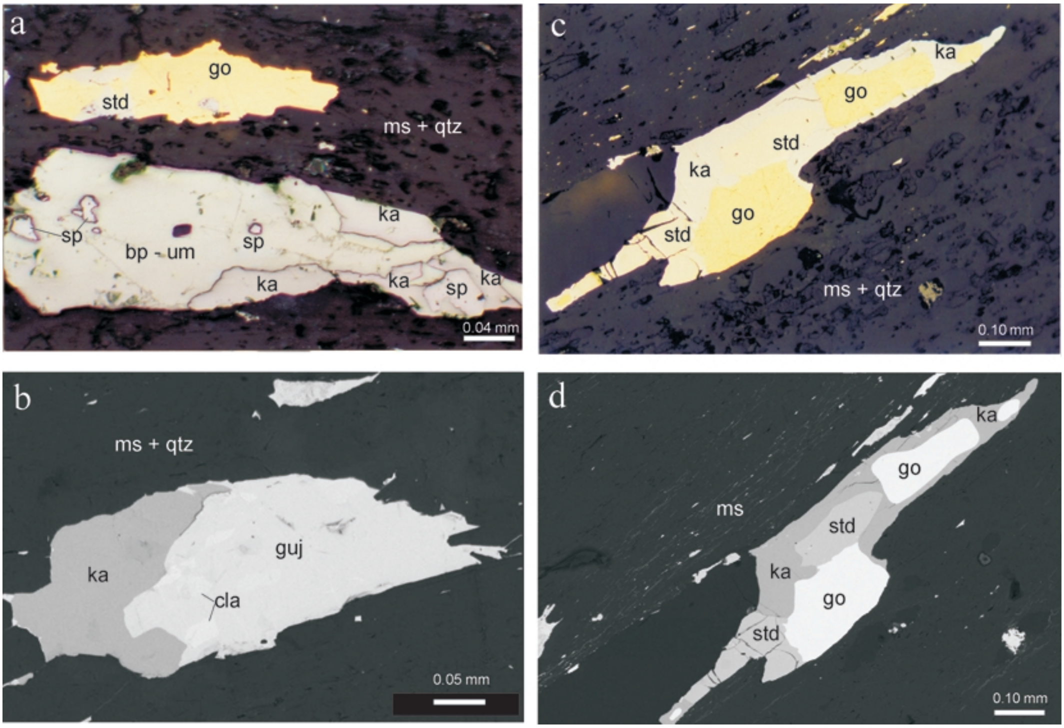

FIG. 2. Reflected light and back-scattered electron (BSE) images of kalungaite and associated minerals. Muscovite (ms) and quartz (qtz) are the gangue minerals. (*a*) Typical occurrence of kalungaite (ka) crystals located at the margins of a composite bohdanowiczite (bp)–unnamed Pb-Bi-Se-S mineral (um) grain, with inclusions of sperrylite (sp), near a composite grain of gold (go) and stibiopalladinite (std). (*b*) BSE image of the association between kalungaite and a grain of guanajuatite (guj) with clausthalite (cla) inclusions. (*c*) Kalungaite associated with gold (go) and stibiopalladinite (std). (*d*) BSE image of the same association from *c*, showing gold grains enveloped by kalungaite. The texture of fine, platy, anhedral kalungaite-bearing aggregates aligned along the foliation planes, marked by muscovite (ms) concentration, can also be seen.

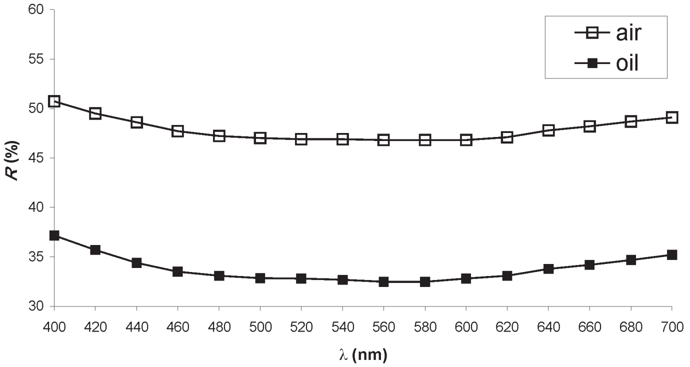

FIG. 3. Reflectance spectra for kalungaite in air (R) and in oil (^{im}R).

In plane-polarized reflected light, the mineral is cream to creamy grey when viewed adjacent to gold grains, has no internal reflections and is isotropic. Reflectance values (Fig. 3) were measured in air and oil (Zeiss oil, n_D = 1.515, DIN 58.884 at 20ºC) relative to a WTiC standard (Zeiss 314), at The Natural History Museum, London, following the methodology of Stanley *et al.* (2002). Reflectance values in air (and in oil) are: 47.5 (33.3) at 470 nm, 46.9 (32.6) at 546 nm, 46.8 (32.6) at 589 nm and 48.0 (34.0) at 650 nm. All measured reflectance data and colour values for kalungaite are presented in Table 1. Optically, kalungaite is similar to minerals of the ullmannite–gersdorffite (NiSbS-NiAsS) series (Anthony *et al.*, 1990), to padmaite (PdBiSe) (Jambor and Puziewicz, 1993) and to the recently described mineral milotaite (PdSbSe) (Paar *et al.*, 2005), which is white, isotropic and lacks internal reflections in plane-polarized light.

TABLE 1. Reflectance data (%) and colour values for kalungaite.

λ (nm)	R	^{im}R	λ (nm)	R	^{im}R
400	50.7	37.2	560	46.8	32.5
420	49.5	35.7	580	46.8	32.5
440	48.6	34.4	600	46.8	32.8
460	47.7	33.5	620	47.1	33.1
480	47.2	33.1	640	47.8	33.8
500	47.0	32.9	660	48.2	34.2
520	46.9	32.8	680	48.7	34.7
540	46.9	32.7	700	49.1	35.2
COM minimum wavelengths					
470	47.5	33.3	589	46.8	32.7
546	46.9	32.65	650	48	34
Colour values: C illuminant					
x	0.309	0.309	λ_d	c565	c563
y	0.313	0.312	P_e%	1	1.6
Y%	47	32.8			
Colour values: A illuminant					
x	0.447	0.448	λ_d	c551	c552
y	0.406	0.405	P_e%	0.5	1
Y%	47	32.8			

Chemical composition

Chemical analyses of kalungaite were carried out using a CAMECA SX50 electron microprobe (University of Brasília) at eight spots in the rim and the core of four crystals in the type material (Table 2). Analytical conditions were: an accelerating beam voltage of 20 kV, a beam current of 40 nA and a beam diameter of 5 μm. The empirical formula from the average spot analysis based on three atoms p.f.u. is $Pd_{1.006}(As_{0.950}Sb_{0.034}Bi_{0.004})_{\Sigma 0.988}(Se_{0.908}S_{0.099})_{\Sigma 1.007}$. The idealized formula is PdAsSe, which requires Pd 40.88, As 28.78, Se 30.33, total 100.00 wt.% (Table 2).

Additional chemical analyses on other samples from different ore bodies of the Buraco do Ouro mine indicate that kalungaite has an homogeneous composition and the same levels of Bi, Sb and S impurities as those found in the type material (Table 2).

X-ray crystallography

A grain of kalungaite was analysed with a Bruker AXS diffractometer equipped with a CCD detector and Ni-filtered Cu-$K\alpha$ radiation. As the grain was not a single crystal of kalungaite and also contained small inclusions of gold, the collection of diffraction data suitable for crystal structure refinement was not possible. Nevertheless, it was possible to obtain and refine a unit cell of 6.087(2) Å.

X-ray powder diffraction data were obtained by exposing a grain of material to Fe-filtered Co-$K\alpha$ radiation in a 114.6 mm diameter Gandolfi camera. Line intensities are from visual estimation. The observed *d* spacings and intensities are presented in Table 3. The strongest seven X-ray powder-diffraction lines [*d* in Å(*I*)(*hkl*)] are: 3.027(75)(002), 1.838(100)(113), 1.172(95)(115, 333), 1.077(80)(044, 144, 334), 0.988(70)(116, 235, 253), 0.929(90)(335) and 0.918(70)(226). The grain also contained gold and these diffraction lines are also included in Table 3. Gold was not used as an internal standard as the exact chemical composition was not known. The pattern was indexed assuming cubic symmetry and a cell dimension of 6.087(2) Å. Sperrylite ($PtAs_2$) has similar X-ray powder patterns (Table 3), symmetry and unit-cell.

The powder data were refined using the *CELREF V3* program (Altermatt and Brown, 1987). A least-squares refinement of 24 lines yielded the following parameters for a cubic unit-cell: a = 6.089(4) Å, V = 225.78 Å^3 , space group $Pa\bar{3}$, Z = 4.

A calculated X-ray diffraction (XRD) pattern, based on space group $Pa\bar{3}$, with a = 6.087(2) and with the x coordinate of As and Se (x = 0.3832) based on the structure of $PtAs_2$ described by Brese and Von Schnering (1994) is presented in Table 3. For the calculation it was assumed that As and Se are disordered at site 8*c*. There is a good match between the intensities calculated by the Rietveld program, *X'pert*, and the observed intensites from the Gandolfi film (Table 3).

Origin of kalungaite

In the Buraco do Ouro mine, no mafic or ultramafic rocks are known close to or in association with the mineralization. The occurrence of relict porphyroclasts of muscovite and of fine muscovite in the mineralized mylonite with

TABLE 2. Electron microprobe analyses of kalungaite in type material and mean of 38 spot analyses in samples from different levels of the Buraco do Ouro mine.

	Type material (*n* = 8)			All samples (*n* = 30)		Ideal formula	Probe standards
Element	Wt.%	Range	Stand. dev.	Wt.%	Stand. dev.	Wt.%	
Pd	41.32	41.07–41.58	0.22	41.32	0.36	40.89	Pd
As	27.49	27.15–27.77	0.21	27.66	0.45	28.78	$FeAs_2$
Bi	0.35	0.27–0.43	0.05	0.38	0.09		Bi
Sb	1.59	1.43–1.80	0.11	1.25	0.41		Sb
Se	27.67	26.73–28.33	0.58	27.94	0.74	30.33	ZnSe
S	1.22	1.00–1.64	0.18	1.15	0.21		FeS_2
Total	99.64			99.70		100.00	

TABLE 3. Observed and calculated XRD data (a = 6.087(2) Å) for kalungaite. The strongest seven XRD lines are highlighted in bold type. Gold (JCPDF file 4-784) and sperrylite (JCPDF file 9-452) values are presented for comparison.

Kalungaite					Gold		Sperrylite	
d_{meas} (Å)	d_{calc} (Å)	I_{meas}	I_{calc}	*hkl*	*d* (Å)	*I*	*d* (Å)	*I*
3.534	3.514	<1	16.1	111			3.430	40
3.027	3.044	75	58.7	002			2.980	60
2.725	2.722	65	56.2	021			2.670	30
2.478	2.485	65	49.3	112			2.430	30
2.346		40		111	2.355	100		
2.152	2.152	40	37.8	022			2.110	50
2.05		10		200	2.039	52		
	2.029		0.6	122				
1.838	**1.835**	**100**	**100**	**113**			1.801	100
1.761	1.757	20	14.1	222			1.719	20
1.685	1.688	30	23.9	023			1.653	20
1.625	1.627	55	10.1	123				
	1.627		23.9	132				
	1.522		1	004			1.595	30
1.475	1.476	<1	0.5	041				
	1.476		0.4	223				
1.441		20		220	1.442	32		
	1.435		0.5	114				
1.400	1.397	10	9.3	133				
1.361	1.361	20	7.7	024			1.368	30
	1.361		7.7	042				
1.329	1.328	20	16.6	142			1.332	40
1.298	1.298	10	8.2	233			1.299	20
1.241	1.243	30	16.3	224			1.272	10
1.230		40		222	1.23	36		
	1.217		0.5	043			1.215	40
	1.194		0.5	134				
	1.194		0.2	143				
				400				
1.172	**1.171**	**95**	**41**	**115**	1.177	12		
	1.171		8	333				
1.131	1.13	60	3.3	025			1.148	70
	1.13		16.6	234				
1.112	1.111	40	8.6	125			1.107	20
	1.111		3.5	152				
1.077	**1.076**	**80**	**34.1**	**044**			1.089	20
	1.06		0.5	144			1.054	40
	1.044		0.2	334				
1.029	1.029	10	2.8	135				
	1.029		2.8	153				
1.015	1.015	30	1	006				
	1.015		15.5	244				
1.000	1.001	10	4.6	061			1.008	40
0.988	**0.987**	**70**	**5.1**	**116**			0.993	40
	0.987		1.9	235			0.980	5
	0.987		11.1	253				
0.963	0.962	50	5.7	026			0.967	10
	0.962		5.7	062				
0.957	0.951	10	0.1	045				
	0.951		0.1	126				
	0.951		1.1	162				
	0.951		0.7	344				
	0.940		0.4	145				
	0.939		0.2	154				
0.935		40			0.936	23	0.943	20
0.929	**0.929**	**90**	**29.8**	**335**				
0.918	**0.918**	**70**	**17.2**	**226**				
0.911		20			0.912	22	0.910	30

the same Ar-Ar age (Massucatto, 2003) and Ti enrichment as in the muscovite phenocrysts from the peraluminous granite allow us to suggest that the Buraco do Ouro orebodies are related to fracture filling and replacement of the granitic rock in the Cavalcante shear zone. These relationships and the ore textures and structures suggest that kalungaite was formed during syn-emplacement deformation and hydrothermal alteration of the peraluminous granite. However, the source of the metals involved in the mineralization remains speculative. A possible source could be the graphite-rich country rocks of the Ticunzal Formation, interpreted as having been derived from anoxic marine sediments, which crop out near the Buraco do Ouro mine and are intruded by the peraluminous granite (Fig. 1). Indeed, marine black shales have been reported by Pasava (1993) as important concentrators of platinum group elements (PGE), with economic concentrations in China, Canada and Poland, as well as in Russia, where some Au-Pt-Pd deposits, considered to be hosted in metamorphosed black shales, are classified as orogenic Au-Pt (-Pd) deposits in carbonaceous metasedimentary rocks by Wilde *et al.* (2003). In the case of the Buraco do Ouro mine, the conditions for complexation, transportation and deposition of Au, Pd, Se and As could be satisfied with saline and acidic fluids of granitic origin interacting with graphite-bearing country rocks enriched in these elements, as discussed by Mountain and Wood (1988), Stanley and Criddle (1990) and Simon *et al*. (1997) in other areas. Considering the available data, we propose that the kalungaite-bearing selenide mineralization at the Buraco do Ouro mine represents an unconventional small hydrothermal PGE deposit.

Acknowledgements

Financial support for this research was provided by the Brazilian Research Council – CNPq. Márcia A. Moura would like to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES (Brazil) and Gema Olivo, respectively, for a research fellowship and support at Queen's University. We are grateful to Leonel Barros Neto, from Penery Mining Ltd, for access to and sampling in the Buraco do Ouro mine, and to Rafael K. Carneiro and Luciano C. Gonçalves for their cooperation at the beginning of the study on the Buraco do Ouro mineralogy. We thank FURNAS Centrais Elétricas and Ana Lívia Silveira for SEM analyses. We are also indebted to Andrew M. McDonald and an anonymous reviewer for their critical comments and constructive suggestions.

References

Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols, M.C. (1990) *Handbook of mineralogy, v.1: Elements, sulfides, sulfosalts.* Mineral Data Publishing, 588 pp.

Altermatt, U.D. and Brown, I.D. (1987) A real-space computer-based symmetry algebra. *Acta Crystallographica*, **A43**, 125–130.

Botelho, N.F. and Moura, M.A. (1998) Granite-ore deposit relationship in central Brazil. *Journal of South American Earth Sciences*, **11**, 427–438.

Botelho, N.F. and Silva, D.V.G. (2004) Caracterização mineralógica e química das mineralizações de ouro (±PGE) da suíte granítica Aurumina, Goiás. *Abstracts of the XLII Congresso Brasileiro de Geologia* (CD Rom).

Brese, N.E and Von Schnering, H.G. (1994) Bonding trends in pyrites and a reinvestigation of the structures of $PdAs_2$, $PdSb_2$, $PtSb_2$ and $PtBi_2$. *Zeitschrift für anorganische und allgemeine Chemie*, **620**, 393–404.

D'el Rey Silva, L.J.H. and Senna, V.F. (1998) Ouro em sericita-quartzo hidrotermalitos controlados por cisalhamentos conjugados brasilianos na região de Cavalcante (GO). *Revista Brasileira de Geociências*, **28**, 405–408.

Jambor, J.L. and Puziewicz, J. (1993) New mineral names. *American Mineralogist*, **78,** 451–452.

Marchetto, C.M.L., Larson, L.T. and Figueiredo A.N. (1993) Platinum group minerals and gold in acid rocks, Cavalcante, Brazil. *I Brazilian Meeting on Platinum Group Elements*, *Extended Abstracts*. Brazilian Geological Society (SBG), pp. 47–51.

Massucato, A.J. (2003) *Caracterização Estrutural do Embasamento do Grupo Araí na Zona Externa da Faixa Brasília (GO)*. Unpublished PhD thesis, University of São Paulo State, Rio Claro, São Paulo, Brazil, 272 pp.

Mountain, B.W. and Wood, S.A. (1988) Chemical controls on the solubility, transport, and deposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. *Economic Geology*, **83**, 492–510.

Paar, W.H., Topa, D., Makovicky, E. and Culetto, F.J. (2005) Milotaite, PdSbSe, a new palladium mineral species from Předbořice, Czech Republic. *The Canadian Mineralogist*, **43**, 689–694.

Pasava, J. (1993) Anoxic sediments – an important environment for PGE: An overview. *Ore Geology Reviews*, **8**, 425–445.

Pimentel, M.M., Fuck, R.A., Jost, H., Ferreira Filho, C.F. and Araújo, S.M. (2000) The basement of the Brasília Fold Belt and the Goiás Magmatic Arc. Pp. 195−230 in: *Tectonic Evolution of South America* (U.G. Cordani, E.J. Milani, A. Thomaz Filho and D.A. Campos, editors). 31st International Geological Congress.

Simon, G., Kesler, S.E. and Essene, E.J. (1997) Phase relations among selenides, sulfides, tellurides, and oxides: II. Applications to selenide-bearing ore deposits. *Economic Geology*, **92**, 468−484.

Stanley, C.J. and Criddle, A.J. (1990) Precious and base metal selenide mineralization at Hope's Nose, Torquay, Devon. *Mineralogical Magazine*, **54**, 485−493.

Stanley, C.J., Criddle, A.J., Förster, H.-J. and Roberts, A.C. (2002) Tischendorfite, $Pd_8Hg_3Se_9$, a new mineral species from Tilkerode, Harz Mountains, Germany. *The Canadian Mineralogist*, **40**, 739−745.

Wilde, A., Edwards, A. and Yakubchuk, A. (2003) Unconventional deposits of Pt and Pd: a review with implications for explorations. *Society of Economic Geologists Newsletter*, **52**, 1−18.

[*Manuscript received 26 April 2005:*
revised 10 January 2006]