

The solid solution between platinum and palladium in nature

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ABSTRACT

Chemical and structural data are reported for platinum–palladium intermediates from two nuggets found at Córrego Bom Sucesso, Minas Gerais, Brazil. Three grains with simple stoichiometries (i.e. Pt_xPd_{1-x} with $x \sim 0.67$, ~ 0.5 and ~ 0.33 , which correspond to Pt₂Pd, PtPd and PtPd₂, respectively) were characterized by single-crystal X-ray diffraction and electron-probe microanalysis. In the absence of single-crystal data it might be tempting to hypothesize that such simple stoichiometries represent distinct mineral species, however structural analyses show that all of the phases are cubic and crystallize in space group $Fm\bar{3}m$. They are, therefore, natural intermediates in the palladium–platinum solid solution. Reflectance and micro-hardness values are reported for the samples and a comparison with the pure metallic elements made. On the basis of information gained from the chemical and structural characterization it can be concluded that there is a complete solid solution between Pt and Pd in nature. These findings corroborate results from experiments on synthetic compounds.

KEYWORDS: platinum, palladium, alloys, chemical composition, unit-cell parameters.

Introduction

STUDIES of the platinum–palladium equilibrium phase diagram show that the two elements form a complete solid solution series (e.g. Bhardwaj *et al.*, 1991); however, platinum with a high palladium content has only been reported in natural specimens relatively recently (e.g. Cabral *et al.*, 2006). Fedortchouk *et al.* (2010) described unusual inclusions of iron-poor and copper-, nickel- and palladium-rich platinum in grains of Pt–Fe alloy from Burwash Creek in the Yukon Territory, Canada. The composition of these inclusions was found to be in the range Pt_{0.48–0.53}Pd_{0.29–0.38}Ni_{0.06–0.08}Cu_{0.06–0.08}, and shows that there is an extensive natural solid

solution between Pt and Pd. However, no structural analyses of grains with these or similar compositions have been reported.

Platinum forms ordered superstructures or intermetallic compounds with elements including Ni, Cu, Sn, In, As, Sb and Bi; if they occur naturally, these phases, which have characteristic structures, qualify as distinct mineral species. In minerals which contain both palladium and platinum, the two elements commonly substitute into the same structural site in a disordered fashion. This type of substitution is present in minerals such as merenskyite, (Pd,Pt)(Te,Bi)₂ (Kingston, 1966); rustenburgite, (Pt,Pd)₃Sn (Mihalik *et al.*, 1975); moncheite, (Pt,Pd)(Te,Bi)₂ (Genkin *et al.*, 1963); isoferroplatinum, (Pt,Pd)₃(Fe,Cu) (Cabri and Feather, 1975); genkinite, (Pt,Pd)₄Sb₃ (Cabri *et al.*, 1977); atokite, (Pd,Pt)₃Sn (Mihalik *et al.*, 1975);

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michenerite, (Pd,Pt)BiTe (Hawley and Berry, 1958); and vincentite, (Pd,Pt)₃(As,Sb,Te) (Stumpfl and Tarkian, 1974). However, there are cases of simple but structurally uncharacterized stoichiometries, such as PtPd (Fleet *et al.*, 2002; Cabral *et al.*, 2006) and the grains of Pt_xPd_{1-x} with $x \sim 0.67$, ~ 0.5 and ~ 0.33 (which correspond to Pt₂Pd, PtPd and PtPd₂, respectively), described herein, which suggest specific, ordered phases.

The characterization of platinum-group minerals (PGM) from a number of Brazilian deposits (e.g. Angeli, 2005; Garuti *et al.*, 2007, 2012) has given us the opportunity to investigate the natural solid solution between platinum and palladium. Chemical and structural analyses of palladium-rich platinum and platinum-rich palladium nuggets from Córrego Bom Sucesso, Minas Gerais, Brazil are reported for the first time. On the basis of the information gained in this study, new crystal-chemical data for these economically important minerals are reported.

Description of the samples and experimental details

The samples described herein are from two nuggets found at Córrego Bom Sucesso, Minas Gerais, Brazil. These nuggets are ~ 1 mm across, rounded in shape and display complex internal zonation (Fig. 1). The Bom Sucesso area is well known to economic geologists; it hosts alluvial deposits of Pt, Pd, Au and detrital diamonds (Cabral *et al.*, 2009a). It is important from a historical perspective as the type locality for palladium (Wollaston, 1805; Hussak, 1906). Furthermore, the PGE minerals in nuggets from the Bom Sucesso area commonly have unusual compositions and microstructures (Hussak, 1906; Cassedanne *et al.*, 1996; Fleet *et al.*, 2002; Cabral *et al.*, 2009b).

Small crystal fragments (40 to 55 μm in size) were hand picked from a polished section for the structural study, which was performed on a Bruker MACH3 single-crystal diffractometer using MoK α radiation. The overall diffraction quality was fairly good and allowed the determination of the a unit-cell parameters for crystal fragments with differing compositions by centring 25 high- θ (22 – 25°) reflections. Measured parameters are 3.9135(2), 3.9059(3) and 3.8894(1) \AA for Pt_xPd_{1-x} with $x \sim 0.67$, ~ 0.50 and ~ 0.33 , respectively.

The chemical composition was determined on the same crystal fragments used in the structural

study at the Eugen F. Stumpfl laboratory at Leoben University, using a Jeol JXA 8200 Superprobe operating in wavelength-dispersive spectrometry (WDS) mode at 20 kV accelerating voltage and 10 nA beam current with a beam diameter of ~ 1 μm . Pure metals were used as standards for Pt, Rh and Pd; synthetic PdSb, SbBi, Pd₃HgTe as standards for Sb, Bi, Hg and Te; and natural chalcopyrite and niccolite as standards for Cu, S and As. The X-ray lines used in the analyses were as follows: K α for S and Cu; L α for Rh, Pt, Pd, As, Te, Bi and Sb; M α for Hg. The following analysing crystals were used: PETJ for S, Hg, Te, Bi; PETH for Rh, Pd, Sb; LIFH for Cu, Pt; and TAP for As. The counting times on the peaks and in the upper and lower background positions were 20 and 10 seconds, respectively. All possible peak overlaps among the selected X-ray lines were

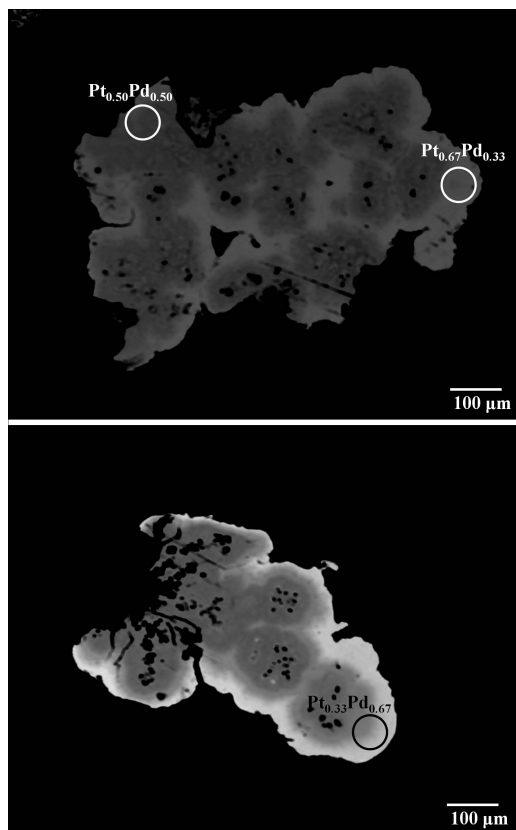


FIG. 1. Backscattered-electron images of the two selected nuggets from Córrego Bom Sucesso, Minas Gerais, Brazil. Circles indicate the regions from which crystal fragments were hand picked.

checked and automatically corrected using the online procedure. Detection limits are as follows: As = 0.09, S = 0.03, Sb = 0.05, Te = 0.05, Bi = 0.05, Hg = 0.09, Cu = 0.03, Rh = 0.07, Pt = 0.1 and Pd = 0.02 wt.%. The backscattered-electron images in Fig. 1 were obtained using the same system that was used for the analyses. Compositions (means of 10 analyses on different spots) and atomic ratios (on the basis of 1 atom) are reported in Table 1. The concentration of Cu, Sb, Bi and As was below instrumental detection limits in every case.

Reflectance measurements were performed in air using a Zeiss MPM-200 microphotometer equipped with an MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. An interference filter was used to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm); data from a 0.1 mm diameter spot were recorded for the specimen and a SiC standard in the same focussing conditions. The reflectance values (in %) determined for Pt_xPd_{1-x} with $x \sim 0.67$, ~ 0.50 and ~ 0.33 , respectively, are as follows: 62.0, 62.8, 63.5 (471.1 nm); 65.2, 66.0, 66.7 (548.3 nm); 66.4, 67.0, 67.8 (586.6 nm); and 68.5, 69.2, 69.9

(652.3 nm). Figure 2 shows that the reflectance values for the minerals studied here lie between those measured for pure platinum (empty squares) and those for pure palladium (empty circles), in agreement with a simple solid solution between the two endmembers.

Micro-indentation hardness measurements on the three fragments with a VHN load of 100 g gave the following values: 314 (range 304–328); 338 (range 330–345); and 351 (range 344–361) $kg\ mm^{-2}$ for Pt_xPd_{1-x} with $x \sim 0.67$, ~ 0.50 and ~ 0.33 , respectively.

Results and discussion

The chemical formulae of the three fragments described herein are close to Pt_2Pd , $PtPd$ and $PtPd_2$ (i.e. they correspond to Pt_xPd_{1-x} solid solutions with $x \sim 0.67$, ~ 0.50 and ~ 0.33 , respectively). In the absence of structural data, grains with such simple stoichiometries might be taken to be good candidates for new mineral species. Indeed Cabral *et al.* (2006) concluded that this was likely for some similar compositions. An important conclusion of this study is that grains with the simple stoichiometric formulae Pt_2Pd , $PtPd$ and $PtPd_2$ have the same crystal

TABLE 1. Electron-probe microanalyses and atomic ratios for the crystal fragments selected for the structural study.

	Mean (wt.%)	Range	Mean (wt.%)	Range	Mean (wt.%)	Range
Rh	0.24	(0.03–0.38)	0.30	(0.26–0.34)	0.10	(0.02–0.15)
Pt	75.28	(74.89–76.59)	57.70	(52.76–59.64)	43.00	(41.86–44.48)
Pd	19.46	(18.97–20.38)	33.25	(32.50–33.99)	55.36	(53.26–56.07)
Te	0.02	(0.00–0.04)	0.03	(0.00–0.07)	0.02	(0.01–0.11)
S	0.26	(0.21–0.31)	0.22	(0.20–0.24)	0.15	(0.09–0.19)
Hg	3.01	(1.00–3.31)	6.73	(5.48–7.98)	1.24	(1.00–1.85)
Total	98.27	(97.29–100.52)	98.23	(98.21–98.26)	99.87	(99.19–101.30)
Elemental composition on the basis of a single atom						
Rh	0.004		0.004		0.002	
Pt	0.649		0.454		0.294	
Pd	0.308		0.479		0.690	
Te	0.000		0.000		0.000	
S	0.014		0.012		0.006	
Hg	0.025		0.051		0.008	
Total	1.000		1.000		1.000	
Simple formula	Pt_2Pd		$PtPd$		$PtPd_2$	

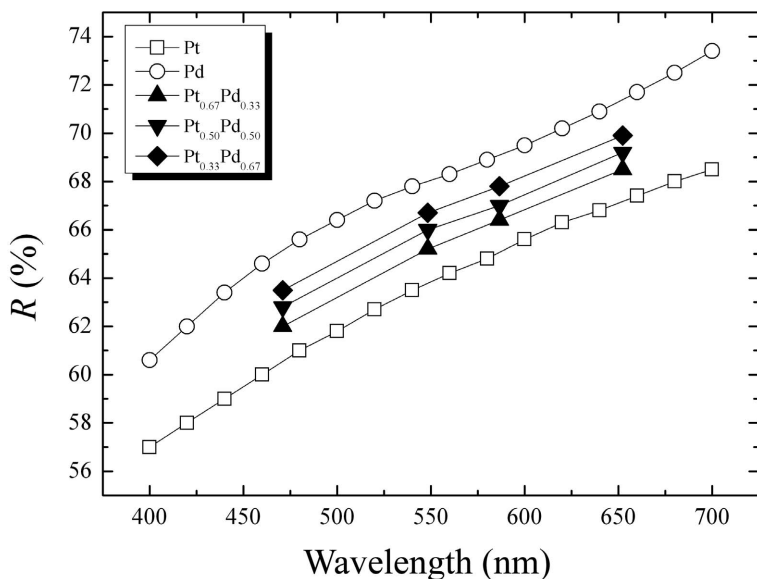


FIG. 2. Reflectivity curves for Pt_xPd_{1-x} in air. Filled upward triangles, downward triangles and diamonds refer to $Pt_{0.67}Pd_{0.33}$, $Pt_{0.50}Pd_{0.50}$ and $Pt_{0.33}Pd_{0.67}$, respectively. Open squares and circles refer to pure platinum and palladium, respectively.

structure as platinum and palladium and are therefore part of a solid-solution series; therefore, they cannot be regarded as distinct mineral species. The rules established by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (Nickel and Grice, 1998) state that in a continuous binary solid solution, only the two endmembers are species. The composition field of a species in such a solid solution extends from the endmember to a composition containing 50 mol.% of the appropriate substituent; this is generally known as the '50% rule'. In the case of multiple homovalent solid-solution series, the 50% rule is interpreted in terms of dominant occupancy at a particular structural site.

The rule described in the foregoing paragraph allows the phase with $x \sim 0.67$ to be described as palladium-rich platinum and the phase with $x \sim 0.33$ is platinum-rich palladium. There is a minor terminological problem for the phase with $x \sim 0.50$, which is at the boundary between the two composition fields: Pt and Pd are disordered in the same site in the cubic $Fm\bar{3}m$ structure and one cannot always use the name platinum or palladium with confidence. This terminological difficulty can be overcome by means of a chemical formula (e.g. $Pt_{0.50}Pd_{0.50}$).

The variation in the cubic a parameter is shown as a function of the Pt content (in a.p.f.u.) in Fig. 3. The a parameter increases with the increasing Pt content according to the equation:

$$a_{\text{pred}} = 3.8896(7) + 0.034(1)Pt$$

where a is the unit-cell parameter in Å and Pt is the platinum content in a.p.f.u. The small amount of Hg that is present in the investigated crystals has an insignificant influence on the linear regression. The equation allows the unit-cell parameter for a particular phase to be determined directly from its chemical composition (which is easily obtained by electron-microprobe analysis). It is of potential use in the absence of precise X-ray data, perhaps due to the paucity of material or intergrowths with other minerals, as is commonly the case for minerals of the platinum group.

The information gained from chemical, optical, physical and structural characterizations of the phases described in this paper, suggests that there is a complete solid solution between platinum and palladium in nature. Although we have discovered grains with simple stoichiometries, including $PtPd$, Pt_2Pd and Pd_2Pt , these phases do not represent new mineral species, but are part of the platinum–palladium solid solution; the occurrence of such simple stoichiometries in an ideal binary solid solution is nonetheless intriguing.

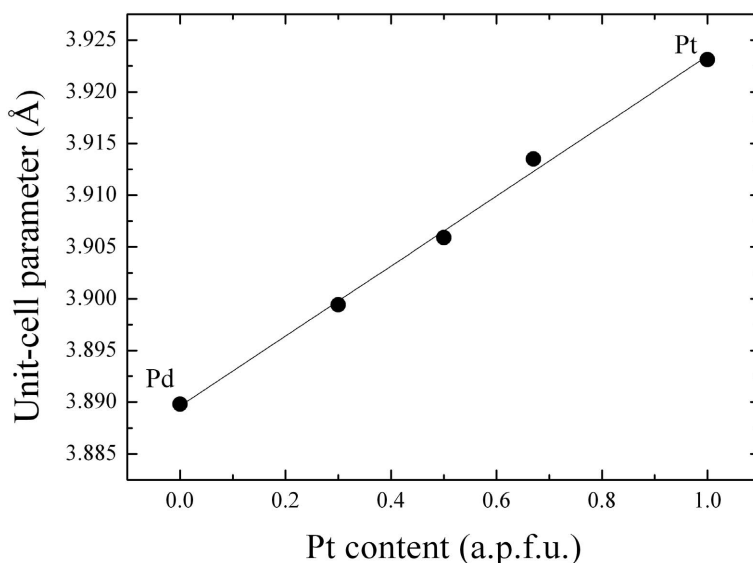


FIG. 3. The Pt content of $\text{Pt}_x\text{Pd}_{1-x}$ in atoms per formula unit vs. the a unit-cell parameter (Å). An analysis of these data indicate a linear relationship ($R^2 = 0.998$).

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