

A silver–palladium alloy from the Bahia lateritic gold deposit, Carajas, Brazil

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Abstract

A silver–palladium alloy with structural formula close to AgPd has been found in laterite from the Bahia lateritic gold deposit. The alloy occurs in a void of an iron oxide nodule, associated with goethite and hematite. The angular shape and protuberances of the alloy grains suggest crystal growth in a lateritic environment, indicating that the alloy is a secondary mineral precipitated during lateritisation. The oxidation of sulphides of the parent rocks probably favoured the migration of palladium and silver as transient thiosulphate and sulphite complexes. Destruction of the thiosulphate and sulphite ligands could result in precipitation of both palladium and silver as an alloy. Eh–pH phase diagrams for Pd–H₂O–Cl and Ag–H₂O–Cl systems show that both palladium and silver are stable in lateritic environments under lower redox potentials. Such an environment may exist at the top of the ferruginous zone due to the abundant organic matter near the surface.

KEYWORDS: silver–palladium alloy, thiosulphate complex, chloride complex, laterite, Bahia gold deposit, Brazil.

Introduction

THE secondary enrichment of platinum-group elements (PGE) in weathering processes has been well documented in recent years (Fuchs and Rose, 1974; Westland, 1981; Bowles, 1986; 1987). However, very little has been reported on the supergene mineralogy of palladium. In this paper a secondary silver–palladium alloy is reported. The alloy was found in an iron oxide nodule of laterite from the Bahia lateritic gold deposit, associated with goethite and hematite at the top of a ferruginous zone. Morphological study and thermodynamic calculation show that the alloy was formed in lateritisation processes. This is the first recorded natural occurrence of the silver–palladium alloy.

The Bahia lateritic gold deposit is located in Serra dos Carajas where the depth of weathering reaches a maximum of 300 metres below the surface. Under the surface soil zone, the lateritic profile consists of a ferruginous zone (about 30 metres thick) where the gold orebodies have been delineated. The ferruginous zone is characterised by iron oxide nodules, pisolites and ferruginous soil with iron oxide patches. In this zone there is a small amount of gibbsite, kaolinite and relict quartz. Beneath the ferruginous zone occurs a mottled zone, which is usually a yellow kaolinite-

rich clay with brown or red ferruginous staining and indurated iron-rich clay patches. Beneath the mottled zone, a poorly developed pallid zone of pale to off-white or greenish white kaolinite-rich clay extends downward to fresh rock. The fresh rock consists mainly of chlorite schist with quartz veinlets, magnetite and sulphide veins (chalcopyrite, bornite, etc.), and associated disseminated sulphides, which suggests hydrothermal mineralisation in the parent rocks.

Laterite

The laterite sample in which the silver–palladium alloy has been found was collected from Test Pit 12, 6.9–10.5 metres below the surface, at the top of the ferruginous zone. The laterite is dark red in colour and is characterised by iron oxide nodules cemented by ferruginous matrices. An analysis by X-ray powder diffraction shows that it consists largely of hematite, goethite, and a small amount of gibbsite, magemite, kaolinite and quartz. The analysis (Table 1) by X-ray fluorescence spectrometry (XRF) shows it to be mainly composed of Fe₂O₃, with a small amount of Al₂O₃, SiO₂, TiO₂ and MnO. In this laterite, iron is strongly enriched while aluminium and silicon are relatively depleted. Alkalis and alka-

Table 1 XRF analysis of laterite

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total
5.60	5.98	75.34	0.38	1.90	0.76	0.02	n.f.	0.08	1.20	8.47	99.73

Total Fe as Fe₂O₃.

L.O.I.=loss on ignition.

n.f.=not found.

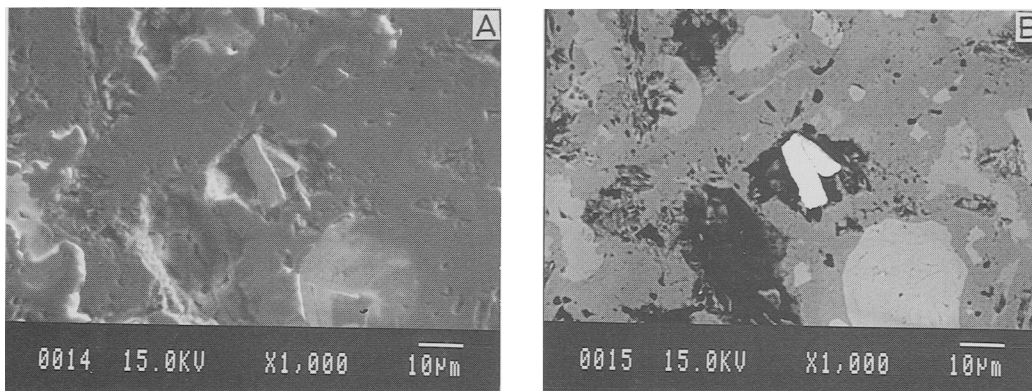


Fig. 1 (A) Scanning electron micrograph of polished thin section with silver–palladium alloy grains (centre) in a void of an iron oxide nodule. (B) Back-scattered electron image of (A), white = silver–palladium alloy; light grey = hematite; dark grey = goethite; black = void.

line earths are strongly depleted. The high content of P₂O₅ suggests the presence of phosphates, especially apatite and monazite which are found to be stable in laterite. Secondary apatite and monazite have also been reported in laterite profiles (Lottermoser, 1988).

Silver–palladium alloy

The micrographs of thin section taken by electron microprobe show two grains of silver–palladium alloy (Fig. 1) occurring in a void of an iron oxide nodule, associated with goethite and hematite, indicating that the alloy crystallised after the formation of the iron oxide minerals. The grains show angular protuberances, 15 µm long and 5 µm wide, suggesting crystal growth in the laterite. These characteristics indicate that the silver–palladium alloy is a secondary mineral in laterite rather than residual from the parent rocks.

With pure metals and cinnabar as standards,

using $L\alpha$ lines for Ag, Pd, Pt, Au, Hg and $K\alpha$ for Cu, microprobe analysis (Table 2) has shown that the alloy contains palladium, silver and minor amount of copper. Platinum, gold and mercury have not been found in the alloy. The atomic ratio of Ag : Pd in the alloy is about 1 : 1 with a structural formula close to AgPd. The calculation of the structural formula suggests that silver is substituted by a very small amount of copper.

Discussion

The silver–palladium alloy occurs in a void of an iron-oxide nodule. The angular shape of the grain can be taken as an evidence of the grain growth in the laterite. In addition ore-microscopic examination and microprobe study failed to show the primary alloy in the parent rocks. Perhaps the primary Pd carriers are sulphides, which are abundant in the parent rocks. Silver probably occurs as electrum inclusions in sulphides as well.

The geochemical study of palladium and silver

has shown that they are mobile during weathering. Chloride complexes and thiosulphate and sulphite complexes are suggested to dissolve and transport them. However, chloride complexation only occur under acidic and oxidising conditions. The weathering of silicates, such as chlorite which is abundant in the parent rocks in this area, will create a neutral to slightly alkaline conditions (Breemen and Wielemaker, 1974). Under such conditions chloride ion complexation must be insignificant whereas thiosulphate and sulphite ions produced from oxidation of sulphides are stable (Fig. 2). These thiosulphate and sulphite complexes are good complex ions to transport both palladium and silver. Palladium thiosulphate complexes may occur as $[\text{Pd}(\text{S}_2\text{O}_3)_2]^{2-}$, $[\text{Pd}(\text{S}_2\text{O}_3)_4]^{6-}$ while palladium sulphite complexes as $[\text{Pd}(\text{SO}_3)_4]^{6-}$, $[\text{Pd}(\text{SO}_3)_2(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Pd}(\text{SO}_3)(\text{H}_2\text{O})_3]^0$ (Plimer and Williams, 1987). Silver can also form thiosulphate and sulphite complexes, such as $[\text{AgS}_2\text{O}_3]^-$, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, $[\text{AgSO}_3]^-$, $[\text{Ag}(\text{SO}_3)_2]^{3-}$ and $[\text{Ag}(\text{SO}_3)_3]^{5-}$. The transportation of palladium and silver may be as a mixed complex of $[(\text{Ag},\text{Pd})(\text{S}_2\text{O}_3)_2]^{3-}$, similar to a mixed complex of $[(\text{Ag},\text{Au})(\text{S}_2\text{O}_3)_2]^{3-}$ suggested by Webster (1986). Palladium and silver, therefore, were probably transported as transient thiosulphate and sulphite complexes during weathering of the parent rocks. As the weathering proceeds the further oxidation of these thiosulphate and sulphite ligands could give rise to the precipitation of both palladium and silver to form a silver-palladium alloy. Metallurgical study indicates that silver and palladium can occur as a complete solid solution (Karakaya and Thompson, 1986), which is similar to silver-gold solid solution.

Chloride however does exist in the weathering environment which is mainly from meteoric precipitation. High concentration of chloride ion exists in saline groundwater in arid areas due to

low rainfall and strong evaporation. In Australia, Mann (1984) reported 0.1 M Cl^- in the laterite profile of Yilgarn Block where chloride leached silver out of the profile causing chemical purification of native gold. Keays and Davison (1976) have noted palladium enrichment in lower sections of the oxide zone at Kambalda, Australia. Travis *et al.* (1976) have noted that palladium is depleted at the surface and strongly enriched in the base of the laterite profile at Gilgarna Rocks, Australia. The depletion of palladium in the upper zone of laterite profiles is probably related to concentration of chloride in ground water. Low rainfall and strong evaporation will increase concentration of chloride in ground water, enhancing the depletion of both silver and palladium. High rainfall, however, will dilute the ground water and lower the chloride concentration, which will increase the stability of palladium and silver in lateritic environment. Another factor influencing stability of silver and palladium is redox potentials. Under low redox potentials stability of both silver and palladium will be increased.

The stability of palladium chloride and silver chloride complexes is illustrated by an Eh-pH diagram for the system Pd-H₂O-Cl and Ag-H₂O-Cl based on thermodynamic data (Wagman *et al.*, 1982). Silver and palladium have been considered separately because no thermodynamic data for a silver-palladium alloy are available. A chloride concentration of $10^{-4.5}$ M is assumed based on the concentration of chloride in both regional precipitation (2.4×10^{-5} M; Stallard and Edmond, 1981) and the lower Amazon river (3.2×10^{-5} M; Stallard, 1980). A silver concentration of 10^{-8} M is assumed based on the concentration of silver in Amazon river (2.2×10^{-9} M; Kharkar *et al.*, 1968). A palladium concentration of 10^{-12} M is taken from Fuchs and Rose (1974). The stability field of lateritic soils is defined based on

Table 2 Microprobe analysis of silver-palladium alloy

No.	Pd	Ag	Pt	Au	Hg	Cu	Total
wt%							
1)	49.70	49.19	n.f.	n.f.	n.f.	0.13	99.02
2)	49.28	49.43	n.f.	n.f.	n.f.	0.09	98.81
number of atoms							
1)	1.010	0.986	-	-	-	0.004	2.000
2)	1.004	0.993	-	-	-	0.003	2.000

n.f.=not found.

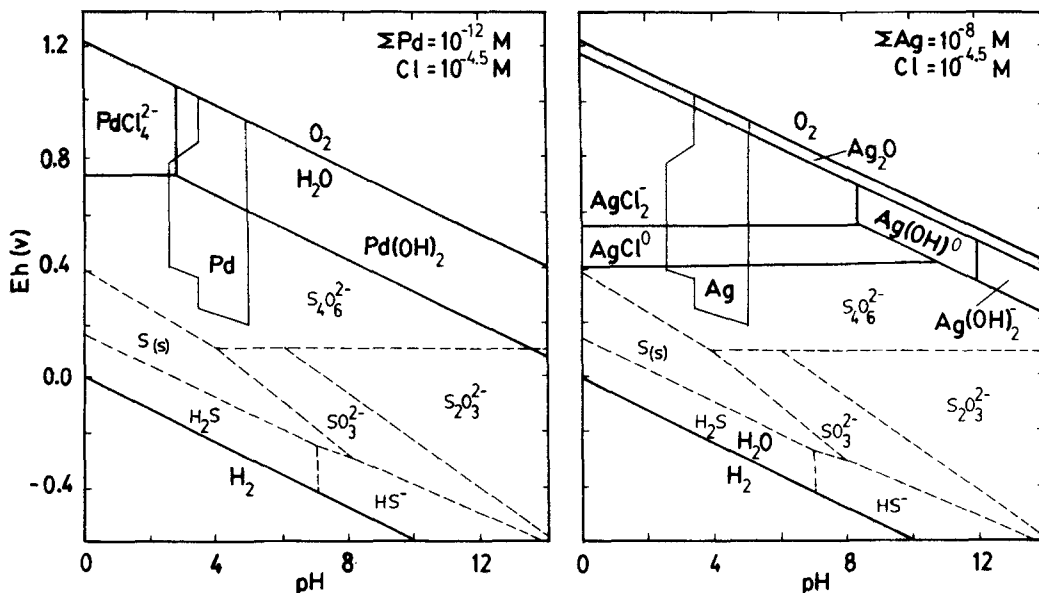


Fig. 2 Eh-pH diagrams for Pd-H₂O-Cl and Ag-H₂O-Cl systems at 25 °C and 1 atm. Heavy solid lines separate stability fields of Pd or Ag species. Upper and lower heavy solid lines define stability limits of H₂O. Light dashed lines separate fields of predominance of the sulphur species (Webster, 1986). Light solid lines show laterite field.

data of Baas Becking *et al.* (1960) and Mann (1984). Also shown in the diagram are the oxidation reactions of palladium and silver to form Pd(OH)₂ and Ag(OH)⁰, Ag(OH)₂⁻ and Ag₂O respectively. The solid phase of Pd(OH)₂ has been used due to the lack of thermodynamic data of aqueous Pd(OH)₂. Stability fields of sulphur species are also shown in the diagrams. From the diagrams it can be seen that under oxidizing conditions both silver and palladium can be leached away from laterite as chloride complexes. Silver is more easily leached out than palladium. Under lower redox potentials, however, both palladium and silver are stable in a lateritic environment. Such an environment may exist at the top of the profiles due to the abundant organic matter in the topsoil, which can lower the redox potentials.

In conclusions the silver-palladium alloy is a secondary mineral precipitated during lateritisation. The oxidation of sulphides of the parent rocks probably favoured the migration of palladium and silver as transient thiosulphate and sulphite complexes. Destruction of the thiosulphate and sulphite ions could account for the precipitation of both palladium and silver. Eh-pH phase diagrams for Pd-H₂O-Cl and Ag-H₂O-Cl systems show that both palladium and silver are stable in lateritic environment under lower redox potentials. Such an environment may exist at the

top of ferruginous zone due to the abundant organic matter near the surface or biological activities. High rainfall in this area prevents high chloride concentrations in ground water which could leach the alloy.

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