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THERMODYNAMIC AND TEXTURAL EVIDENCE FOR AT LEAST TWO STAGES OF Au–Pd MINERALIZATION AT THE CAUÊ IRON MINE, ITABIRA DISTRICT, BRAZIL

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ABSTRACT

The Cauê mine, in the Itabira District of Brazil, contains a unique precious-metal-bearing mineral assemblage that includes palladian gold, pure gold, native palladium, palladseite, arsenopalladinite and palladium–copper oxide minerals. Thermodynamic calculations indicate that some of these phases are out of equilibrium with each other, and therefore cannot be cogenetic. At least two mineralizing events are required to explain the textures and paragenesis of the Cauê deposits. The main mineralizing event occurred during, or prior to, regional Transamazonian orogenesis, whereas the later event was probably related to more recent weathering of the hypogene ore. Minerals that formed during the main ore-forming episode include palladian gold, palladseite and arsenopalladinite. Textural evidence suggests that this event was synchronous with the *D*1 deformation. The precious metals were most likely transported as chloride complexes by high-temperature brines, and deposited as a result of changes in pH or $f(O_2)$ (or both) accompanying interaction of ore fluids with dolomitic iron-formation. In contrast, thermodynamic and textural relationships involving palladium oxide, pure gold and pure palladium indicate that these minerals could not have survived regional metamorphism, and were more likely formed during recent weathering of the primary hypogene ore. Weathering also resulted in leaching of selenium from the rock, with possible remobilization of palladium and gold as simple hydroxy complexes.

Keywords: gold, palladium, iron formation, *jacutinga*, weathering, Cauê, Itabira, Brazil.

SOMMAIRE

La mine de Cauê, du district d'Itabira, au Brésil, possède un assemblage unique de minéraux de métaux précieux, comprenant l'or palladifère, l'or pur, le palladium natif, la palladséite, l'arsénopalladinite et les oxydes de palladium et cuivre. Les calculs thermodynamiques indiquent que certains de ces minéraux ne sont pas en équilibre entre eux et, par conséquent, ne peuvent être cogénétiques. Au moins deux événements minéralisateurs sont nécessaires pour expliquer les textures et assemblages du gisement de Cauê. L'événement minéralisateur principal a eu lieu pendant ou avant l'orogenèse transamazonienne, alors que l'événement tardif est probablement associé à la météorisation plus récente. Les minéraux formés pendant l'épisode principal sont l'or palladifère, la palladséite et l'arsénopalladinite. D'après les textures, cet événement serait contemporain de la déformation *D*1. Les métaux précieux ont probablement été transportés sous forme de complexes chlorurés par des saumures à hautes températures. Leur déposition serait liée à un changement de pH ou $f(O_2)$ (ou des deux) dû à la réaction entre les fluides minéralisateurs et la formation de fer dolomitique encaissante. Par contre, les relations thermodynamiques et les textures impliquant l'oxyde de palladium, l'or pur et le palladium pur indiquent que ces minéraux n'ont pu survivre au métamorphisme régional et ont probablement été formés pendant la météorisation des minéraux primaires hypogènes. La météorisation a provoqué le lessivage du sélénium de la *jacutinga*, avec une possible remobilisation de l'or et du palladium sous forme de complexes hydroxylés.

Mots-clés: or, palladium, formation de fer, *jacutinga*, météorisation, Cauê, Itabira, Brésil.

INTRODUCTION

An unusual palladium-bearing gold deposit is being exploited at the Cauê iron mine, located in the Itabira District, southern São Francisco Craton, Minas Gerais, Brazil. Gold ore reserves in the entire Itabira District are estimated at 100,000 t grading 30 g/t Au (Leão de Sá & Borges 1991), and the annual production is approximately 500 kilograms of palladium-bearing gold bullion (Olivo *et al.* 1995). The Cauê deposit is one of five palladium-bearing gold deposits in the southern São Francisco craton that are hosted by Lake-Superior-type iron-formations within the Proterozoic Minas Supergroup.

The precious-metal deposit of the Cauê mine is hosted by *jacutinga*, a weathered, metamorphosed, and sheared oxide-facies iron-formation of the Minas Supergroup (Olivo *et al.* 1995). The main precious metal minerals are gold, palladian gold, and native palladium, as well as oxides, selenides, and arsenide–antimonides of palladium. All of these ore minerals were previously interpreted to have formed at high temperatures (up to 600°C) and high oxidation state (hematite stable), synchronous with shearing and regional metamorphic events (Olivo *et al.* 1994, 1995, Olivo & Gauthier 1995, Olivo *et al.* 1996). This interpretation was mainly based on textural data of the gold–palladium ore. However, weathering in the Cauê mine extends to a depth of more than 200 meters, and considerable evidence indicates that gold and the platinum-group elements can be mobile in surficial environments (*e.g.*, Mann 1984, Bowles 1986, Butt 1988, Lawrance 1988, Wood & Vlassopoulos 1990, Benedetti & Boulègue 1991, Wood, 1991, Zang *et al.* 1992, Bowell *et al.* 1993, Jedwab *et al.* 1993, Bowles *et al.* 1994, Augé & Legendre 1994, Jedwab 1994, 1995). Therefore, it is necessary to consider whether some or all of these minerals could have formed under near-surface conditions.

In this paper, we review the probable conditions of transport and deposition of gold and palladium minerals from the Cauê *jacutinga* based on thermodynamic calculations. We also discuss the chemical mobility of Pd and Au under conditions of weathering. Finally, we propose a multistage deposition-and-remobilization model to explain the mineralogy and textures of this deposit.

THE CAUÊ PALLADIUM-BEARING GOLD DEPOSIT

The geological setting of the Cauê deposit has been described by Olivo *et al.* (1995, 1996), and the ore mineralogy in the iron formation, by Olivo *et al.* (1994) and Olivo & Gauthier (1995). At the Cauê mine, the iron formation that hosts the Pd–Au deposits of interest is part of the Early Proterozoic Itabira Group, of the Minas Supergroup. This unit consists of itabirite, *jacutinga*, and massive hematite bodies. Itabirite is the most abundant facies, and is composed of alternating bands of quartz and hematite. *Jacutinga* is the auriferous iron-formation, and is described below. The iron-formation was affected by three phases of folding and thrust faulting (Olivo *et al.* 1995). Early *D*1 and *D*2 structures were generated by a progressive simple-shear regime with a transport direction consistently east-over-west. A later *D*3 event formed open folds with an associated crenulation cleavage. The iron formation is in thrust contact with the underlying Archean volcano-sedimentary sequence of the Rio das Velhas Supergroup and with the overlying quartzite unit of the Minas Supergroup. Slices of Archean amphibolite and talc schist are commonly imbricated into the iron-formation unit (Olivo *et al.* 1995, 1996).

The Cauê gold deposit comprises five small, disconnected orebodies, each of which is hosted by *jacutinga* (Olivo *et al.* 1995). The *jacutinga* horizons have a mineralogy that is distinct from the more widespread itabirite iron-formation. In addition to quartz + hematite ± magnetite, *jacutinga* contains abundant white phyllosilicates (talc or phlogopite + kaolinite) with minor tourmaline, apatite and monazite. Dorr & Barbosa (1963) and Olivo *et al.* (1995) have proposed that *jacutinga* represents dolomite-bearing itabirite that has subsequently been hydrothermally altered to an assemblage of oxide and silicate minerals.

The highest grades of palladium and gold occur in quartz veins (Corpo Y orebody) or in hematite veins with minor concentrations of quartz (Corpo X, Central and Aba Leste orebodies). Precious-metal ore also is found in bands of hematite or white phyllosilicate (talc, phlogopite and kaolinite) parallel to *S*1 foliation of *jacutinga* (Fig. 3 in Olivo *et al.* 1994). In the Corpo Y, Corpo X, Aba Leste, and Central orebodies, the auriferous veins are parallel to the *S*1 mylonitic foliation, are dismembered by the progressive high bulk-shear deformation, and are repeated by tight folds generated during the *D*2 progressive deformation (Olivo *et al.* 1995). In contrast to the other orebodies, gold at the Aba Norte deposit occurs in a boudinaged hematite vein parallel to *S*2, which cuts *S*1 and *S*0.

Although the occurrence of palladian gold in *jacutinga* was recognized as early as the 19th century in the southern São Francisco craton, as referred by Hussak (1906) and Bensusan (1929), the textures and compositions of this mineral were only recently described by Olivo *et al.* (1994) at the Cauê mine (Table 1, Fig. 1A). In addition to palladian gold, pure gold crystals were found in the Aba Leste orebody. Pure gold also occurs at Corpo Y in the kaolinite-rich bands (Fig. 1B) or as late coatings surrounding palladium minerals (Figs. 1C, D).

In the Itabira region, Pd-bearing minerals other than palladian gold were previously described by Clark *et al.* (1974), who examined concentrates of residual minerals produced during the washing of the gold ore. They found arsenopalladinite, isomertieite [$(Pd,Cu)_5(Sb,As)_2$], atheneite [$(Pd,Hg)_3As$], palladium–mercury oxide, and a palladium selenide, later identified as palladseite by Davis *et al.* (1977). More recently, Jedwab *et al.* (1993) and Jedwab (1995) reported the presence of palladinite (palladium oxide), isomertieite and gold grains containing inclusions of Pt–Fe and Pd–Fe oxides in the concentrates obtained from the tailings of the Cauê iron mine. Although interesting, it is impossible to reconstruct the paragenesis of these mineral occurrences, as the original textures and relationships with the surrounding rocks have been destroyed. In contrast, Olivo & Gauthier (1995) have described the *in situ* occurrence of palladseite, arsenopalladinite, palladium, and palladium oxide from *jacutinga* at the Cauê mine (Figs. 1B–D, Table 1).

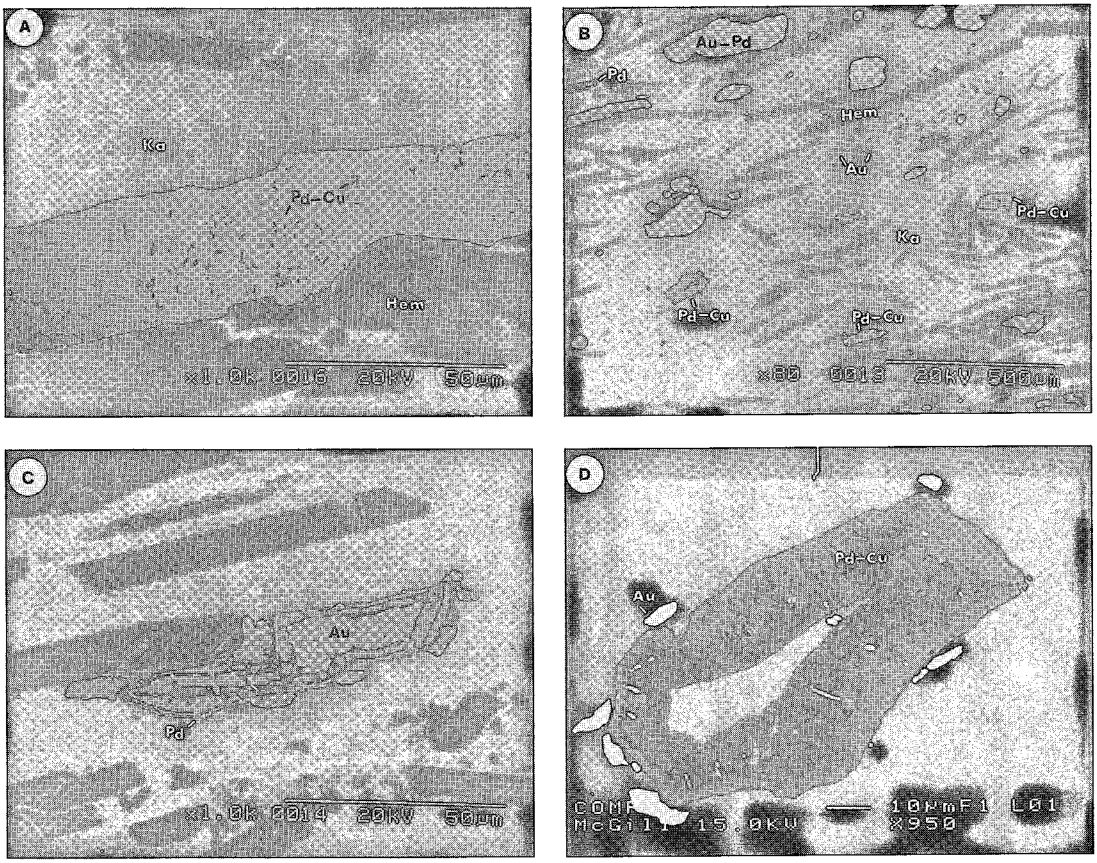


FIG. 1. A. Back-scattered electron image showing a grain of gold, elongate parallel to $S1$ foliation, with inclusions of palladium–copper oxide (Pd–Cu) in *jacutinga* from Corpo Y orebody (Hem: hematite, Ka: kaolinite). B. Back-scattered electron image showing gold (Au), palladian gold (Au–Pd), native Pd (Pd) and Pd–Cu oxide (Pd–Cu) grains in kaolinite-rich band (Ka) in *jacutinga* from Corpo Y orebody (Hem: hematite). C. Back-scattered electron image showing a grain of native palladium (Pd) coated with gold and with the corroded interior replaced by pure gold (Au), in *jacutinga* from Corpo Y. D. Back-scattered electron image showing a zoned palladium–copper oxide (Pd–Cu) with inclusions of gold (Au) in *jacutinga* from Corpo Y orebody. This grain was coated with gold, which was partially removed by repeated polishing.

ORE-MINERAL STABILITIES

In previous studies of the Cauê mine, Olivo and co-investigators have proposed that all of the palladium-bearing minerals present in the deposit could have formed in a single hydrothermal event ($D1$-shearing event). However, the following analysis of ore-mineral stabilities shows that some of these ore minerals are out of equilibrium with each other, and therefore cannot be cogenetic.

Pd–PdO

The temperature dependence of the Pd–PdO redox boundary, along with some other important redox buffers, is summarized in Figure 2. High oxygen fugacities are required to stabilize PdO relative to pure metallic Pd, and these values increase with increase in temperature (*e.g.*, $\sim 10^{-30}$ bars at 25°C to $\sim 10^{-2}$ bars at 600°C). Whereas the Pd–PdO boundary was calculated assuming pure mineral compositions, both phases at the Cauê mine contain significant impurities (Table 1). However, because these effects are mutually offsetting, the position of the Pd–PdO boundary in Figure 2 should not change significantly at the scale of the diagram. Oxygen fugacities in the Cauê hydrothermal fluids were most likely buffered by the hematite–magnetite pair at 600°C (below 10^{-10} bars; Olivo *et al.* 1994) and under these conditions, PdO could not be stable. In contrast, at low temperature, any fluid that equilibrated with atmospheric oxygen [equilibrium $f(O_2) \approx 0.2$ bars] would lie well within the PdO stability field, suggesting that PdO at the Cauê mine probably formed at low temperature by interaction with near-surface waters, as discussed below.

TABLE 1. Pd–Au MINERALS FOUND IN SITU IN JACUTINGA FROM THE CAUÊ MINE

	Structures and textures	Compositions (in weight %)	References	Interpretation (this paper)
Palladian gold	This mineral occurs as free grains and as inclusions in tourmaline and quartz parallel to S1 mylonitic foliation; in the Corpo Y and Corpo X orebodies, these grains are commonly rich in Pd–Cu oxides; in the Aba Leste orebody, Au and Pd are homogeneously alloyed.	Au (78.5–99 %) Pd (1–19 %) Cu (up to 4.6%) Ag (up to 0.6%) Fe (up to 3.2%) Zn (up to 3%)	Olivo et al. (1994); Olivo et al. (1995)	Hypogene
Gold	This mineral occurs as fine grains in kaolinite-rich bands, or coating palladium minerals, or filling cavities in palladium grains.	Au (100%)	Olivo et al. (1995); this paper	Secondary
Arsenopalladinite ($Pd_8(As,Sb)_3$)	One grain recovered from disaggregated jacutinga (Corpo Y) exhibits alternating bands of palladium oxide and arsenopalladinite.	Pd (77.6%) As (17.1%) Sb (5.3%)	Olivo & Gauthier (1995)	Hypogene
Palladseite ($Pd_{17}Se_{15}$)	This mineral occurs in a core of a palladium grain that is coated with pure gold in the kaolinite–rich band (Corpo Y).	Pd (54.5–60.0%) Cu (2.5–3.0%) Hg (3.0–3.8%) Se (33.6–36.9%) Au (up to 0.1%) Fe (up to 0.7%)	Olivo & Gauthier (1995)	Hypogene
Palladium	Grains occur in quartz and kaolinite–rich bands (Corpo Y). These grains are coated with pure gold, and generally have corroded interiors, which are partially replaced by gold.	Pd (92.5%) Cu (1.31%) Au (1.98%) Fe (1.31%)	Olivo & Gauthier (1995)	Secondary
Pd–Cu oxide	This mineral occurs commonly as euhedral concentrically zoned grains in kaolinite–rich bands (Corpo Y).	Pd (73.1–79.8%) Cu (3.4–6.3%) Hg (up to 1.4%) Au (up to 0.6%)	Olivo & Gauthier (1995)	Secondary

Au–Pd

Okamoto & Massalski (1985), among others, have shown that the Au–Pd system forms a complete solid-solution at all temperatures up to the melting point of gold (1064°C). Although Pd and Au are commonly alloyed in the Cauê mine, grains of nearly pure gold and nearly pure palladium also have been found, in some cases in contact with each other. The occurrence of native palladium in contact with native gold is a disequilibrium texture because at any temperature below 1064°C, these metals should instead combine to form an alloy of intermediate composition. The main barrier to any such reaction is the rate of diffusion of Au and Pd within the solid phase. Whereas this rate is much too slow to allow any compositional changes at 25°C, the reverse is likely to be the case at temperatures corresponding to hydrothermal alteration and metamorphism in the Cauê area. For example, Gammons & Williams-Jones (1995a) have recently shown that grains of electrum (Au–Ag solid solution) will quickly homogenize during high-grade metamorphism (*e.g.*, <1 to >100 years at 600°C, depending on the grain size). Although no data were found for diffusion rates in the Au–Pd system, they are unlikely to be much different than for Au–Ag, since all three metals have similar atomic radii (in the range 1.75 to 1.79 Å) and a similar *fcc* crystal structure. Even if complete homogenization did not occur, diffusion gradients would surely be found near any palladium–gold contact. Instead, the grains observed from the Cauê mine have sharp compositional boundaries, indicating that negligible diffusion has occurred. Therefore, the pure gold and palladium grains could not have precipitated together, in contact, during (or before) peak metamorphism, but were more likely the result of low-temperature processes, as discussed below.

Pd–$Pd_{17}Se_{15}$

Published phase relationships in the Pd–Se system (Okamoto 1992) indicate that pure palladium and palladseite ($Pd_{17}Se_{15}$) are out of equilibrium at all temperatures and are separated by several Pd-selenide phases of intermediate composition (Pd_4Se, Pd_7Se_2, Pd_3Se_{11}, Pd_7Se_4) or Pd–Se melt ($T > 385°C$). At the Cauê mine, a grain of native palladium was found that completely encloses a smaller grain of palladseite ($Pd_{17}Se_{15}$). It is therefore obvious that: 1) native palladium and palladseite could not have formed at the same time, and 2) that the texture in question could not have survived a prograde metamorphic event.

On the basis of the above observations, it is clear

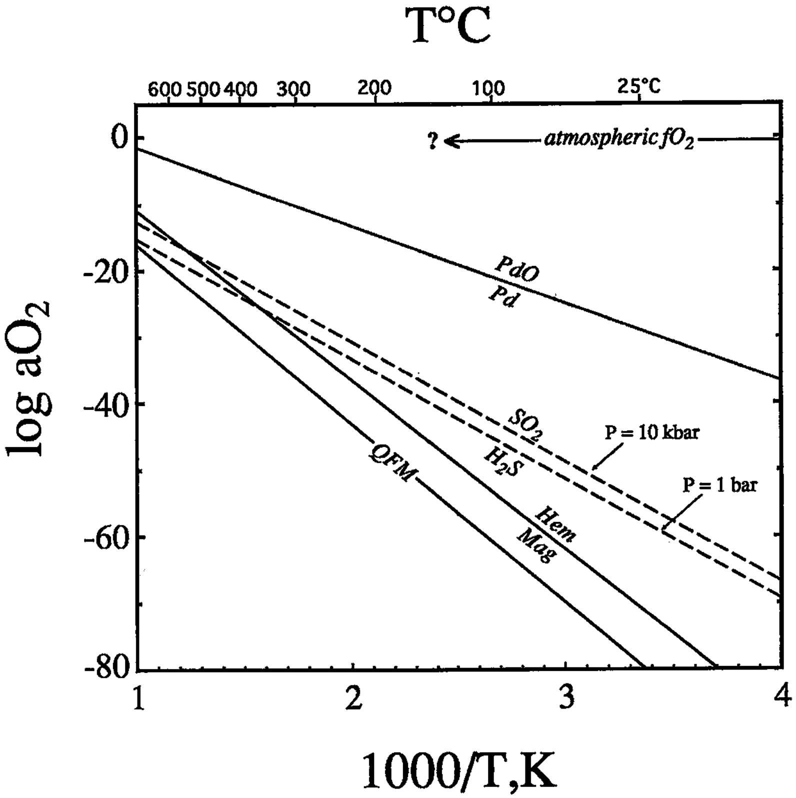


FIG. 2. Temperature dependence of the Pd–PdO redox boundary, along with some other important redox buffers. The diagram illustrates that PdO is not stable under the reducing conditions typical of high temperature metamorphic environments, as represented by the SO_2–H_2S, Hem–Mag (hematite – magnetite) and QFM (quartz – fayalite – magnetite) buffers. In contrast, PdO will be stable relative to Pd in oxygenated, near-surface waters. Thermodynamic data for the Pd–PdO boundary were taken from Mallika *et al.* (1983). Data for QFM and Hem–Mag are from Barton & Skinner (1979). Data for SO_2–H_2S are from Robie *et al.* (1979), and have been contoured for 1 bar and 1 kbar.

that at least two mineralizing events are required to explain the textures and paragenesis of the Cauê mine. The first event, during which the bulk of the precious metals was introduced, may have occurred synchronously with *D*1 deformation. The second event happened much later, probably during recent weathering or possibly during an episode of low-temperature alteration. These ideas are expanded in the following sections.

MAIN MINERALIZING EVENT

In previous studies, Olivo and co-investigators have proposed that the main mineralizing event at the Cauê mine occurred synchronously with development of the *S*1 mylonitic foliation and associated *D*1 structures, and that this deformation was roughly coincident with peak thermal metamorphism (Olivo *et al.* 1994, 1995). This interpretation is supported by the fact that the orebody geometries as a whole have been strongly deformed by progressive shear (Olivo *et al.* 1995). It is also consistent with certain ore-mineral textures, including: (1) grains of palladian gold that occur as isolated minerals or as inclusions within syn-*D*1 tourmaline in the core of dismembered sheath folds, (2) grains of palladian gold that are elongate parallel to the elongation lineation, and (3) grains of palladian gold enclosed by quartz veins, which are themselves stretched parallel to the elongation lineation in the plane of the *S*1 mylonitic foliation (Olivo *et al.* 1994). Oxygen isotopic studies of quartz–hematite pairs parallel to *S*1 yield temperatures appropriate for the regional Transamazonian orogenic event in this part of the craton (610°C; Hoefs *et al.* 1982). As well, Pb–Pb isotopic results obtained from quartz, palladian gold and specular hematite parallel to *S*1 yield an age of 1.83 ± 0.10 Ga, which also corresponds to the Transamazonian event (Olivo *et al.* 1996).

Two contrasting types of fluids are needed to explain the introduction of gold and palladium during the main mineralizing event, depending on whether the precious metals were mobilized as chloride or bisulfide complexes. To stabilize bisulfide complexes, the ore fluid should have been reduced, H_2S-rich and near-neutral (Gammons & Bloom 1993, Pan & Wood 1994). However, this seems very unlikely, given the complete absence of sulfide minerals in both itabirite and *jacutinga* in the Cauê area (Bensusan 1929, Dorr & Barbosa 1963, Guimarães 1970, Schorscher *et al.* 1982, Leão de Sá & Borges 1991, Olivo *et al.* 1995). Although it may be argued that sulfide minerals may have been lost during prograde devolatilization reactions, Olivo *et al.* (1995) have shown that sulfides are well preserved in adjacent Archean mafic rocks, all of which have been subjected to the same peak metamorphic conditions.

For chloride complexes to dominate, the ore fluid should have been hot, acidic, oxidized, and highly saline (Gammons *et al.* 1992, Gammons & Williams-Jones 1995b). This is consistent with the model of Olivo *et al.* (1995), who proposed that palladium and gold were mobilized during the *D*1 shear event as chloride complexes under moderately oxidizing conditions (hematite-stable), and then deposited within *jacutinga* horizons owing to the presence of dolomite in the protolith of this rock type. Fluid–rock interaction would have dissolved dolomite and replaced it by talc and phlogopite, resulting in an increase in solution pH and subsequent deposition of precious metals. Although we have no fluid-inclusion data to estimate the salinity of the paleo-ore fluids, circumstantial evidence suggests that brines were present in the region prior to the regional orogeny. For example, in the Quadrilátero Ferrífero, southern São Francisco Craton, gold at the Ouro Preto, Passagem and Morro de Santana mines is hosted by a tourmalinite layer near the base of the Minas Supergroup iron-formation unit (Fleischer & Routhier 1973, Ladeira 1991). The origin of this tourmalinite has been explained by greenschist-facies metamorphism in the presence of a B-rich, connate brine (Fleischer & Routhier 1973). Assuming that this brine-rich layer was also present in the Cauê area, high-salinity fluids may have been mobilized, along with precious metals, during high-grade metamorphism.

It has been proposed that oxidized, saline fluids introduced precious metals as chloride complexes at the Coronation Hill U–Au–Pd–Pt deposit of the Northern Territories, Australia (temperature of formation ~150–200°C; Bloom *et al.* 1992, Mernagh *et al.* 1994). Similar Au–PGE occurrences have been described in the south Devon area of England (temperature of formation ~100°C; Leake *et al.* 1991). At Coronation Hill, the ore is hosted by weakly deformed and metamorphosed sediments of early Proterozoic age that unconformably overly highly deformed and metamorphosed gneiss, schists and metavolcanic rocks of Archean age. The main ore minerals include electrum, native palladium, palladium antimonides, and palladium selenides (including palladseite) (Mernagh *et al.* 1994).

Considering the similarities between the geological setting and ore mineralogy at the Coronation Hill and Cauê deposits, the possibility that the main mineralizing event at Cauê was *pre*-metamorphic must also be addressed. It is possible that much of the gold and palladium at the Cauê mine was introduced during an early event in which migrating basinal brines within the Proterozoic Minas Supergroup encountered horizons of dolomite-bearing itabirite and precipitated metals owing to changes in pH or $f(O_2)$ (or both). This model differs from that proposed by Olivo *et al.* (1995) only in the timing of ore deposition relative to regional metamorphism. In fact, it is impossible to differentiate between a pre- or synmetamorphic origin for Au–Pd mineralization at the Cauê mine, on the basis of the evidence in hand. Amphibolite-grade metamorphism and deformation would likely have destroyed any textural evidence that the ore was of low-temperature origin, and would also have reset the oxygen and lead isotopic fingerprints. In addition, some remobilization of metals and other components may have occurred during deformation, which could explain certain textures, such as inclusions of Pd-bearing gold within syntectonic tourmaline (Olivo *et al.* 1994, 1995). Metamorphic remobilization, if it occurred, could well have contributed to the very high grade of the Cauê deposits, which average 30 g/t of gold.

EFFECTS OF WEATHERING

The Cauê Au–Pd deposits have been intensely weathered (Olivo *et al.* 1995). The main secondary minerals in *jacutinga* are goethite and kaolinite, the former replacing hematite and magnetite, and the latter replacing talc, phlogopite, and K-feldspar (Fig. 1B). Dissolution of quartz grains also is evident, especially along grain contacts (Fig. 12C in Olivo *et al.* 1995). Open space is partially filled with secondary kaolinite, resulting in a friable rock. On the basis of the earlier discussion of ore-mineral stabilities, it is clear that weathering has also resulted in some redistribution of precious metals within each orebody, which led to new phases such as pure gold, pure palladium and Pd–Cu oxides. To better understand these processes, $f(O_2)$–pH diagrams have been constructed for the Se–H_2O, Au–Se–Cl–H_2O, and Pd–Se–Cl–H_2O systems at 25°C (Figs. 3 to 5). Thermodynamic data used to construct these diagrams are summarized in Table 2.

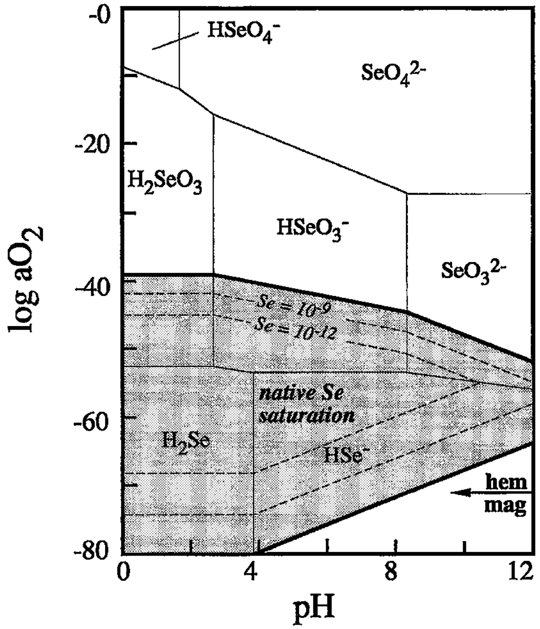
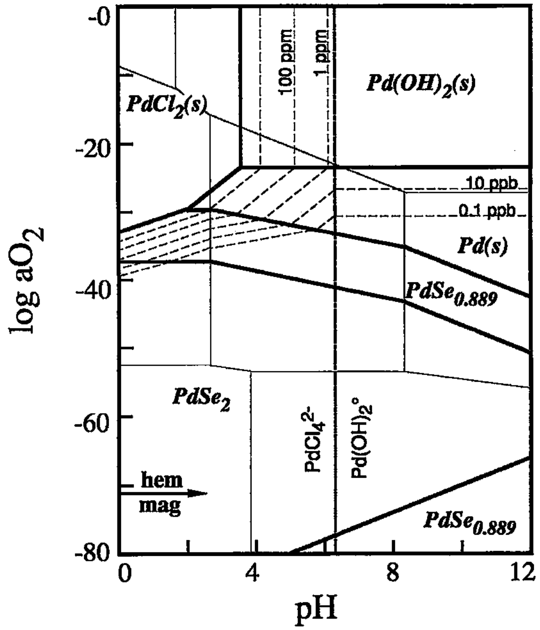


FIG. 3. Log $f(O_2)$–pH diagram summarizing the distribution of aqueous selenium-bearing species at 25°C, 1 bar. The shaded region shows the field of saturation with selenium metal, assuming a total aqueous Se concentration of 10^{-6} molal. Solubility contours are also shown for 10^{-9} and 10^{-12} molal ΣSe_{aq}. The arrow shows the approximate location of the hematite–magnetite redox boundary. Thermodynamic data used to construct this diagram, as well as Figures 4 and 5, are summarized in Table 1.



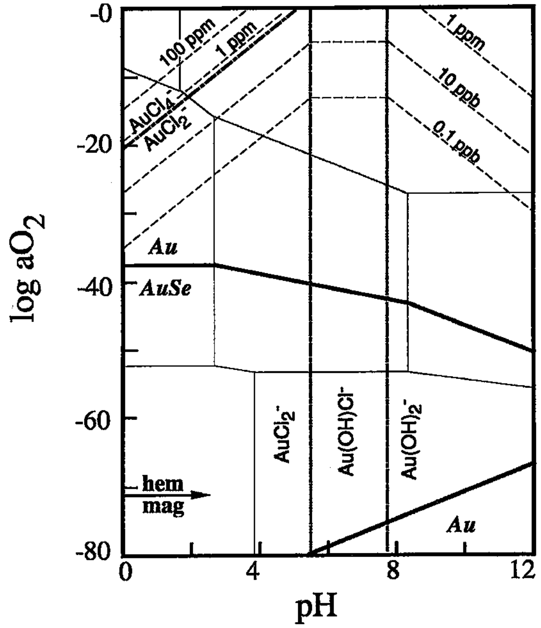


FIG. 5. Log $f(O_2)$–pH diagram summarizing the mineralogy, solubility, and aqueous speciation of gold at 25°C, 1 bar. See captions to Figures 3 and 4 for more details.

FIG. 4. Log $f(O_2)$–pH diagram summarizing the mineralogy, solubility, and aqueous speciation of palladium at 25°C, 1 bar. The activities of Cl^- ion and total aqueous selenium are fixed at 0.1 and 10^{-6} molal, respectively. Sulfur is not included in the diagram, for simplicity. Boundaries between solids are shown by bold solid lines, and between aqueous palladium species by bold dashed lines. Isoactivity boundaries for aqueous selenium species (unlabeled) are given by thin solid lines. Metal solubility contours are shown by thin dashed lines, and are labeled in ppm (mg/kg) or ppb (µg/kg) units. See Figure 3 for more details.

TABLE 2. SELECTED THERMODYNAMIC DATA (25°C, 1 bar)

species [a]	ΔG°f, kJ·mol^{-1}	source [b]	species [a]	ΔG°f, kJ·mol^{-1}	source
Pd(s)	0.0	-	Se(s)	0.0	-
$PdSe_2$(s)	-59.0	1,2	$H_2Se°$	+22.2	12
$PdSe_{.889}$(s)	-46.4	1,2	HSe^-	+43.9	"
Pd^{2+}	+176.6	3	$H_2SeO_3°$	-426.2	"
$PdCl_4^{2-}$	-418.8	4	$HSeO_3^-$	-411.3	"
$Pd(OH)_2°$	-272.8	5	SeO_3^{2-}	-363.6	"
$Pd(OH)_2$(s)	-303.3	6	$HSeO_4^-$	-450.9	"
$PdCl_2$(s)	-125.1	7	SeO_4^{2-}	-441.4	"
Au(s)	0.0	-	Cl^-	-131.3	13
AuSe(s)	-9.6	8	H_2O(l)	-237.1	"
$AuCl_4^-$	-235.1	8,9	OH^-	-157.3	"
$AuCl_2^-$	-151.0	8,9	H^+	0.0	-
$Au(OH)Cl^-$	-219.2	8,10	O_2(g)	0.0	-
$Au(OH)_2^-$	-276.1	8,11			

[a] All species are aqueous complexes unless otherwise stated. [b] Sources of data: [1] Mountain & Wood (1988); [2] Mills (1974); [3] calculated from log K = 10.6 for the reaction: $Pd + 2H^+ + 1/2O_2(g) = Pd^{2+} + H_2O$ (Wood et al. 1992); [4] calculated from log K = 12.33 for the reaction: $Pd^{2+} + 4Cl^- = PdCl_4^{2-}$ (Wood et al. 1992); [5] calculated from log K = +23.6 for the reaction: $Pd^{2+} + 2OH^- = Pd(OH)_2°$ (Nabivanets & Kalabina 1970); [6] calculated from log K = -5.36 for the reaction $Pd(OH)_2(s) = Pd(OH)_2°$ (Nabivanets & Kalabina 1970); [7] Wagman et al. (1982); [8] Shenberger (1985); [9] Nikolaeva et al. (1972); [10] Gadet & Pouradier (1972); [11] Baranova & Ryzhenko (1981); [12] D'Yachkova & Khodakovskiy (1968); [13] Cobble et al. (1982).

Ore oxidation

Figure 3 indicates that selenium is insoluble under reduced conditions, but is highly soluble in oxidized surface-waters as aqueous selenate (SeO_4^{2-}) or selenite ($HSeO_3^-$, SeO_3^{2-}). In the weathering environment, the stable solid form of palladium is either the native metal or the oxide, depending on $f(O_2)$ (Fig. 4). The following reactions describe the sequential oxidation of palladseite to palladium, and palladium to PdO:

$$\tfrac{1}{17}Pd_{17}Se_{15}(s) + \tfrac{45}{34}O_2(g) + \tfrac{15}{17}H_2O = Pd(s) + \tfrac{15}{17}SeO_4^{2-} + \tfrac{30}{17}H^+ \qquad (1)$$

$$Pd(s) + \tfrac{1}{2}O_2(g) = PdO(s) \qquad (2)$$

In the case of palladian gold, it is the Pd *component* in the Au–Pd alloy that is oxidized, rather than a pure palladium phase. Reaction (2) may be rewritten accordingly:

$$Pd_xAu_{1-x}(s) + \tfrac{x}{2}O_2(g) = xPdO(s) + (1-x)Au \qquad (3)$$

Reactions (1) to (3) help explain many of the textures summarized in Table 1 and in previous investigations of the Cauê deposits, including: (a) the presence of palladseite grains coated by pure palladium, (b) the presence of discrete grains of (Pd,Cu) oxide coated by pure gold, and (c) the presence of grains of palladium-bearing gold with inclusions of (Pd,Cu) oxides. The first texture is readily explained by reaction (1), and needs no further comment. The second texture can be explained either by the complete pseudomorphic replacement of Pd-bearing gold by PdO + Au (reaction 3), or by sequential precipitation of PdO, and then Au, from soil or groundwater. It is interesting to note that the larger grains of Pd–Cu oxide commonly show delicate compositional zoning. This may reflect replacement of an initially zoned precursor phase, or, more likely, could be due to oscillatory changes in groundwater chemistry (*e.g.*, in response to seasonal fluctuations in temperature or rainfall). Similarly zoned Pt–Fe oxides were recently described in alluvial concentrates from New Caledonia by Augé & Legendre (1994), who also favored a supergene origin for these unusual phases. The third texture can be explained by reaction 3, but only if O_2(g) is able to infiltrate into the interior of the Au–Pd grains. Selective dissolution of palladium during weathering (see below) from an initially homogeneous Au–Pd alloy is one possible mechanism for the generation of the required microporosity.

Solubility of gold and palladium

Figures 4 and 5 may be used to evaluate the solubility of palladium- and gold-bearing minerals under conditions of weathering. Both diagrams were drawn for a Cl^- activity of 0.1 molal. Although this value is almost certainly too high for groundwaters in the vicinity of the Cauê mine, it was chosen to emphasize a few points. Inspection of Figures 4 and 5 indicates that both Pd and Au are highly insoluble under reducing conditions, but that they become marginally soluble under strongly oxidizing conditions. In the case of palladium, a maximum solubility of close to 1 ppm is attained in the stability field of Pd-oxide or hydroxide as the hydroxy complex, $Pd(OH)_2^0$. Although much higher Pd solubilities are possible at lower pH as the chloride complex ($PdCl_4^{2-}$), this species will probably be unimportant at the lower salinities of soil and groundwaters at the Cauê mine. In the case of gold, solubilities of >10 ppb are possible at near-neutral pH as chloride or hydroxy-chloride complexes (Fig. 5). In the absence of chloride ions, gold mobility in the ppb range is still possible as the hydroxy complex, $Au(OH)_2^-$. It should be mentioned that the experimental data of Vlassopoulos & Wood (1990) would predict much higher solubilities of gold as hydroxy complexes (>1,000 ppm for air-saturated water at neutral pH). However, the validity of these data has been questioned (Krupp & Weiser 1992), and they were therefore not used in the present study. Other complexes of gold and palladium (*e.g.*, with cyanide, organic acids or sulfur species) could further enhance metal solubility, if ligand concentrations were sufficiently high [see Wood *et al.* (1992), for a detailed discussion]. This is unlikely in the case of the sulfur species (polysulfide, thiosulfate), owing to the general absence of sulfide minerals in the *jacutinga* horizons at the Cauê mine.

On the basis of the above observations, we conclude that both palladium and gold may be mobilized in the weathering environment as simple hydroxy complexes by air-saturated water, but that these metals will quickly reprecipitate upon entering a more reducing environment. The controls on $f(O_2)$ in soil and weathered bedrock are extremely complicated, and are a sensitive function of variables such as rainfall, biological activity, diffusion of $O_2(g)$ and $H_2(g)$ through pore waters, and interaction of groundwaters with inorganic reductants such as magnetite and Fe-bearing silicate minerals. For this reason, it is difficult to predict the extent to which gold and palladium could be remobilized, and how far these metals would be dispersed. Metal dispersion would, in general, be augmented by surface topography, as this would result in the downslope advection of groundwater and (during rain events) soil water, along with their dissolved metals. In contrast, if topography is negligible (as at the Cauê mine), near-surface waters could locally remain saturated with phases such as PdO and Au for years, with minimal lateral dispersion. Significant redistribution of metals in a vertical direction could, however, be caused by seasonal fluctuations in rainfall or positioning of the water table. Secondary enrichment in metals (especially of palladium) is quite possible in this scenario.

CONCLUSIONS

A consideration of the textural relationships, experimental data and thermodynamic stability of mineral assemblages at the Cauê deposits indicates that many of the ore minerals are out of equilibrium with each other, and therefore could not have formed during a single event. Palladian gold, palladseite, and arsenopalladinite were most likely deposited during the main hypogene mineralizing event synchronous with *D*1 deformation, as supported by textural studies, Pb–Pb isotope relationships, and thermodynamic data. A model for this main-stage mineralization invokes transport of palladium and gold as chloride complexes by oxidized, saline brines. The mineralogy and textural relationships of the deposit were modified by more recent weathering of the *jacutinga* units. Selenium was leached from the rock, and new phases such as pure gold, native palladium, and palladium–copper oxide were formed. Remobilization of palladium and gold as simple hydroxide complexes probably occurred during weathering and lateritization, and may have locally increased the average grade of the deposit.

As is widely known, the interpretation of ore mineral textures is commonly prone to ambiguity. This study is just one example that shows how thermodynamics may be used, in combination with careful petrographic observations, to help unravel the paragenetic sequence of events of complexly mineralized orebodies.

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