ABSTRACT

The Caú 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 Caú 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 D1 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(O2) (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, Caú, Itabira, Brazil.

INTRODUCTION

An unusual palladium-bearing gold deposit is being exploited at the Caú 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 Caú 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 Caú 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 iron–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 D1 and D2 structures were generated by a progressive simple-shear regime with a transport direction consistently east-over-west. A later D3 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 t alc schist are commonly imbricated into the iron-formation unit (Olivo et al. 1995, 1996).
On Pd-MINERALIZATION

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., ~10⁻³⁰ bars at 25°C to ~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(O₂) = 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.
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–Pd17Se15

Published phase relationships in the Pd–Se system (Okamoto 1992) indicate that pure palladium and palladseite (Pd17Se15) are out of equilibrium at all temperatures and are separated by several Pd-selenide phases of intermediate composition (Pd2Se, Pd3Se2, Pd4Se11, Pd7Se4) 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 (Pd17Se15). 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...
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 D1 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 S1 mylonitic foliation and associated D1 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-D1 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 S1 mylonitic foliation (Olivo et al. 1994). Oxygen isotopic studies of quartz–hematite pairs parallel to S1 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

---

**Figure 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 SO₂–H₂S, 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 SO₂–H₂S are from Robie et al. (1979), and have been contoured for 1 bar and 1 kbar.
isotopic results obtained from quartz, palladian gold and specular hematite parallel to S1 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$_2$S-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, Schorsch 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 D1 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 palladsite) (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$_2$O, Au–Se–Cl–H$_2$O, and Pd–Se–Cl–H$_2$O 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 $\Sigma Se_{aq}$. 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. 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. Iso-activity 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.

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.
Ore oxidation

Figure 3 indicates that selenium is insoluble under reduced conditions, but is highly soluble in oxidized surface-water as aqueous selenate (SeO$_4^{2-}$) or selenite (HSO$_3^-$). 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 palladite to palladium, and palladium to PdO:

\[
\frac{1}{17} \text{Pd}_4\text{Se}_{15}(s) + \frac{45}{4} \text{O}_2(g) + \frac{15}{4} \text{H}_2\text{O} = \text{Pd}(s) + \frac{15}{17} \text{SeO}_3^{2-} + \frac{9}{17} \text{H}^+ \quad (1)
\]

\[
\text{Pd}(s) + \frac{1}{2} \text{O}_2(g) = \text{PdO}(s) \quad (2)
\]

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:

\[
\text{Pd}_{x}\text{Au}_{1-x}(s) + \frac{1}{2} \text{O}_2(g) = x\text{PdO}(s) + (1-x)\text{Au} \quad (3)
\]

Reactions (1) to (3) help explain many of the textures summarized in Table 1 and in previous investigations of the Cauè deposits, including: (a) the presence of palladite 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 Cauè 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)$_3$$_2$. Although much higher Pd solubilities are possible at lower pH as the chloride complex (PdCl$_2^-$), this species will probably be unimportant at the lower salinities of soil and groundwaters at the Cauè mine. In the case of gold, solubilities of >10 ppb are possible at near-neutral pH as chloride or hydroxy-chloride complexes (Fig. 5). In the absence of chloride ions, gold mobility in the ppb range is still possible as the hydroxy complex, Au(OH)$_3$. 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 Cauè mine.

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### Table 2. Selected Thermodynamic Data (25°C, 1 bar)

<table>
<thead>
<tr>
<th>Species $^a$</th>
<th>$\Delta G^0_{298}$, kJ·mol$^{-1}$</th>
<th>Source $^b$</th>
<th>Species $^a$</th>
<th>$\Delta G^0_{298}$, kJ·mol$^{-1}$</th>
<th>Source $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(s)</td>
<td>0.0</td>
<td>-</td>
<td>Se(s)</td>
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<td>-</td>
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<td>Pd(Se)</td>
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<td>HgSe</td>
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<td>12</td>
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<tr>
<td>Pd(Se)$_3$</td>
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<td>1.2</td>
<td>HgSe</td>
<td>$+43.9$</td>
<td>12</td>
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<td>PdO</td>
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<td>3</td>
<td>HgSe$_2$</td>
<td>$-426.2$</td>
<td>1</td>
</tr>
<tr>
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<td>1</td>
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<td>5</td>
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<td>1</td>
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<td>Pd(OH)$_2$(s)</td>
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<td>AuSe(s)</td>
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<td>$-237.1$</td>
<td>-</td>
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<td>AuCl$_2^-$</td>
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<td>Off</td>
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<td>SeO$_3^2-$</td>
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<td>Au(OH)$_2^-$</td>
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<td>8.11</td>
<td>SeO$_4^{2-}$</td>
<td>$-237.1$</td>
<td>-</td>
</tr>
</tbody>
</table>

On the basis of the above observations, we conclude that both palladium and gold may be mobilized in the weathering environment as simple hydroxyl complexes by air-saturated water, but that these metals will quickly reprecipitate upon entering a more reducing environment. The controls on f(O₂) in soil and weathered bedrock are extremely complicated, and are a sensitive function of variables such as rainfall, biological activity, diffusion of O₂(g) and H₂O(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. Palladiun gold, palladaseite, and arsenopalladinite were most likely deposited during the main hypogene mineralizing event synchronous with D1 deformation, as supported by textural studies, Pb–Pb isotope relationships, and thermodynamic data. A model for this main-stage mineralization involves 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 thermodynamic 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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