БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 43 • SOFIA • 2005

Au-Ag-Te-Se deposits
IGCP Project 486, 2005 Field Workshop, Kiten, Bulgaria, 14-19 September 2005

S/Se ratios in palladiferous gold coexisting with palladseite, Cauê iron ore deposit, Itabira district, Quadrilátero Ferrífero of Minas Gerais, Brazil

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Abstract. Selenium and sulphur contents in palladiferous gold coexisting with palladseite from hematitic, Au–Pd–Pt-bearing veins hosted by itabirite at the Cauê iron ore deposit, Itabira district, Minas Gerais, Brazil, indicate S/Se ratios of >1. Sulphur, at concentrations of a few hundred ppm, is present in solid solution within palladiferous gold. Oxidising conditions, i.e., sulphate >> reduced sulphur species, prevented sulphur from forming sulphide minerals, but led it to be partitioned into palladseite and, subordinately, palladiferous gold. In the absence of sulphide minerals, sulphur as a trace element in gold should reflect highly oxidising conditions of the fluid system.

Key words: S/Se ratios, palladiferous gold, palladseite, *jacutinga* veins, Cauê iron ore deposit, Itabira district, Quadrilátero Ferrífero, Minas Gerais, Brazil

Introduction

Little is known about the distribution of selenium and sulphur in native gold. Apparently, native gold has not routinely been analysed for selenium and sulphur, even in microanalytical trace element investigations using the proton microprobe (e.g., Maetz et al., 1997). As a result, ratios of S/Se in native gold and their applicability to ore genesis and provenance studies (*cf.* Hattori et al., 2004) have not been assessed.

Sporadic descriptions suggest that gold *per se* may have S/Se ratios that reflect the redox conditions of the fluid system from which it derived. Selenium contents of up to 4.5 wt.% in native gold have recently been reported from Au–Se deposits in the western Qinling Mountains, China (Liu et al., 2000). At the Serra Pelada bonanza-style Au–Pd–Pt deposit, northern Brazil (Carajás), palladiferous gold hosts occasional inclusions of seleniferous minerals of palladium with and without platinum (Cabral et al., 2002a, b). Both deposits possibly formed under oxidising conditions where sulphate was stable. Another palladiferous gold bearing mineralization characterised by high oxidation state is located at the Cauê hematite deposit in the Quadrilátero Ferrífero, Minas Gerais, Brazil. At Cauê, part of its palladiferous gold coexists with palladseite, a Cu–Hg-bearing selenide of palladium (Davis et al., 1977; Olivo and Gauthier, 1995; Cabral et al., 2002c).

In this contribution, we report preliminary results of an electron-microprobe study on the distribution of selenium and sulphur in palladiferous gold coexisting with palladseite from Cauê. The study further documents the remarkably high ratios of Pd/Ag and discusses the possible application of the S/Se ratio as a palaeo-redox indicator in bonanza-style gold deposits.

Geological setting and palladiferous gold-bearing veins

Cauê is the northernmost hematite deposit of the Itabira district, situated in the north-eastern part of the Quadrilátero Ferrífero. A location map can be found elsewhere (e.g., Rosière and Rios, 2004). The world-class Itabira district consists of iron ore deposits hosted by the Itabira iron formation of Harder and Chamberlin (1915), later designated as the Itabira Group (Dorr, 1969). The Palaeoproterozic Itabira Group comprises a lower itabirite unit, the Cauê Formation, and a conformably overlying unit of carbonate rocks, the Gandarela Formation. The Itabira Group defines a major chemical sequence within the clastic Minas Supergroup, which unconformably rests upon Archaean greenstone rocks of the Rio das Velhas Supergroup.

Two main deformational events affected the Quadrilátero Ferrífero: (i) the 2.1–2.0 Ga Transamazonian orogeny, with regional folding and uplifting of gneissic domes; and (ii) the 0.8–0.6 Ga Brasiliano thrust belt (e.g., Chemale et al., 1994). This west-verging thrust belt resulted in a deformational gradient, from predominantly low-strain brittle faulting in the western part of the Quadrilátero Ferrífero, to high-strain ductile shearing eastward (Rosière and Rios, 2004). The Itabira district is located in the eastern high-strain domain, where a pervasive tectonic foliation, defined by the planar arrangement of hematite in itabirites and iron ores, is ascribed to the Brasiliano orogeny (Alkmim and Marshak, 1998; Rosière and Rios, 2004).

Regional metamorphism ranges from greenschist facies in the western and central parts of the Quadrilátero Ferrífero to almandine-amphibolite facies eastward (Pires, 1995). The Itabira district displays metamorphic mineral assemblages of upper greenschist–lower amphibolite facies (Dorr and Barbosa, 1963; Pires, 1995), with $\delta^{18}O$ values of quartz–iron oxide pairs indicating metamorphic temperatures ranging from 408 to 660°C (Hoefs et al., 1982).

Jacutinga veins

Jacutinga is the local designation for auriferous veins hosted by itabirites of the Itabira iron formation. These crosscutting veins consist essentially of specular hematite with variable amounts of quartz and subordinate kaolinite, talc, limonite and manganese oxide (Henwood, 1871; Hussak, 1904). Gold is typically palladiferous (Hussak, 1904) and occurs as nuggets and threads (Henwood, 1871). Much of the gold extracted from the area around the baroque village of Ouro Preto is presumed to have come from *jacutinga* veins, whose gold is peculiarly black. Such *ouro preto* (black gold) is characterised by a dark coating of iron oxides and, distinctively, Pd–O species on palladiferous gold (e.g., Cabral et al., 2003).

The *jacutinga* veins from the Itabira district were described by Olivo and Gauthier (1995) as orebodies parallel to the itabirite tectonic foliation and, therefore, coeval with peak metamorphic conditions at about 660°C (Hoefs et al., 1982). A late Transamazonian age of 1.83 ± 0.10 Ga was attributed to *jacutinga* mineralisation sampled at Cauê (Olivo et al., 1996), but this age has a large error with a MSWD of 7.55 in the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram. The lead isotopic data come in part from mixed populations of old martite (hematite pseudomorph after magnetite) and specular hematite from both the host itabirite and *jacutinga*, and should reflect an inheritance from old martite. These data also show that samples with the most radiogenic lead fall below the 1.83 Ga reference isochron, a fact that indicates disturbance of the lead isotope systematics during a younger event. On the other hand, detailed mapping by mine geologists has demonstrated that the *jacutinga* veins truncate the tectonic foliation (Galbiatti 1999). Because this pervasive foliation is considered to have been generated during the ductile phase of the 0.8–0.6 Ga Brasiliano orogeny (e.g., Rosière and Rios, 2004), the cross-cutting relationships suggest a late Brasiliano age for the Cauê *jacutinga* veins.

Sample material and analytical technique

Auriferous aggregates of fine-grained massive magnetite were sampled from hematitic (*jacutinga*) veins at the Cauê opencast. They represent fragments from the wall-rock (itabirite) within the veins. Palladiferous gold and palladseite occur (i) as inclusions in coarse-grained, chaotically dispersed laths of hematite and (ii) in the interstices of the fine-grained magnetite matrix (Cabral et al., 2002c). Magnetite has chromium contents of up to 7.5 wt.%, and is extensively oxidised to hematite (martite). Palladseite is invariably rimmed by a dark grey Pd–O halo. Electron microprobe analyses of palladiferous gold and palladseite found in massive magnetite fragments are published elsewhere (Cabral et al., 2002c).

Electron-microprobe analyses for trace elements in palladiferous gold were performed under 15 kV and 100 nA using a Cameca SX100 at the Laboratoire de Microanalyse, Université Laval, Canada. The beam size was set at 2 µm and counting times were 20–40 s and 0–10 s on peak and background, respectively. Standards and X-ray lines were as follows: chalcopyrite (Cu*K*α), pyrite (S*K*α), G4PdS (Pd*L*α), pure metal (Ag*L*β) and $Se_{90}As_{10}$ (Se*L*α). Under these analytical conditions, the detection limits were 28 ppm for sulphur, 55 ppm for selenium, 168 ppm for silver, 176 ppm for palladium and 360 ppm for copper.

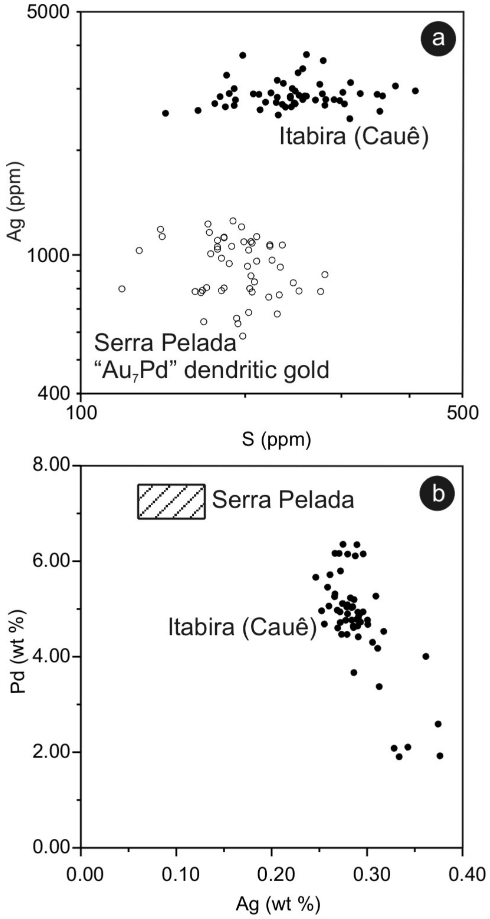

Fig. 1. Diagrams of (a) S vs. Ag and (b) Ag vs. Pd in palladiferous gold coexisting with palladseite from Cauê, Itabira district (black dots). Data from the Serra Pelada "Au_7Pd" palladiferous gold are shown for comparison (Cabral et al., 2002a, b, in press)

Results

Fifty-seven microanalyses on forty-nine crystals of gold adjacent to, or in contact with, palladseite assayed 1.91–6.35 wt.% Pd, <360–11,226 ppm Cu, 2,462–3,763 ppm Ag, 143–410 ppm S and <55–126 ppm Se. Most

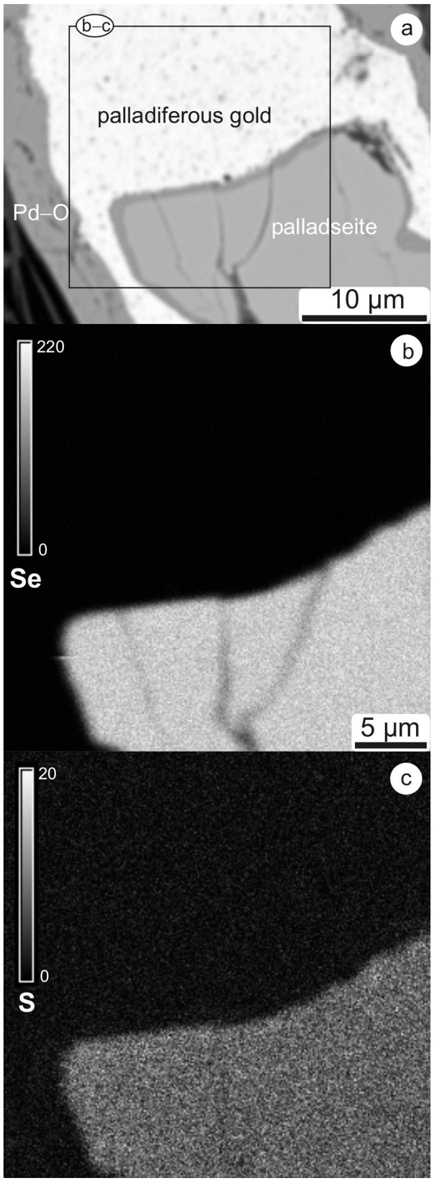

Fig. 2. (a) Back-scattered electron image of palladiferous gold in contact with palladseite, which is partially oxidised to a Pd–O phase. X-ray mapping for selenium (b) and sulphur (c)

microanalyses (n = 44) were below the detection limit for selenium (55 ppm), indicating S/Se ratios of >1. Sulphur has no correlation with silver (Fig. 1a) or any other element analysed. Silver shows a broad negative correlation with palladium (Fig. 1b). The Pd/Ag ratios range from 5 to 23. For comparison, data from Serra Pelada palladiferous gold are also plotted in Fig. 1.

X-ray mapping for selenium and sulphur in gold that is in contact with palladseite (Fig. 2a) indicates that selenium was fractionated into selenide (palladseite), leaving no traces (detectable by the electron microprobe) in the adjoining gold (Fig. 2b). Sulphur, though preferentially partitioned into the selenide phase, is also distributed in the palladiferous gold (Fig. 2c). Palladseite has up to 0.4 wt.% S (Cabral et al., 2002c). No gradient in sulphur abundance was observed at the palladseite–gold boundary.

Discussion

Primary (hypogene) gold generally has silver in amounts higher than 1 wt.%, but palladium is rarely present in substantial quantities (Boyle, 1979). Hypogene gold, therefore, should commonly have Pd/Ag ratios of $<10^{-3}$. However, high Pd/Ag ratios of >5 characterise the Cauê palladiferous gold coexisting with palladseite. The ratios are comparable to those found in the dendritic gold from the near-surface, bonanza-style Au–Pd–Pt deposit of Serra Pelada (Cabral et al., in press). Palladiferous gold from both deposits has low silver contents, <0.4 wt.% Ag (Fig. 1a). Such low Ag contents are also found in secondary (supergene) gold from ferruginous lateritic profiles (e.g., Mann, 1984). Experimental investigation demonstrates that high palladium mobilities and Pd/Ag chloride complexes ratios are restricted to unusually saline, highly oxidising fluids (Gammons et al., 1993). The reason why palladiferous gold is devoid of significant silver can be explained by the fact that such oxygenated brines are in the stability field of cerargyrite (AgCl), where silver solubility is independent of pH and oxidation state. As a result, pH neutralisation or reduction would not affect silver, but palladium solubility, leading to separation of silver from palladium (Gammons et al., 1993).

Sulphur is apparently in solid solution in palladiferous gold from Cauê. This hypothesis is supported by the absence of sulphide inclusions in gold. It could be argued that the sulphur detected might be an artefact from the carbon coating. Test microanalyses on carbon-coated hematite crystals from an iron ore deposit in the Quadrilátero Ferrífero (Gongo Soco) indicated that sulphur contents are below, or slightly above, the detection limit of 20 ppm S. Therefore, sulphur is indigenous to the palladiferous gold.

S/Se ratios greater than unity are found in palladiferous gold from Cauê, in Minas Gerais, and Serra Pelada, in northern Brazil. The presence of sulphur in gold should reflect the redox conditions under which gold precipitated. Deposition of selenide minerals, represented by palladseite, requires $f\mathrm{Se}_2/f\mathrm{S}_2$ ratios greater than unity, a condition attained in oxidising systems in which aqueous sulphur is in the form of sulphate while selenium occurs as aqueous selenide species (Simon et al., 1997). Such conditions (above the hematite–magnetite buffer) are too oxidising for precipitation of sulphide minerals, allowing sulphur not only to substitute for selenium in palladseite, but also to be eventually incorporated into the concomitant gold (Figs. 1a, 2). This unexpected partition of sulphur into solid solution in alloys seems to take place in systems of high oxidation state, i.e. in the absence of sulphide minerals. One example comes from platiniferous hematite–quartz veins in the Waterberg deposit, South Africa, where cupriferous platinum has up to 4 wt.% S in solid solution (McDonald et al., 1999).

Palladiferous gold is associated with seleniferous minerals of palladium and platinum at Cauê and Serra Pelada. In the presence of selenium, palladium is strongly partitioned into selenide phases, rather than into any alloy phase (*cf.* Gammons et al., 1993). Nevertheless, palladiferous gold occurs in amounts exceeding by far those of seleniferous minerals, suggesting that the total palladium solubility was higher than that of selenium in the hydrothermal fluids.

Conclusions

Palladiferous gold coexisting with palladseite has sulphur in solid solution in amounts of a few hundred ppm. S/Se ratios of >1 in palladiferous gold are the result of selenium partitioning into selenide (palladseite). Because the ore-bearing fluids were oxidising, i.e. sulphate >> reduced sulphur species, sulphur did not form sulphide minerals, but it was incorporated into palladseite and, subordinately, palladiferous gold. It is thus suggested that, in the absence of sulphide minerals, sulphur as a trace element in gold should reflect highly oxidising conditions of the fluid system. This proposition is supported by observations from relatively selenium-poor, oxidising hydrothermal deposits at Serra Pelada, in northern Brazil, and Waterberg deposit, in South Africa. Further investigation is necessary, particularly determination of, and comparison with, S/Se ratios of gold from sulphide-bearing systems.

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