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HYDROGEN IN A NATURAL Pd–O COMPOUND FROM GONGO SOCO, MINAS GERAIS, BRAZIL

Alexandre Raphael CABRAL[§] and Bernd LEHMANN

Institut für Mineralogie und Mineralische Rohstoffe, Technische Universität Clausthal,
Adolph-Roemer-Str. 2A, D-38678 Clausthal-Zellerfeld, Germany

Dieter GRAMBOLE[¶] and Folker HERRMANN

Forschungszentrum Rossendorf e.V., Institut für Ionenstrahlphysik und Materialforschung,
PF 510119, D-01314 Dresden, Germany

Abstract

The existence of hydrogen in Pd–O-bearing aggregates, which together with iron oxides form the characteristic dark encrustation of an *ouro preto* nugget of Gongo Soco, Minas Gerais, Brazil, is confirmed by elastic recoil detection analysis with a heavy-ion microbeam (micro-ERDA). Hydrogen is lost from Pd–O-bearing areas during the micro-analyses, but not from goethite. The data indicate that the Pd–O–H phase is unstable compared to goethite, giving support to previous observations that it is a transient phase in a transformation to native palladium.

Keywords: hydrogen, elastic recoil detection analysis, Pd–O-bearing compound, *ouro preto* nugget, Gongo Soco, Minas Gerais, Brazil.

Sommaire

L'existence d'hydrogène dans des aggrégats contenant une phase à Pd–O, qui constitue, avec des oxydes de fer la patine sombre caractéristique d'une pépite de *ouro preto* prélevée à Gongo Soco, Minas Gerais, Brazil, est confirmée par une analyse par détection du recul élastique avec un micro-faisceau d'ions lourds (technique micro-ERDA). L'hydrogène est libéré des régions contenant la phase Pd–O au cours des analyses, mais non de la goethite. Les données montrent ainsi que la phase à Pd–O–H est instable par rapport à la goethite, et étayent l'hypothèse fondée sur les observations antérieures qu'il s'agit d'une phase transitoire dans une transformation en palladium natif.

(Traduit par la Rédaction)

Mots-clés: hydrogène, analyse par détection du recul élastique, composé contenant Pd–O, pépite de *ouro preto*, Gongo Soco, Minas Gerais, Brésil.

Introduction

Evidence for the existence of natural oxygen-bearing compounds of palladium dates back to the nineteenth century (Gardner 1826, Johnson & Lampadius 1837), but their occurrence has only recently been confirmed. The presence of oxygen has been indicated by qualitative energy-dispersion (ED) analysis and also by quantitative electron-microprobe wavelength-dispersion (WD) analysis, from which the oxygen content is calculated by stoichiometry (*e.g.*, Clark *et al.* 1974, Vuorelainen *et al.* 1982, Jedwab 1995, Olivo & Gauthier 1995, Salpéteur *et al.* 1995, Hey 1999, Moreno *et al.* 1999, Nickel 2002), as well as by quantitative measurement of the intensity of an oxygen peak with the electron microprobe (*e.g.*, McDonald *et al.* 1999, Varajão *et al.* 1999, Tolstykh *et al.* 2000, Cabral *et al.* 2001, 2002a). However, the existence of possible H_2O- or OH-bearing Pd–O compounds has remained essentially conjectural. The anhydrous nature of a Pd–Pb oxide from Penikat, Finland, was inferred by infrared-absorption spectroscopy (Barkov *et al.* 1999). On the other hand,

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[§] *Present address*: Rua Coelho Neto, no. 32/apt. 704, 22231-110 Rio de Janeiro – RJ, Brazil. *E-mail address*: cabral70tricolor@yahoo.com.br

[¶] *E-mail address*: d.grambole@fz-rossendorf.de

the presence of hydrogen has been suggested for a Pd–O phase or phases from Lavatravo, Madagascar, on the basis of excess oxygen compared to stoichiometric palladium monoxide, PdO (McDonald *et al.* 1999). Low analytical totals and the formation of microcracks under the electron beam have been considered indicative of an unanalyzed volatile component, H_2O or OH, in Pd–O aggregates from Minas Gerais, Brazil (Cabral *et al.* 2002b, 2003).

We here report data from elastic recoil detection analysis with a heavy-ion microbeam (micro-ERDA), which provide the first confirmation of hydrogen in Pd–O-bearing *ouro preto*. The Pd–O material from Minas Gerais is a distinctive component of the ferruginous encrustations that give the characteristic dark color to the historically famous *ouro preto* (Jedwab 1995, Jedwab & Cassedanne 1998, Cabral *et al.* 2001, 2003, and references therein). The material occurs as an oxidation-induced halo on a precursor Pd-bearing mineral and is unstable, *i.e.*, it tends to evolve to native palladium (Cabral & Lehmann 2003).

EXPERIMENTAL

Sample material

The sample material is a gold nugget about 1.5 cm across, recovered in a Knelson concentrator at the Gongo Soco iron ore plant. This gold nugget (sample GS–Au–22) and the specular-hematite-rich vein-style Au–Pd mineralization of Gongo Soco are described elsewhere (Cabral 2003). The gold is alloyed with silver (~8 wt.% Ag), with subordinate amounts of palladium (up to 0.3 wt.% Pd), but it contains abundant inclusions of Pd-bearing selenide minerals, including chrisstanleyite, $Ag_2Pd_3Se_4$, and unnamed Sb–Ag–Hg-bearing selenides of palladium (Cabral 2003). The gold nugget studied consists of fragments of gold cemented by specular hematite, with which goethite and, the Pd–O compound occur. These minerals, of which the Pd–O compound is characteristic, give the typical dark color of *ouro preto*. It differs, nevertheless, from other nuggets of *ouro preto* from Gongo Soco, which commonly have higher contents of palladium alloyed with gold and inclusions of arsenide–antimonides of palladium compositionally close to mertieite-II, $Pd_8(Sb,As)_3$, and isomertieite, $Pd_{11}Sb_2As_2$ (Cabral *et al.* 2002c).

Two sites of gold-encrusting Pd–O-bearing aggregates of specular hematite were investigated in this study. At the first site, the Pd–O phase has abundant microcracks and is situated between an aggregate of platy hematite and a goethite-like phase (Fig. 1a). At the second site, the Pd–O phase looks more massive, *i.e.*, it lacks the prominent microcracks observed at the first site, and occurs in the interstices of crystals of platy hematite (Fig. 2a). Reconnaissance electron-microprobe analyses indicate that the Pd–O phase contains a considerable amount of copper (up to 13 wt.%), subordinate gold, iron and manganese (amounting to a few wt.%), and traces of mercury (<1 wt.%) (Table 1). The analytical totals are below 100 wt.%; oxygen is the only missing element detected by energy-dispersion analysis. However, the metal content indicated in some microanalyses (totaling 94–95 wt.%) suggests that the amount of oxygen is insufficient to account for a PdO-type compound, *i.e.*, some of the Pd–O phase under investigation may represent oxygen-deficient Pd–Cu compounds.

Hydrogen measurement

The distribution of hydrogen in Pd–O-bearing areas was obtained by micro-ERDA using the nuclear microprobe at the 3 MV Tandetron accelerator of the Forschungszentrum Rossendorf, Dresden (Herrmann & Grambole 1995). The Pd–O-bearing samples were bombarded with 16 MeV Si^{5+} ions at an incident angle of 20° relative to the sample surface. The beam, focused to a diameter of about 3 μm, was electromagnetically scanned over the sample. Because of the glancing incidence, a lateral resolution of about 3×10 μm^2 was obtained. The recoiled hydrogen atoms were measured by a silicon surface-barrier detector covered by a 10 μm Al foil to stop the Si ions scattered in the sample. In this way, it was possible to measure hydrogen (in principle also helium, but no heavier elements) up to a depth of some hundred nanometers. Simultaneously to the detection of the hydrogen ion, the X-rays induced by the Si beam were detected by a Si(Li)-PIXE (Particle Induced X-ray Detection) detector. The detectors for measuring the hydrogen ions and the X-rays were situated at angles of 30° and 150°, respectively, relative to the incident beam. The amplified signals of the detectors were analyzed with two analog-to-digital converters (ADC). These digital data were stored, together with the X–Y coordinates of the scanned beam, event by event on a hard disk. During the measurement, up to four element-distribution maps and the spectra could be observed

TABLE 1. RESULTS OF RECONNAISSANCE ELECTRON-MICROPROBE ANALYSES OF THE Pd–O COMPOUND, GONGO SOCO, MINAS GERAIS, BRAZIL

	1	2	3	4	5	6	7	8	9	10
Pd	77.48	74.61	74.42	75.25	78.89	76.55	77.28	77.64	78.08	78.27
Cu	7.43	7.87	9.59	7.09	12.02	11.93	12.97	12.88	11.99	12.16
Au	2.84	2.21	3.32	2.00	1.00	1.00	1.49	2.22	1.78	1.22
Hg	<0.2	<0.2	0.72	0.22	0.54	0.45	0.44	0.51	0.48	0.41
Fe	0.24	0.23	0.68	0.81	1.08	0.42	2.58	0.82	0.87	1.72
Mn	1.45	2.21	0.99	3.05	0.53	0.65	0.64	0.75	1.14	0.52
Total	89.44	87.13	89.72	88.42	94.06	91.00	95.40	94.82	94.34	94.30

The electron-microprobe analyses were performed at 20 kV and 40 nA with a Cameca SX100 (TU Clausthal). The following X-ray lines and standards were used: pure metals (Au$L\alpha$, Cu$K\alpha$, Pd$L\alpha$, Pt$L\alpha$, Se$K\alpha$), HgTe (Hg$L\alpha$), Fe_2O_3 (Fe$K\alpha$), $MnSiO_3$ (Mn$K\alpha$) and InSb (Sb$L\alpha$). Platinum, selenium and antimony were sought, but are below the detection limit of 0.3, 0.2, 0.1 wt.%, respectively. Column headings: 1–4: first site (Fig. 1a), 5–10: second site (Fig. 2a). Compositions are reported in wt.%.

online. By reason of this event-by-event storage, the loss of hydrogen during ion bombardment and also differences in the elemental composition could be evaluated off-line (*i.e.,* after the measurement) for several areas in the sample.

RESULTS AND DISCUSSION

The distribution of hydrogen is shown in Figures 1 and 2. At the first site (Fig. 1a), hydrogen is present within the Pd-rich domain (Pd–O phase, Figs. 1b, c), but concentrated in Fe-rich domains (Figs. 1c, d). The Fe-rich areas with hydrogen (*e.g.*, domain 2 in Fig. 1c) and without hydrogen (*e.g.*, domain 3, Fig. 1c) correspond respectively to a goethite-like mineral (domain 2) and hematite (domain 3). At the second site (Fig. 2a), hydrogen is associated with Pd-rich areas containing a Pd–O phase (Figs. 2b, c).

The hydrogen in the Pd–O areas is unstable. During micro-analysis of the first site, hydrogen was lost from the Pd–O-bearing area (Fig. 3a). However, the hydrogen content of the goethite-like mineral of domain 2 remained constant (Fig. 3b). Hydrogen also was lost from the Pd–O-bearing area of the second site (Fig. 3c). This behavior suggests that there are two types of hydrogen bonds, of which those of the goethite-like mineral are more or less stable and not broken by the incident ions, but the kind of linkage cannot be distinguished by this method.

The concentrations of hydrogen in the samples were calculated by a PC algorithm for ERDA (Spaeth *et al.* 1998) using values of stopping power from Ziegler (1980). They were averaged over the whole domain and over a depth of about 50 to 250 nm, *i.e.*, no surface hydrogen was included into the evaluation. Since hydrogen was lost during the measurement (Fig. 3), the concentration was extrapolated to a charge of $Q = 0$ nC. The concentrations are as follows: 1) Domain 1, Pd–O phase (Fig. 1c): 6.3 ± 2.4 at.% H, 2) Domain 2, goethite-like phase (Fig. 1c): 11.2 ± 2.2 at.% H, and 3) Domain 4, Pd–O phase (Fig. 2c): 8.1 ± 2.7 at.% H. The errors quoted arise mainly by the fitting procedures used (Fig. 3). Here, it should be noted that the measured content of hydrogen in domain 2 is less than that of ideal goethite, FeOOH (25 at.% H). The reason for this difference may be attributed to: (1) the spectrum summation from parts beyond the boundary of the goethite-like mineral, and (2) probable inhomogeneity of the mineral surface. The hydrogen escape on ion bombardment follows an exponential curve in the Pd–O–H phase (Figs. 3a, c) and a relatively stable hydrogen "background" can be observed in Figure 3c at about 25 counts/262 nC, which corresponds to about 4.0 at.% H.

This study demonstrates that the Pd–O-bearing phase, which characterizes an *ouro preto* nugget of Minas Gerais, contains hydrogen. The hydrogen is most likely related to H_2O, as suggested by the desiccation-like microcracks at the first site (Fig. 1a), and the fact that the hydrogen content of the Pd–O-bearing domains decreases during measurement. This behavior is different from that displayed by goethite, where hydrogen remains constant. In other words, the Pd–O–H-bearing compound is unstable compared to goethite. In the supergene environment, where goethite is stable, the Pd–O–H-bearing species would thus be metastable. This fact would explain why such compound is deficient in oxygen, eventually giving rise, *via* a deoxygenation–dehydration process, to native palladium (Cabral & Lehmann 2003; *cf.* McDonald *et al.* 1999, Cabral *et al.* 2003). Native palladium would therefore seem to be the stable phase of palladium under supergene conditions.

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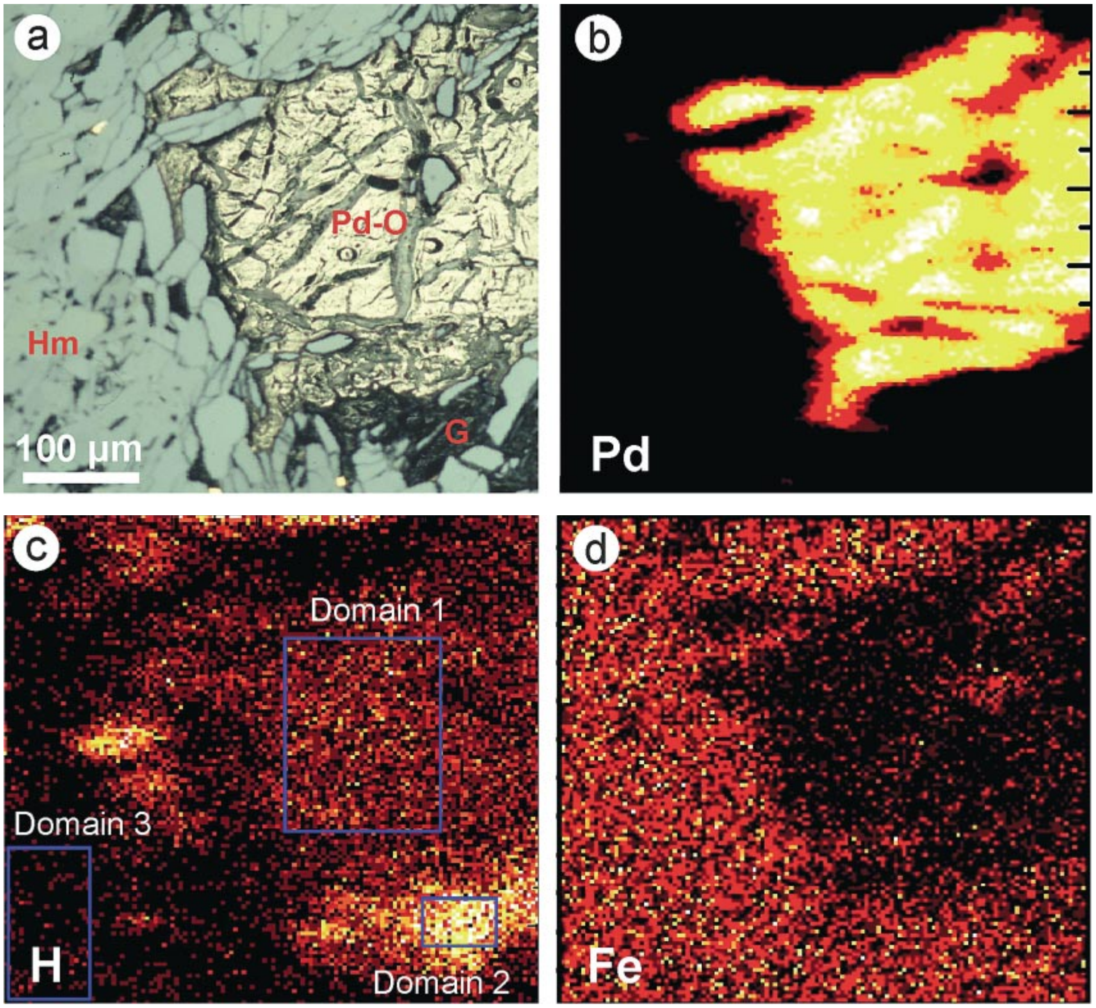

FIG. 1. a. Photomicrograph (reflected light, oil immersion) of a Cu-bearing Pd–O phase (Pd–O), with abundant microcracks, located between an aggregate of hematite (Hm) and a goethite-like phase (G). Originally, the Pd–O phase had a dark grey color. It acquired a whitish color after ion bombardment. b, d. Distribution of palladium (b) and iron (d), obtained by micro-PIXE with a beam of 16 MeV Si^{5+} (Q = 229.4 nC). c. Distribution of hydrogen, obtained by micro-ERDA with a beam of 16 MeV Si^{5+} (Q = 2.03 µC).

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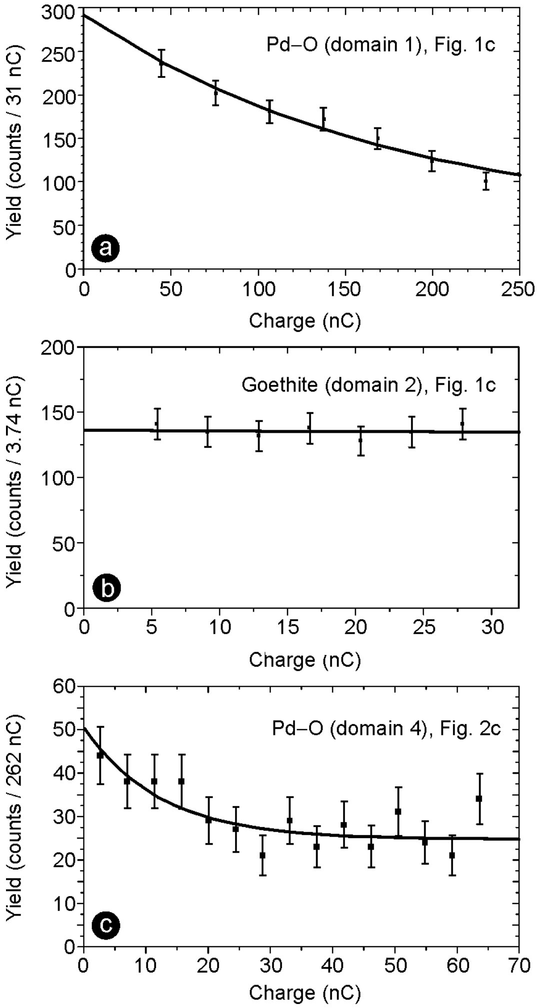

FIG. 3. a–c. Yield of the recoiled hydrogen atoms according to the hydrogen concentration as a function of accumulated charge of the incident Si ions for (a) Pd–O in domain 1 (Fig. 1c), (b) goethite-like phase in domain 2 (Fig. 1c) and (c) Pd–O in domain 4 (Fig. 2c).

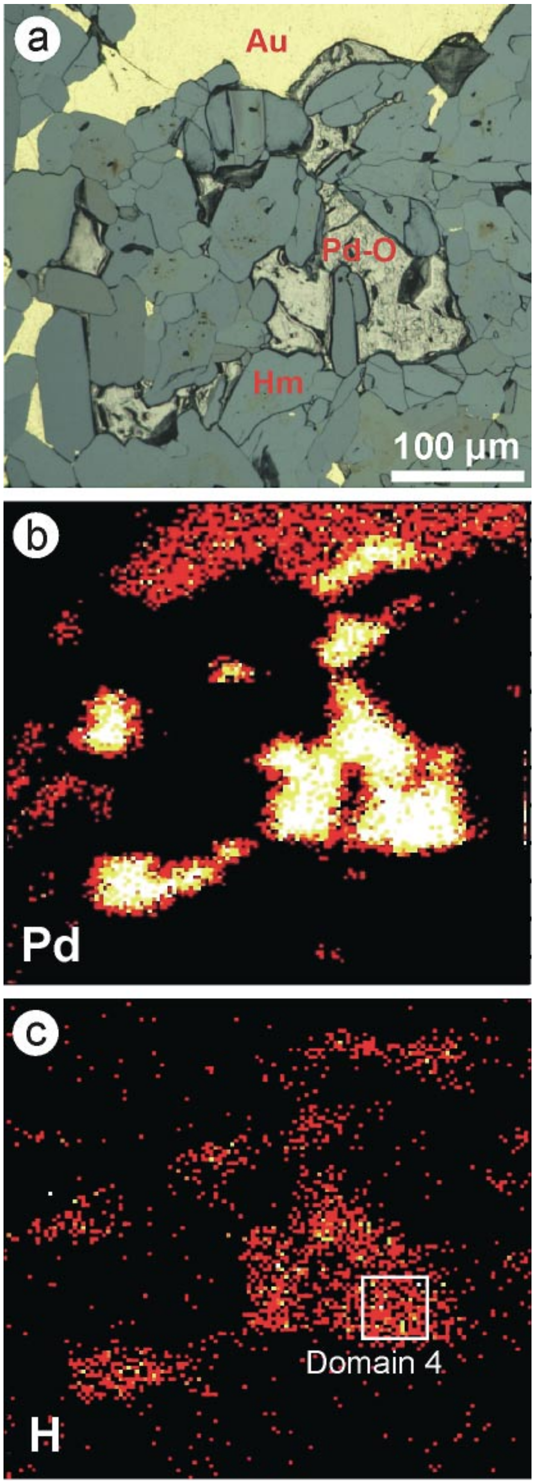

FIG. 2. a. Photomicrograph (reflected light, oil immersion) of a Cu-bearing Pd–O phase (Pd–O) interstitial to crystals of platy hematite (Hm). The hematite and Pd–O phase are part of a dark encrustation on a fragment of gold (Au) that makes up a nugget of *ouro preto*. The whitish color of the Pd–O phase arose from ion bombardment; its original color was dark grey. b. Distribution of palladium, obtained by micro-PIXE with a beam of 16 MeV Si^{5+} (Q = 16.4 nC). c. Distribution of hydrogen, obtained by micro-ERDA with a beam of 16 MeV Si^{5+} (Q = 4 µC).

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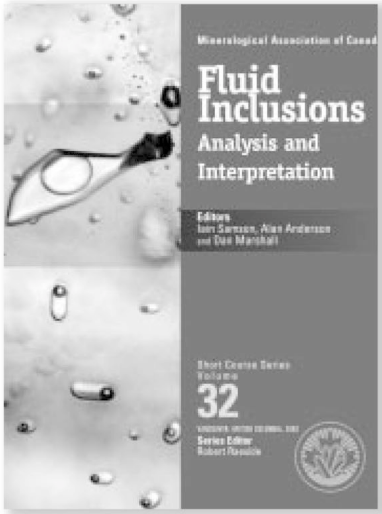

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