

*The Canadian Mineralogist*  
Vol. 42, pp. 1745-1755 (2004)

## JAGUÉITE, $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , A NEW MINERAL SPECIES FROM EL CHIRE, LA RIOJA, ARGENTINA

WERNER H. PAAR<sup>§</sup> AND DAN TOPA

*Department of Geography, Geology and Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria*

EMIL MAKOVICKY

*Geological Institute, University of Copenhagen, Østervoldgade 10, DK-1350 Copenhagen K, Denmark*

RICARDO J. SUREDA

*Cátedra de Mineralogía, Facultad de Ciencias Naturales, Universidad Nacional, 4400 Salta, Argentina*

MILKA K. DE BRODTKORB

*Consejo Nacional de Investigaciones Científicas y Técnicas, University of Buenos Aires,  
Paseo 258-9A, 1640 Martínez, Argentina*

ERNEST H. NICKEL

*Exploration and Mining, CSIRO, Private Bag no.5, PO Wembley, W.A. 1613, Australia*

HUBERT PUTZ

*Department of Geography, Geology and Mineralogy, University of Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Austria*

### ABSTRACT

Jaguéite, with the simplified formula  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , the copper analogue of chrisstanleyite, was discovered in a telethermal selenide vein-type deposit at the El Chire prospect, Los Llantenes District of La Rioja Province, Argentina. The new mineral species is generally associated with chrisstanleyite, particularly in intimate intergrowths, clausenthalite, naumannite, tiemannite, klockmannite, berzelianite, umangite and aguilarite. Mercurian silver, native gold, and two unnamed compounds, chemically  $(\text{Ag,Cu})_6\text{Hg}_2\text{Pd}_2\text{Se}_3$  and  $(\text{Ag,Cu})_8\text{Hg}_3(\text{S,Se})_7$ , occur as rare constituents. The selenide vein is hosted by metasedimentary rocks of Carboniferous age that belong to the Precordilleran terrane. Jaguéite occurs in anhedral grains that lack a distinct morphology. Aggregates of intergrown jaguéite and chrisstanleyite measure up to  $100 \times 20 \mu\text{m}$ ; single grains, however, do not exceed  $60 \mu\text{m}$ . The mineral is megascopically creamy yellowish in color, opaque and lacks internal reflections. It has a metallic luster and a black streak. It is brittle with an uneven fracture and without observable cleavage.  $\text{VHN}_{25}$  ranges between 464 and 772 (mean 612)  $\text{kg/mm}^2$ , corresponding to a Mohs hardness of 5. In plane-polarized light, it is weakly to moderately birefractant and slightly pleochroic, from light buff to creamy buff. Jaguéite is anisotropic; the rotation tints are brownish – bluish – greenish. The prominent spindle-shaped twins are almost identical to those in chrisstanleyite. The measured values of reflectance in air and oil, respectively, are 41.0–50.1, 27.0–31.9 (470 nm), 44.1–51.8, 29.2–33.8 (546 nm), 44.6–51.7, 29.4–33.7 (589 nm), 45.1–52.0, 30.2–34.1 (650 nm); values for 400–700 nm are tabulated. As an average, eight electron-microprobe analyses gave: Cu 15.7, Ag 1.59, Pd 42.04, Se 40.15, total 99.48 wt.%, corresponding to  $(\text{Cu}_{1.91}\text{Ag}_{0.11})_{\Sigma 2.02}\text{Pd}_{3.05}\text{Se}_{3.93}$  (basis: 9 atoms per formula unit). The ideal formula is  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , which requires Cu 16.68, Pd 41.88, Se 41.44, total 100.00 wt.%. Jaguéite has a monoclinic cell with  $a$  5.672(5),  $b$  9.910(9),  $c$  6.264(6) Å,  $\beta$  115.40(2)°,  $V$  318.1(5) Å<sup>3</sup>, space group  $P2_1/c$  and  $Z=2$ . The calculated density is 8.01  $\text{g/cm}^3$ . The crystal structure was solved from single-crystal data obtained on a four-circle diffractometer with an area detector. The strongest eight lines in the calculated powder-diffraction pattern [ $d$  in Å( $hkl$ )] are: 2.759(23)( $\bar{1}31$ ), 2.676(100)(121), 2.630(64)( $\bar{1}22$ ), 2.508(31)(202), 2.269(27)(041), 1.950(27)(122), 1.920(36)( $\bar{1}23$ ) and 1.866(24)( $\bar{2}41$ ). Jaguéite and chrisstanleyite form a limited solid-solution series. The mineral is named after the village of Jagué, which is the closest settlement to the El Chire mine. Both the mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names (IMA 2002-060).

<sup>§</sup> E-mail address: werner.paar@sbg.ac.at

**Keywords:** jaguëite, new mineral species, platinum-group mineral, Cu–Pd selenide, electron-microprobe data, reflectance data, X-ray-diffraction data, crystal structure, El Chire, Los Llantenes, La Rioja, Argentina.

### SOMMAIRE

La jaguëite, dont la formule simplifiée serait  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , est l'analogue à dominance de cuivre de la chrisstanleyite; cette espèce nouvelle a été découverte dans un gisement de sélénures téothermal en veines, l'indice de El Chire, district de Los Llantenes, province de La Rioja, en Argentine. La nouvelle espèce est généralement associée à la chrisstanleyite, surtout en intercroissances intimes, et à clausenthalite, naumannite, tiemannite, klockmannite, berzélianite, umangite et aguilarite. Lui sont associés, mais plus rarement, argent mercurifère, or, et deux phases sans nom, de composition  $(\text{Ag,Cu})_6\text{Hg}_2\text{Pd}_2\text{Se}_3$  et  $(\text{Ag,Cu})_8\text{Hg}_3(\text{S,Se})_7$ . La veine de sélénures recoupe des roches métasédimentaires d'âge carbonifère faisant partie du socle pré-Cordillère. La jaguëite se présente en grains xénomorphes, sans morphologie distincte. Les agrégats de jaguëite et de chrisstanleyite en intercroissance atteignent  $100 \times 20 \mu\text{m}$ ; les grains monocristallins, par contre, ne dépassent pas  $60 \mu\text{m}$ . Le minéral est crème jaunâtre à l'oeil, opaque et sans réflexions internes. Il possède un éclat métallique et une rayure noire. Il est cassant, avec une fracture inégale et sans clivage évident. Sa dureté  $\text{VHN}_{25}$  va de 464 à 772 (en moyenne, 612)  $\text{kg/mm}^2$ , ce qui correspond à une dureté de Mohs de 5. En lumière polarisée, la jaguëite est légèrement à modérément biréfléctante et légèrement pléochroïque, de beige pâle à crèmeux. Elle est anisotrope; les teintes de rotation sont brunâtre – bleuâtre – verdâtre. Les macles biseautées proéminentes ressemblent beaucoup à celles de la chrisstanleyite. Les valeurs de la réflectance, dans l'air et dans l'huile, respectivement, sont 41.0–50.1, 27.0–31.9 (470 nm), 44.1–51.8, 29.2–33.8 (546 nm), 44.6–51.7, 29.4–33.7 (589 nm), 45.1–52.0, 30.2–34.1 (650 nm); nous présentons les valeurs pour l'intervalle 400–700 nm. En moyenne, les huit analyses à la microsonde électronique ont donné: Cu 15.7, Ag 1.59, Pd 42.04, Se 40.15, total 99.48% (poids), ce qui correspond à  $(\text{Cu}_{1.91}\text{Ag}_{0.11})_{\Sigma 2.02}\text{Pd}_{3.05}\text{Se}_{3.93}$  (base de neuf atomes par formule unitaire). La formule idéale,  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , requiert Cu 16.68, Pd 41.88, Se 41.44, total 100.00%. La jaguëite possède une maille monoclinique,  $a$  5.672(5),  $b$  9.910(9),  $c$  6.264(6) Å,  $\beta$  115.40(2)°,  $V$  318.1(5) Å<sup>3</sup>, groupe spatial  $P2_1/c$  et  $Z=2$ . La densité calculée est 8.01  $\text{g/cm}^3$ . La structure cristalline a été résolue sur monocristal avec un diffractomètre à quatre cercles muni d'un détecteur à aire. Les huit raies les plus intenses du spectre de diffraction (méthode des poudres) [ $d$  en Å( $hkl$ )] sont: 2.759(23)( $\bar{1}31$ ), 2.676(100)(121), 2.630(64)( $\bar{1}22$ ), 2.508(31)(202), 2.269(27)(041), 1.950(27)(122), 1.920(36)( $\bar{1}23$ ) et 1.866(24)(241). La jaguëite et la chrisstanleyite forment une solution solide limitée. Le nom choisi rappelle le village de Jaguë, le plus proche de la mine El Chire. La nouvelle espèce et son nom ont reçu l'approbation de la Commission pour les nouveaux minéraux et les noms de minéraux (IMA 2002–060).

Traduit par la Rédaction)

**Mots-clés:** jaguëite, nouvelle espèce minérale, minéral du groupe du platine, sélénure de Cu–Pd, données de microsonde électronique, données de réflectance, données de diffraction X, structure cristalline, El Chire, Los Llantenes, La Rioja, Argentine.

### INTRODUCTION

The association of platinum-group elements (PGE), especially palladium and to a minor extent platinum, and selenide mineralization, is known from several occurrences worldwide (Cabral *et al.* 2002a, b, Clark & Criddle 1982, Jedwab 1997, Jedwab *et al.* 1999, Johan *et al.* 1970, Johan 1989, Kwitko *et al.* 2002, Nickel 2002, Paar *et al.* 1998, 2005, Roberts *et al.* 2002, Stanley *et al.* 2002, Wallis 1994). We have documented the presence of platinum-group minerals (PGM) in selenide mineralization of La Rioja, Argentina, as a result of a detailed microscopic and electron-microprobe investigation (Paar *et al.* 2000, 2002a, b, 2004). All the selenide occurrences carrying platinum-group elements have very small reserves, and they thus do not have economic potential.

Our study of the microparagenesis of the high-grade selenide mineralization at El Chire, Argentina, exposed in a small exploration drift, led to the discovery of the new mineral jaguëite, ideally  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ . It is named after the small village of Jaguë, which is located in the homonymous "Bolson de Jaguë" (depression of Jaguë),

the starting point for expeditions to both the selenide districts of Los Llantenes and Sierra de Cacho (west of the Sierra de Umango). The same mineral had been noticed in the Pilbara region of Australia by Nickel (2002), who considered it the Cu-dominant analogue of chrisstanleyite,  $\text{Ag}_2\text{Pd}_3\text{Se}_4$ . The mineral and the mineral name have been approved by the Commission of New Minerals and Mineral Names, IMA (2002–060). The holotype specimens (polished section and two ore fragments) are deposited in the systematic reference collections of the Department of Geography, Geology and Mineralogy, Division of Mineralogy and Material Sciences, University of Salzburg, and are registered under catalogue numbers 14938 and 14939 a, b.

### LOCATION AND GEOLOGY

El Chire is a small occurrence of selenide mineralization west of the depression of Jaguë, which is some 30 km northwest of the village of Vinchina in La Rioja Province of Argentina (Fig. 1a). According to the topographic map Tinogasta (scale 1:250000), sheet 2969–II (1986), the mine is situated 30 km west of the small

village of Alto Jagué, and 5.5 km south–southwest of Punta del Agua, at an altitude slightly above 3100 m above sea level. The coordinates are 28°38.3' S (longitude) and 68°44.3' W (latitude), as deduced from the map.

El Chire is situated at the southwestern corner of the selenium ore district of Los Llantenes (Guerrero 1969, Angelelli 1984, Brodtkorb 1990, 1993), which belongs to the Precordillera terrane accreted onto the South American continent during the Early Paleozoic (Famatinian) orogeny (Astini *et al.* 1995). The outcrops of the selenium mineralization are located on the steep flanks of a rugged mountain range with difficult access.

The host rocks of the structurally controlled vein-type mineralization are Carboniferous sandstones, arkoses, conglomerates and lutites of the Volcán Formation (= Cerro Minutas Formation; Guerrero 1969), hydrothermally altered to a brownish or reddish rock with abundant hematite in the vicinity of the calcite-bearing single selenide-bearing vein.

This vein has been explored underground both along strike and dip (Fig. 1b). It pinches out after a few meters which is, in fact, typical for most of the selenide occurrences in that region. The width of the calcite vein on the surface varies between one and two centimeters, but increases underground to almost six centimeters. Symmetrical banding (Fig. 1c), vugs and sections of brecciated vein can be observed, with fragments of the altered country-rock cemented by calcite and selenide minerals (Fig. 1d).

The selenide mineralization occurs as massive layers in the vein up to two centimeters in thickness, in pods of irregular shape and varying size, and finely disseminated in the calcite vein matrix. Microscopically, the selenides (tiemannite, naumannite, jaguéite and chrisstanleyite) occur in lobate inclusions in, and occasionally along, grain boundaries of calcite.

The dominant selenides are tiemannite, HgSe, and naumannite, Ag<sub>2</sub>Se, the latter decreasing with depth. Clausthalite, PbSe, is a common but minor associate, whereas eucairite, AgCuSe, umangite, Cu<sub>3</sub>Se<sub>2</sub>, klockmannite, CuSe, and berzelianite, Cu<sub>2</sub>Se, are rare. Aguilarite, Ag<sub>4</sub>SeS, has only once been observed, as microscopic grains associated with naumannite and tiemannite. An unnamed phase containing Ag, Cu, Hg, S and Se is present in trace amounts. Native gold with no detectable content of palladium is especially abundant in the strongly oxidized portion of the vein and is embedded as irregularly shaped grains and thin flakes (foils) up to several millimeters in length in the calcite and, rarely, in the selenide matrix.

Three platinum-group minerals are associated with the selenide mineralization: (1) jaguéite, chemically (Cu,Ag)<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>, the new species described herein, (2) chrisstanleyite, (Ag,Cu)<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub> (Paar *et al.* 1998), and (3) an unnamed selenide of Ag(Cu), Hg and Pd (Figs. 2a–d). Chemical data on ore fragments we picked from

El Chire are compared with data from other selenide occurrences in La Rioja (Table 1).

Jaguéite and chrisstanleyite commonly occur as intimate intergrowths in the calcite (and malachite) matrix, and rarely as isolated grains in the tiemannite–naumannite ore (Figs. 2a, c). The unnamed PGM forms a rim around grains of chrisstanleyite, too thin (4–20 μm) to be extracted for X-ray study (Fig. 2d). A silver–mercury alloy (mercurian silver; Cipriani *et al.* 1993) is associated with the unnamed phase in porous patches up to 500 × 250 μm, and more commonly in irregular grains (30 × 30 μm) and microveinlets. The intergrowth relationships suggest the following order of crystallization for the selenide assemblage: chrisstanleyite and jaguéite → (clausthalite) → naumannite and tiemannite → umangite and klockmannite → Pd-free native gold.

The presence of umangite provides an important constraint on temperature of formation during the mineralizing event. Chakrabarti & Laughlin (1981) have shown that umangite is only stable below 112°C, at which temperature it decomposes to berzelianite and high klockmannite. Abundant hematite, which accompanies the selenide mineralization, is further evidence for selenide formation from highly oxidizing fluids, whose source is, as yet, unknown.

Secondary minerals such as chalcocite (in mm-sized crystals and crystal clusters up to 1 cm), malachite (as thin crusts and small veinlets) and trace amounts of molybdomenite – olsacherite – kerstenite occur in cavities that are especially abundant in the weathered portions of the vein.

#### APPEARANCE AND PHYSICAL PROPERTIES

The new mineral species occurs in small amounts in most of the 37 polished sections prepared from selenide specimens collected from the vein outcrop. Lobate aggregates of jaguéite and chrisstanleyite up to 500 μm across, partly as oriented intergrowths, are embedded in a calcite matrix, and may cover areas up to 4 × 1 mm (maximum). More commonly, jaguéite can be observed as dust-like inclusions of anhedral grains in tiemannite

TABLE 1. GRADES<sup>1</sup> OF PRECIOUS METALS IN SELENIDE ORE FROM EL CHIRE AND ADJOINING LOCATIONS, LA RIOJA, ARGENTINA

Location	Pd	Pt	Au	Ag	
El Chire	8.49	1.96	0.06	7.98	>> nau
	13.10	8.98	16.90	0.17	< nau, > tie
	2.79	1.74	0.08	5.43	> nau, < tie
Los Llantenes	0.52	2.06	1.72	0.18	
Las Asperzas	0.75	4.40	9.60	0.56	

<sup>1</sup> Actlabs, Ancaster, Ontario, Canada. Concentrations are reported in ppm, except for Ag (wt%). Methods used and detection limits (in ppb): fire assay – ICP-OES: Au (2), Pt (5), Pd (4); four acid ICP (ICP-OES): Ag (0.3). Symbols: nau naumannite, tie tiemannite; >> abundant, < minor constituent.

(preferably) and naumannite. These grains vary in size between a few micrometers up to 40–50  $\mu\text{m}$  across and do not show obvious forms. Spindle-shaped deformation twins are common.

In plane-polarized light, jagu ite cannot be distinguished from the intergrown chrisstanleyite (Fig. 2a). When using crossed polars or back-scattered electron imaging (Figs. 2b, c), however, a sharp boundary between the two selenides is evident. The intergrowth tex-

tures are indicative of the earlier crystallization of chrisstanleyite, which then was replaced by solutions with  $a_{\text{Cu}} > a_{\text{Ag}}$ , leading to the formation of the new species.

The larger aggregates of jagu ite–chrisstanleyite occasionally show a random decomposition into a mixture of Cu–Ag–Hg–Pd–Se–(?)O compounds (Figs. 2a–c), which optically are characterized by a strong anisotropy, similar to that of minerals with a sheet-like

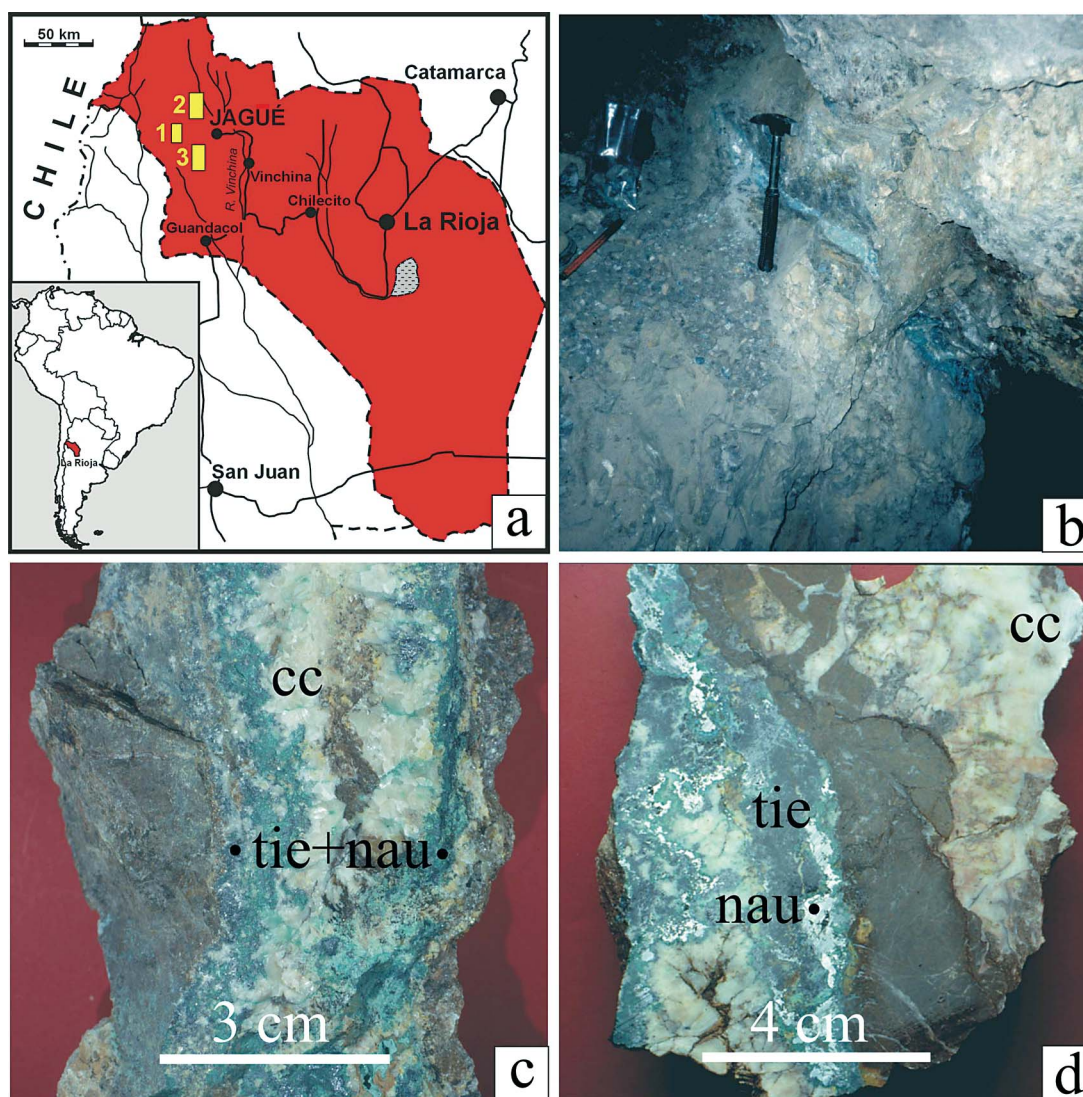


FIG. 1. a) Province of La Rioja (in red) and its selenide districts: 1) El Chire, 2) Los Llantenes, 3) Cerro Cacho (including Las Asperzas, Tuminico). b) El Chire mine, underground, with an exposure of the oxidized selenide vein. c) Symmetrically banded selenide vein in altered country-rock. The coating of malachite is a consequence of weathered primary copper selenides. Symbols: tie tiemannite, nau naumannite, cc calcite. d) Polished slab of a brecciated vein section with fragments of country rock. The metallic phases are an intergrowth of naumannite–tiemannite. Other symbols as in c).

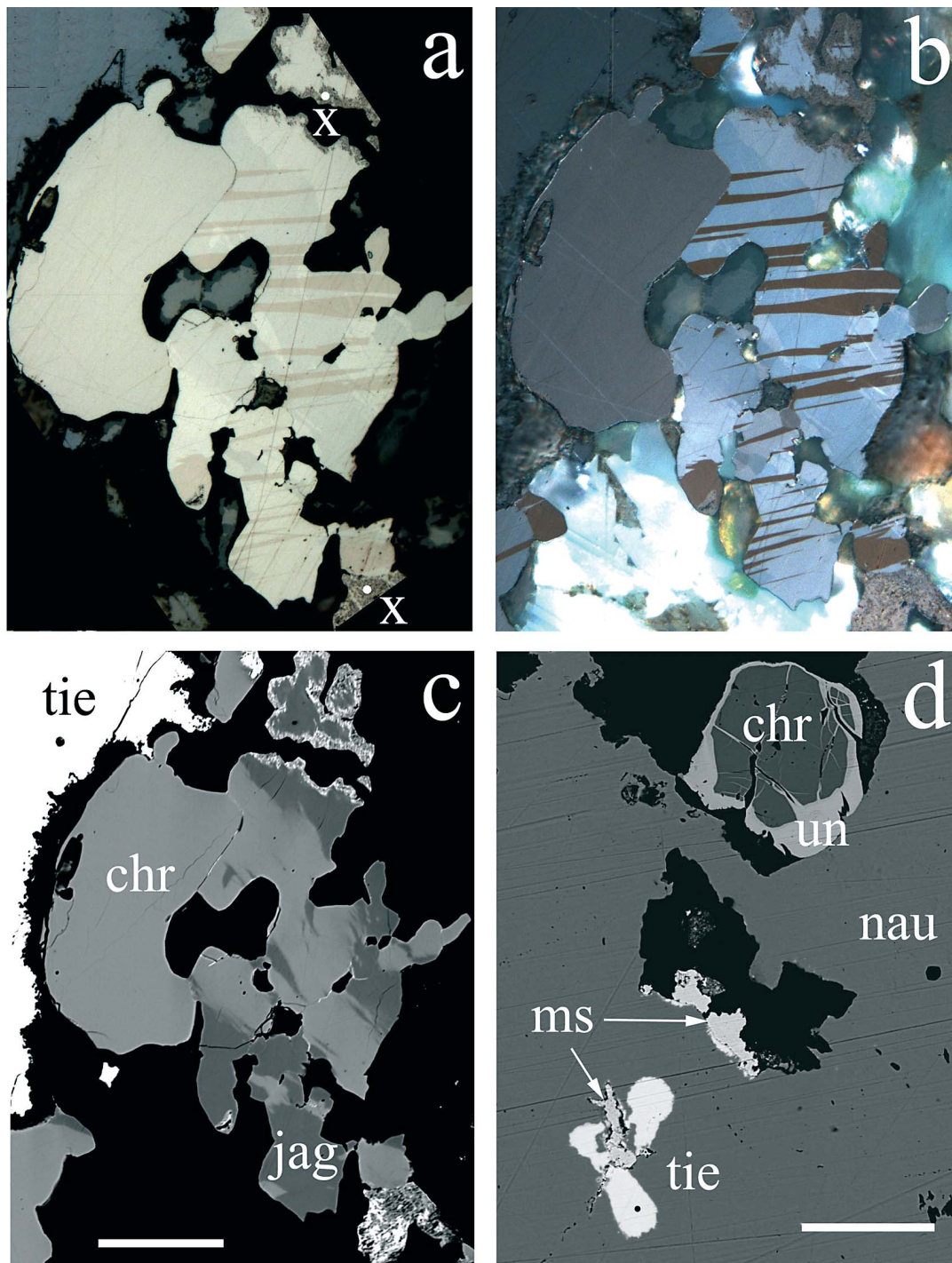


FIG. 2. a) Lobate grains of chrisstanleyite, which randomly is replaced by jaguéite, in calcite; tie is tiemannite. The Cu–Ag–Hg–Pd–(?)O compound (x) rims jaguéite and chrisstanleyite. Oil immersion, uncrossed polars. EC 2002. b) Same as a) but X polars. c) Same as a) but BSE image; bars indicate 50  $\mu$ m. d) An unnamed (un) Ag(Cu)–Hg–Pd–Se compound rims chrisstanleyite; mercurian silver (ms) is closely associated with tiemannite.

structure. Fine grain-sizes and complicated interlocking features cause a problem in obtaining accurate analyses, and preclude attempts to extract them for further study.

Jaguéite has a distinctly creamy-yellowish color, to the naked eye strongly resembling that of pyrite, especially where adjacent to tiemannite, which then is greyish with a weak violet tint. The new mineral species is opaque, has a metallic luster, a black streak, is brittle and has an uneven fracture. Neither cleavage nor parting is evident in polished sections. The VHN<sub>25</sub> measured from seven indentations is in the range 464–772, mean 612 kg/mm<sup>2</sup>, thus distinctly higher than VHN<sub>100</sub> for chrisstanleyite (mean 395 kg/mm<sup>2</sup>; Paar *et al.* 1998) and the compositionally related mineral oosterboschite (VHN<sub>50–100</sub> = 340 kg/mm<sup>2</sup>; Johan *et al.* 1970). Using the equation by Young & Millmann (1964), a corresponding Mohs hardness of about 5 can be calculated.

It turned out to be impossible to extract pure grains of sufficient size to determine the density of the mineral. The density calculated on the basis of the empirical formula and  $Z = 2$  is 8.02 g/cm<sup>3</sup>, which is distinctly lower than the densities of the related minerals chrisstanleyite and oosterboschite (8.33 and 8.48 g/cm<sup>3</sup>, respectively).

#### OPTICAL PROPERTIES

In plane-polarized light (~3200 K), the reflectance of jaguéite is slightly higher than that of chrisstanleyite with which it is generally associated. The differences, however, are quite small (less than 2%) and barely detectable.

Jaguéite is opaque and lacks internal reflections. The bireflectance is weak to moderate (air) and more distinct in oil. The mineral is pleochroic from a light buff to a creamy buff. Between crossed polars, it is distinctly anisotropic (enhanced in oil), and the rotation tints (from extinction) are: brownish – bluish – greenish. The most

characteristic feature is twinning, which is typified by spindle-shaped lamellae of varying thickness in one direction. These were likely formed mechanically. Deformation or mechanical twins have variable thickness, of branching and tapering character (Blenkinsop 2000). This kind of twinning is distinctly different from that reported for oosterboschite (Johan *et al.* 1970, p. 477), which shows fine polysynthetic and parquet-like lamellae, which are generally straight and of constant thickness, and may be interpreted as growth twins.

The reflectance measurements (400–700 nm) of jaguéite were made at intervals of 20 µm using a Leitz MPV–SP microscope-spectrophotometer and a WTiC reflectance standard for the air and oil (Leica  $N_D = 1.518$ ) determinations (Table 2, Fig. 3). The spectra are compared with those of chrisstanleyite from Hope's Nose, United Kingdom (Paar *et al.* 1998) and oosterboschite, Musonoi, Democratic Republic of Congo (Johan *et al.* 1970). The reflectances of chrisstanleyite from El Chire, which differs by its copper content from the copper-free chrisstanleyite from Hope's Nose, are not included in Figure 3 because they do not show apparent deviations from those of jaguéite.

The shape of the spectra for jaguéite and chrisstanleyite (Hope's Nose) is very similar, with a slight increase of R toward higher wavelengths (jaguéite). Jaguéite is slightly more strongly reflecting (<1–3%) and bireflectant ( $\leq 2\%$ ) than chrisstanleyite. The spectra of jaguéite ( $R_1$ ) and chrisstanleyite are "bracketed" by those of oosterboschite, which has a distinctly different dispersion (Fig. 3).

#### CHEMICAL DATA

Quantitative chemical data for jaguéite and the associated phases were obtained with an electron microprobe (JEOL Superprobe JXA–8600, controlled by LINK–eXL system, operated at 25 kV, 30 nA, 20 s counting time for peaks and 7 s for background). The following natural (n) and synthetic (s) standards and X-ray lines were used: n–Cu<sub>3</sub>Se<sub>2</sub> (CuK $\alpha$ , SeK $\alpha$ ), n–HgS (HgL $\alpha$ , SK $\alpha$ ), n–Sb<sub>2</sub>S<sub>3</sub> (SbL $\alpha$ ) and pure metals for AgL $\beta$  and PdL $\alpha$ . The raw data were corrected with the on-line ZAF–4 procedure. Results of two to 12 point analyses obtained from a homogeneous grain or an individual phase in an aggregate were averaged. These mean compositions are compiled in Table 3. The mean analytical result obtained for the jaguéite grain used for the structure study, as well as results illustrating the small range in composition of jaguéite and chrisstanleyite, are compared with literature data from Nickel (2002) and Johan *et al.* (1970). The empirical formula of jaguéite, normalized to nine atoms per formula unit (*apfu*), which is the content of the two asymmetric units as determined by the structure analysis, is (Cu<sub>1.91</sub>Ag<sub>0.11</sub>) $\Sigma_{2.02}$ Pd<sub>3.05</sub>Se<sub>3.93</sub>. The simplified formula of jaguéite can be written Cu<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>. It requires: Cu 16.68, Pd 41.88, Se 41.44, total 100.0 wt.%. The results of all individual analyses

TABLE 2. REFLECTANCE DATA (IN AIR AND OIL) FOR JAGUÉITE

$\lambda$ (nm)	$R_1$ %	$R_2$ %	${}^mR_1$ %	${}^mR_2$ %
400	36.1	46.0	23.7	28.5
420	37.5	46.9	24.5	29.6
440	39.0	48.0	25.8	30.6
460	40.5	49.2	26.7	31.7
470	<b>41.0</b>	<b>50.1</b>	<b>27.0</b>	<b>31.9</b>
480	41.7	50.6	27.6	32.3
500	42.8	51.5	28.2	33.0
520	43.5	51.8	28.7	33.5
540	44.0	51.8	29.2	33.8
546	<b>44.1</b>	<b>51.8</b>	<b>29.2</b>	<b>33.8</b>
560	44.4	51.8	29.3	33.7
580	44.6	51.7	29.4	33.7
589	44.6	<b>51.7</b>	<b>29.4</b>	<b>33.7</b>
600	44.7	51.8	29.7	33.7
620	45.0	51.9	29.9	33.7
640	45.1	52.0	30.1	34.0
650	<b>45.1</b>	<b>52.0</b>	<b>30.2</b>	<b>34.1</b>
660	45.3	52.0	30.3	34.2
680	45.6	52.1	30.4	34.3
700	45.8	52.3	30.7	34.3

TABLE 3. COMPOSITION OF JAGUÉITE, CHRISSTANLEYITE, ASSOCIATED PHASES FROM EL CHIRE, ARGENTINA, AND LITERATURE DATA

No.	Mineral	Location/Sample	<i>n</i> <sup>1</sup>	Cu	Ag	Pd	Hg	S	Se	Total	<i>N</i> <sup>2</sup>
1	jaguéite	El Chire, su-2002*	8	15.70(15)	1.59(9)	42.04(18)			40.15(16)	99.48(38)	9
2	jaguéite	El Chire, 98/18-d	4	14.35(18)	3.19(9)	41.21(6)			40.90(23)	99.64(29)	9
3	jaguéite, theoretical composition			16.68		41.88			41.44	100	9
4	chrisstanleyite	El Chire, su-2002	12	3.09(14)	20.55(25)	38.64(14)			37.54(16)	99.84(38)	9
5	chrisstanleyite	El Chire, 98/18-h	9	4.42(18)	18.67(35)	38.38(15)			38.62(25)	100.09(39)	9
6	chrisstanleyite, theoretical composition			25.36		37.52			37.12	100	9
7	aguilarite	El Chire, 98/18	5	1.43(28)	79.88(47)		1.04(43)	5.90(25)	11.58(57)	99.79(26)	6
8	mercurian Ag	El Chire, 01/119	2	0.67(19)	51.63(21)		47.29(5)		n.d.	99.80(2)	3
9	unnamed 1	El Chire, 98/18	5	2.14(4)	44.59(26)		33.58(28)	7.68(16)	11.63(15)	99.62(19)	18
10	unnamed 2	El Chire, 01/119	3	1.29(1)	40.50(16)	14.28(11)	28.07(24)		15.74(7)	99.88(4)	13
11	jaguéite	Pilbara <sup>3</sup>		16.80	0.92	40.09			41.33	99.17	9
12	chrisstanleyite	Pilbara <sup>3*</sup>		2.05	24.07	35.48	0.36		38.50	101.16	9
13	oosterboschite	Musunoi <sup>4</sup>		16.90		44.50			39.00	100.40	5

Notes: The compositions are expressed in terms of weight % constituents; standard deviation is shown in parentheses; <sup>1</sup> number of spot analyses; <sup>2</sup> number of atoms per formula unit, used for formula calculations. \* Crystal used for structural investigation. <sup>3</sup> Nickel (2002); <sup>3\*</sup> contains 0.7 wt.% Pt; <sup>4</sup> mean result of two analyses from Johan *et al.* (1970).

Empirical formulae: 1) (Cu<sub>1.91</sub>Ag<sub>0.11</sub>)Σ<sub>2.02</sub>Pd<sub>3.05</sub>Se<sub>3.95</sub>, 2) (Cu<sub>1.75</sub>Ag<sub>0.23</sub>)Σ<sub>1.98</sub>Pd<sub>3.00</sub>Se<sub>4.02</sub>, 3) Cu<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>, 4) (Cu<sub>0.41</sub>Ag<sub>1.59</sub>)Σ<sub>2.00</sub>Pd<sub>3.03</sub>Se<sub>3.97</sub>, 5) (Cu<sub>0.57</sub>Ag<sub>1.43</sub>)Σ<sub>2.00</sub>Pd<sub>2.97</sub>Se<sub>4.03</sub>, 6) Ag<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>, 7) (Cu<sub>0.12</sub>Ag<sub>4.04</sub>Hg<sub>0.03</sub>)Σ<sub>4.19</sub>(S<sub>1.01</sub>Se<sub>0.80</sub>)Σ<sub>1.81</sub>, 8) (Cu<sub>0.04</sub>Ag<sub>1.98</sub>)Σ<sub>2.03</sub>Hg<sub>0.97</sub>, 9) (Cu<sub>0.61</sub>Ag<sub>7.43</sub>)Σ<sub>8.04</sub>Hg<sub>3.01</sub>(S<sub>4.30</sub>Se<sub>2.65</sub>)Σ<sub>6.95</sub>, 10) (Cu<sub>0.30</sub>Ag<sub>5.62</sub>)Σ<sub>5.92</sub>Pd<sub>2.01</sub>Hg<sub>2.09</sub>Se<sub>2.98</sub>, 11) (Cu<sub>2.03</sub>Ag<sub>0.07</sub>)Σ<sub>2.10</sub>Pd<sub>2.89</sub>Se<sub>4.01</sub>, 12) (Cu<sub>0.33</sub>Ag<sub>1.84</sub>)Σ<sub>2.17</sub>(Pd<sub>2.76</sub>Hg<sub>0.02</sub>Pt<sub>0.03</sub>)Σ<sub>2.81</sub>Se<sub>4.03</sub>, 13) (Cu<sub>2.71</sub>Pd<sub>4.26</sub>)Σ<sub>6.97</sub>Se<sub>5.03</sub>.

of jaguéite and chrisstanleyite from El Chire, plotted in the diagram Pd–Cu–Ag (Fig. 4), together with literature data, indicate that jaguéite and chrisstanleyite form a limited solid-solution series.

X-RAY-DIFFRACTION DATA

The small size of the crystal extracted, the presence of twinning, and the small amount of material available, commonly intergrown with chrisstanleyite, restricted the X-ray studies to the use of a single-crystal diffractometer with an area-detector system. The crystal-structure determination (Topa *et al.*, in prep.) indicates that jaguéite is monoclinic, space group *P*2<sub>1</sub>/*c*, *a* 5.6719(45), *b* 9.9095(87), *c* 6.2636(55) Å, β 115.403(24)°, *V* 318.0(8)Å<sup>3</sup>, *Z* = 2, with all of its unit-cell parameters very close to those of chrisstanleyite (Paar *et al.* 1998). As powder data could not be obtained because of insufficient material, a powder pattern was calculated with PowderCell 2.3 software (Kraus & Nolze 1999) for Debye–Scherrer geometry and CuKα radiation (λ = 1.540598 Å), without the anomalous dispersion correction (Table 4), using cell parameters, space group, atom positions, site occupancies and isotropic displacement factors from the results of the single-crystal structure refinement. These data, together with the theoretical powder-diffraction pattern for chrisstanleyite (Fig. 5), illustrate the small, but clear, differences in *d*-values for the two minerals.

TABLE 4. CALCULATED POWDER-DIFFRACTION DATA FOR JAGUÉITE

<i>I</i> <sub>calc</sub>	<i>d</i> <sub>calc</sub>	<i>h k l</i>	<i>I</i> <sub>calc</sub>	<i>d</i> <sub>calc</sub>	<i>h k l</i>
15	4.551	1 1 0	1	1.878	2 2 1
16	4.476	1 1 1	18	1.871	0 5 1
1	3.728	0 2 1	24	1.866	2 4 1
2	3.562	1 2 0	2	1.864	0 4 2
5	3.525	1 2 1	4	1.856	3 0 2
1	3.028	1 1 1	2	1.849	1 5 0
14	2.853	0 3 1	4	1.840	1 1 1
6	2.829	0 0 2	1	1.836	2 2 3
22	2.776	1 3 0	13	1.825	3 1 2
23	2.759	1 3 1	2	1.785	1 3 2
17	2.726	2 1 1	13	1.781	2 4 0
100	2.676	1 2 1	9	1.763	1 4 2
64	2.630	1 2 2	1	1.762	1 3 3
8	2.562	2 0 0	12	1.751	2 2 1
31	2.508	2 0 2	6	1.738	2 2 2
5	2.480	2 1 0	3	1.708	3 0 0
1	2.478	0 4 0	3	1.683	3 1 0
5	2.461	2 2 1	2	1.670	1 5 2
2	2.432	2 1 2	2	1.652	0 6 0
8	2.291	1 3 1	1	1.649	3 1 3
3	2.276	2 2 0	1	1.638	0 3 3
27	2.269	0 4 1	2	1.629	3 1 1
10	2.262	1 3 2	2	1.618	3 3 2
3	2.238	2 2 2	2	1.615	3 2 0
1	2.230	1 4 0	1	1.611	1 4 2
3	2.221	1 4 1	1	1.594	1 4 3
1	2.074	1 1 2	5	1.590	2 0 2
2	2.039	1 1 3	4	1.572	1 6 0
4	2.024	2 3 0	2	1.570	2 4 1
19	1.988	2 1 1	1	1.570	2 1 2
1	1.954	1 4 1	10	1.569	1 6 1
27	1.950	1 2 2	1	1.552	2 0 4
15	1.938	2 1 3	1	1.546	1 1 3
3	1.936	1 4 2	2	1.545	2 4 3
36	1.920	1 2 3			

The data for jaguéite are: calculated *I* values, followed by calculated *d* (Å), based on the crystal-structure parameters (Topa *et al.* 2004).

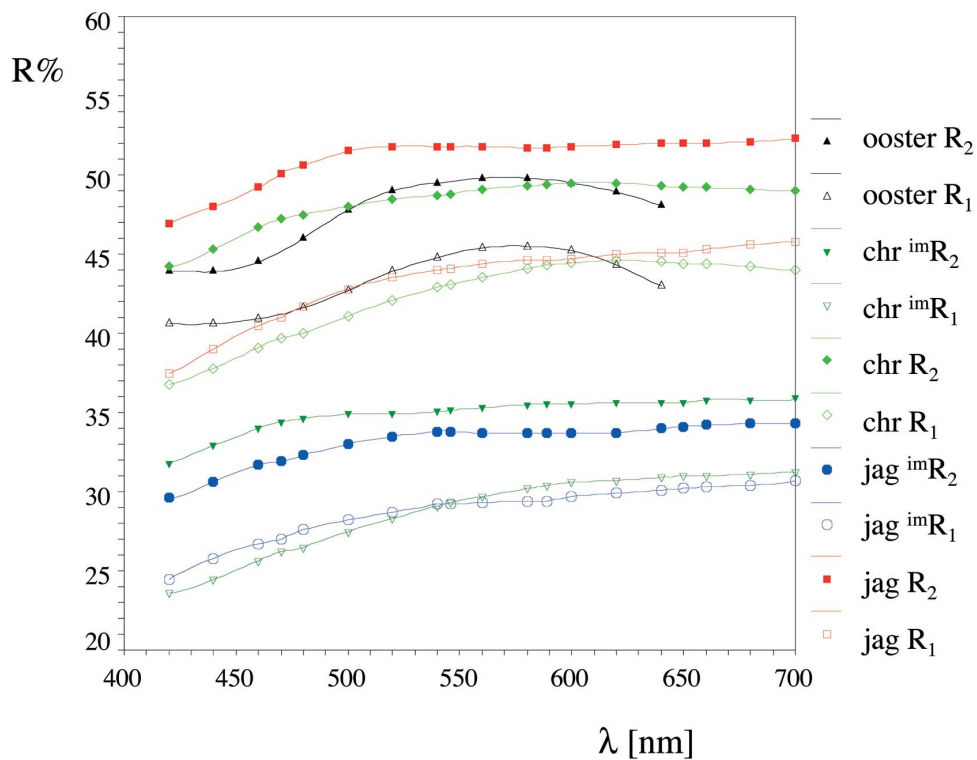


FIG. 3. Reflectance data for jaguéite, chrisstanleyite and oosterboschite.

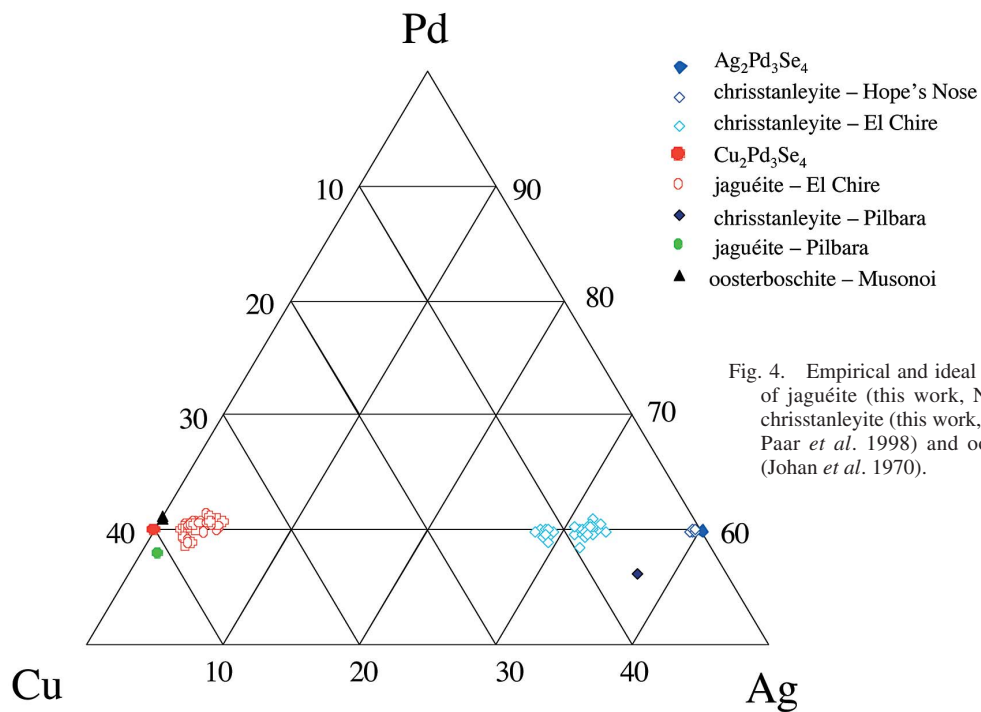


Fig. 4. Empirical and ideal compositions of jaguéite (this work, Nickel 2002), chrisstanleyite (this work, Nickel 2002, Paar *et al.* 1998) and oosterboschite (Johan *et al.* 1970).



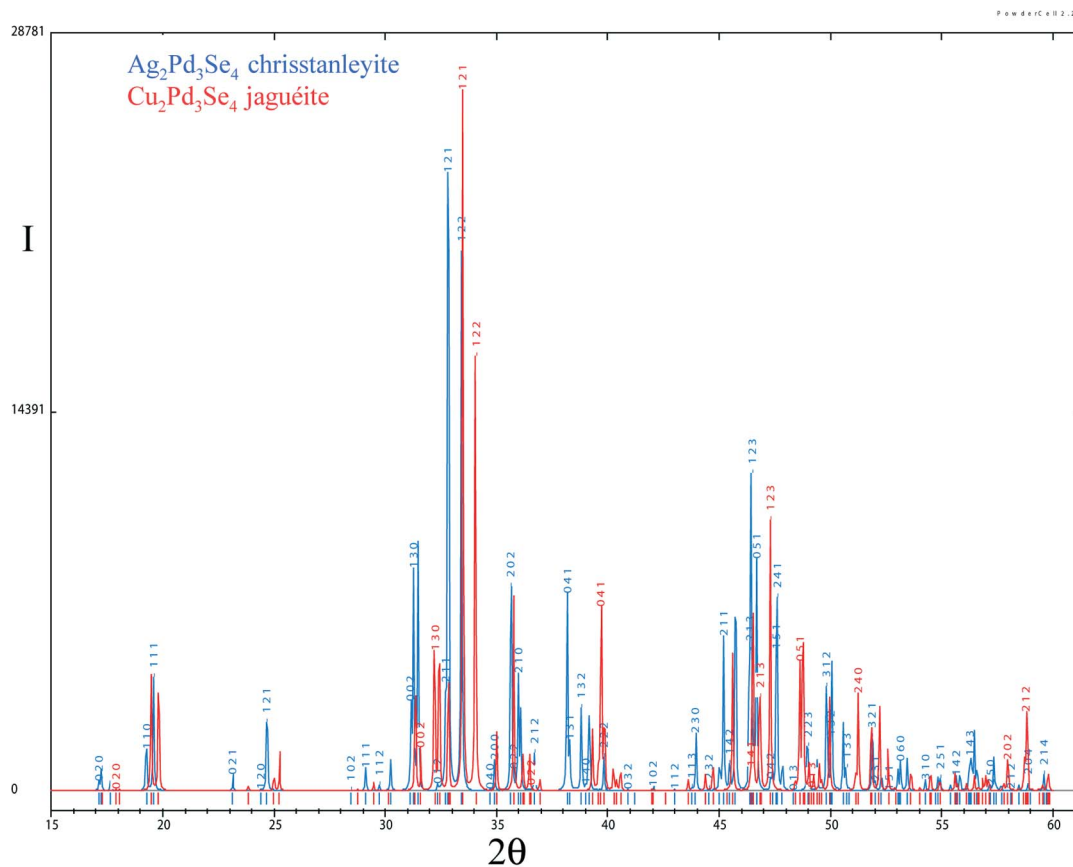


FIG. 5. Calculated powder-diffraction patterns for jaguéite and chrisstanleyite.

#### RELATED SPECIES

A Cu–Pd–Se mineral with a chemical composition very close to jaguéite was described by Nickel (2002), who also observed a phase which he identified as oosterboschite. Roberts *et al.* (2002) investigated ore concentrates from Musonoi and determined two compounds in the ternary system Cu–Pd–Se associated with verbeekite,  $\text{PdSe}_2$ . One compound is compositionally jaguéite. Routine X-ray investigations on this compound, however, gave a pattern very close to that of oosterboschite. The second compound penetrates verbeekite along fractures and corresponds to  $\text{CuPd}_2\text{Se}_3$ .

Jaguéite is the Cu-dominant analogue of chrisstanleyite. The monoclinic cell ( $P2_1/c$ ) of chrisstanleyite with a composition  $\text{Ag}_{1.6}\text{Cu}_{0.4}\text{Pd}_3\text{Se}_4$  has  $a$  5.675(4),  $b$  10.329(7),  $c$  6.340(4) Å and  $\beta$  115.13(1)° (Topa *et al.*, in prep.). Palladium atoms are coordinated by four selenium atoms in both structures, in a square coordination that is completed by one or two close Pd–Cu, and Pd–Ag contacts, respectively. The very irregular, elongate

tetrahedra of Cu and Ag, respectively, are the only elements differing appreciably in size, although not in shape, between the two structures. This difference is responsible for the distinction in  $b$  dimensions. Jaguéite and chrisstanleyite are isotypes, but the difference in the size of Cu and Ag polyhedra may lead to the apparent miscibility-gap between these compounds (Fig. 4).

Jaguéite is compositionally very similar to the mineral oosterboschite, which is the other natural compound in the ternary system Cu–Pd–Se. Although the ratio Pd/Cu (1.5) in jaguéite is very close to the Pd/Cu value (1.57) in oosterboschite, the  $Me/Se$  ratios differ considerably, *i.e.*, 1.25 in jaguéite and 1.4 in oosterboschite. There are also significant differences in the optical properties, especially in the dispersion of the two minerals (Fig. 3). The unit-cell parameters and the space group are different. A re-investigation of the holotype material of oosterboschite, especially an attempt to solve its crystal structure, would shed light on the possible relationship of the two species. Several efforts made to

obtain oosterboschite for study purposes, were unsuccessful, however.

In an ongoing investigation on the synthetic system Cu–Pd–Se, Karup-Møller & Makovicky (unpubl. data) have found  $\text{Cu}_2\text{Pd}_3\text{Se}_4$  to be a well-defined compound, clearly separated from the copper-containing selenides of palladium and maintaining its stoichiometric composition.  $\text{Cu}_2\text{Pd}_3\text{Se}_4$  has been synthesized at 300° and 400°C, but it is absent at 550° and 650°C.

#### ACKNOWLEDGEMENTS

Field studies and laboratory work, in Argentina and Austria, respectively, were funded by the Austrian Science Foundation (FWF) through grants P 11987 and 13974 to the first author. This support is gratefully acknowledged. The editorial care of R.F. Martin, as well as suggestions of N.J. Cook, J.A. Mandarino, A.R. Cabral and L. Bindi are very much appreciated. We owe sincere thanks to Gerhard Amann and Klaus Robl for assistance in the field. Georg Zagler is thanked for the reflectance measurements. Appreciation is extended to Winfried Waldhör for the preparation of high-quality polished sections, to Margit Ebner and Gudrun Riegler who typed the manuscript.

#### REFERENCES

- ANGELELLI, V. (1984): Yacimientos metalíferos de la República Argentina. *Comisión de investigaciones científicas, Provincia de Buenos Aires* **II**, 553-560.
- ASTINI, R.A., BENEDETTO, J.L. & VACCARI, N.E. (1995): The early Paleozoic evolution of the Argentine Precordillera as a Laurentian rifted, drifted, and collided terrane; a geodynamic model. *Geol. Soc. Am., Bull.* **107**, 253-273.
- BLENKINSOP, T. (2000): *Deformation Microstructures and Mechanisms in Minerals and Rocks*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- DE BRODTKORB, M.K., GAY, H.D. & SUREDA, R.J. (1990): Carboniferous epithermal mineralizing activity in the Precordillera. The polymetallic selenide–sulphide minerals of Los Llantenes mining district, La Rioja, Argentina. Eighth Int. Symposium on Andean Geodynamics (Grenoble, France), Extended Abstr., 66-67.
- \_\_\_\_\_, \_\_\_\_\_ & \_\_\_\_\_ (1993): Polymetallic selenide–sulphide minerals of the Los Llantenes mining district, La Rioja, Argentina. *Proc. 8<sup>th</sup> Quadrennial IAGOD Symp.* **1**, 119-125.
- CABRAL, A.R., LEHMANN, B., KWITKO-RIBEIRO, R. & CRAVO COSTA, C.H. (2002a): Palladium and platinum minerals from the Serra Pelada Au–Pd–Pt deposit, Carajás mineral province, northern Brazil. *Can. Mineral.* **40**, 1451-1463.
- \_\_\_\_\_, \_\_\_\_\_, \_\_\_\_\_, GALBIATTI, H.F. & PEREIRA, M.C. (2002b): Palladseite and its oxidation: evidence from Au–Pd vein-type mineralization (jacutinga), Cauê iron-ore mine, Quadrilátero Ferrífero, Minas Gerais, Brazil. *Mineral. Mag.* **66**, 327-336.
- CHAKRABARTI, D.J. & LAUGHLIN, D.E. (1981): The Cu–Se (copper–selenium) system. *Bull. Alloy Phase Diagrams* **2**, 305-315.
- CIPRIANI, C., BERNARDINI, G.P., CORAZZA, M., MAZZETTI, G. & MOGGI, V. (1993): Reinvestigation of natural and synthetic silver amalgams. *Eur. J. Mineral.* **5**, 903-914.
- CLARK, A.M. & CRIDDLE, A.J. (1982): Palladium minerals from Hope's Nose, Torquay, Devon. *Mineral. Mag.* **46**, 371-377.
- GUERRERO, M.A. (1969): Informe del distrito minero Los Llantenes, depto. Gral. Sarmiento La Rioja. Serv. Min. Nac. Buenos Aires, Argentina, Unpubl. Rep.
- JEDWAB, J. (1997): Minéralogie des métaux du groupe de platine au Shaba, Zaïre. In Colloque International CORNET. *Mém. Acad. R. Sci. Outre-Mer (Brussels)*, 325-355.
- \_\_\_\_\_, TARKIAN, M., CORNELISEN, B., MOËLO, Y. & DEUDON, C. (1999): Mineralogy of palladium, platinum, rhenium and gold in the sulfide ores of Shinkolobwe, Katanga, Congo. In Proc. of the 5<sup>th</sup> Biennial SGA Meeting and the 10<sup>th</sup> Quadrennial IAGOD Meeting, (London). A.A.Balkema, Rotterdam, The Netherlands (abstr., 171-174).
- JOHAN, Z. (1989): Merenskyite,  $\text{Pd}(\text{Te},\text{Se})_2$ , and the low-temperature selenide association from the Předbořice uranium deposit, Czechoslovakia. *Neues Jahrb. Mineral. Monatsh.*, 179-191.
- \_\_\_\_\_, PICOT, P., PIERROT, R. & VERBEEK, T. (1970): L'oosterboschite,  $(\text{Pd},\text{Cu})_7\text{Se}_5$ , une nouvelle espèce minérale, et la trogtalite cupro-palladifère de Musonoï (Katanga). *Bull. Soc. Fr. Minéral. Cristallogr.* **93**, 476-481.
- KRAUS, W. & NOLZE, G. (1999): *Powder Cell for Windows* (version 2.3). BAM, Berlin, Germany.
- KWITKO, R., CABRAL, A.R., LEHMANN, B., LAFLAMME, J.H.G., CABRI, L.J., CRIDDLE, A.J. & GALBIATTI, H.F. (2002): Hongshiite, PtCu, from itabirite-hosted Au–Pd–Pt mineralization (jacutinga), Itabira District, Minas Gerais, Brazil. *Can. Mineral.* **40**, 711-723.
- NICKEL, E.H. (2002): An unusual occurrence of Pd, Pt, Au, Ag and Hg minerals in the Pilbara Region of Western Australia. *Can. Mineral.* **40**, 419-433.
- PAAR, W.H., AMANN, G., SUREDA, R.J. & BRODTKORB, M.K. (2002b): Selenium mineralization associated with precious metals in the Sierra de Umango, Argentina. *Eighth Gen. Meeting, Int. Mineral. Assoc. (Edinburgh)*, Abstr., 265-266.
- \_\_\_\_\_, \_\_\_\_\_, TOPA, D. & SUREDA, R.J. (2000): Gold and palladium in the Sierra de Umango and Los Llantenes selenide districts, La Rioja, Argentina. *Mem. XIV Congreso Geológico Boliviano (La Paz)*, 465-469.

- \_\_\_\_\_. BRODTKORB, M.K. DE, TOPA, D. & SUREDA, R.J. (2004): Palladium, platinum, gold and silver in selenide districts of NW-Argentina. *Thirty-second Int. Geol. Congress (Florence), Abstr.*, 277.
- \_\_\_\_\_. ROBERTS, A.C., CRIDDLE, A.J. & TOPA, D. (1998): A new mineral, chrisstanleyite,  $\text{Ag}_2\text{Pd}_3\text{Se}_4$ , from Hope's Nose, Torquay, Devon, England. *Mineral. Mag.* **62**, 257-264.
- \_\_\_\_\_. TOPA, D., MAKOVICKY, E. & CULETTO, F.J. (2005): Milotaite,  $\text{PdSbSe}$ , a new palladium mineral, from Předbořice, Czech Republic. *Can. Mineral.* **43** (in press).
- \_\_\_\_\_. \_\_\_\_\_, ROBERTS, A.C., CRIDDLE, A.J., AMANN, G. & SUREDA, R. (2002a): The new mineral species brodtkorbite,  $\text{Cu}_2\text{HgSe}_2$ , and the associated selenide assemblage from Tuminico, Sierra de Cacho, La Rioja, Argentina. *Can. Mineral.* **40**, 225-237.
- ROBERTS, A.C., PAAR, W.H., COOPER, M.A., TOPA, D., CRIDDLE, A.J. & JEDWAB, J. (2002): Verbeekite, monoclinic  $\text{PdSe}_2$ , a new mineral from the Musonoi Cu-Co-Mn-U mine, near Kolwezi, Shaba Province, Democratic Republic of Congo. *Mineral. Mag.* **66**, 173-179.
- STANLEY, C.J., CRIDDLE, A.J., FÖRSTER, H.J. & ROBERTS, A.C. (2002): Tischendorfite,  $\text{Pd}_8\text{Hg}_3\text{Se}_9$ , a new mineral species from Tilkerode, Harz Mountains, Germany. *Can. Mineral.* **40**, 739-745.
- \_\_\_\_\_. \_\_\_\_\_ & LLOYD, D. (1990): Precious and base metal selenide mineralization at Hope's Nose, Torquay, Devon. *Mineral. Mag.* **54**, 485-493.
- WALLIS, E. (1994): *Erzparagenetische und mineralchemische Untersuchung der Selenide im Harz*. Unpubl. Diploma thesis, University of Hamburg, Hamburg, Germany.
- YOUNG, B.B. & MILLMAN, A.P. (1964): Microhardness and deformation characteristics of ore minerals. *Trans. Inst. Mining Metall.* **73**, 437-466.

Received April 8, 2004, revised manuscript accepted August 13, 2004.