

Hansblockite, (Cu,Hg)(Bi,Pb)Se₂, the monoclinic polymorph of grundmannite: a new mineral from the Se mineralization at El Dragón (Bolivia)

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ABSTRACT

Hansblockite, ideally (Cu,Hg)(Bi,Pb)Se₂, is a new selenide from the El Dragón mine, Bolivia. It typically occurs in thin subparallel plates intergrown with two unnamed Cu–Hg–Pb–Bi–Se species, clausthalite, Co-rich penroseite and petrovicite. It also forms subhedral to anhedral grains up to 150 µm long and 50 µm wide. Hansblockite is non-fluorescent, black and opaque with a metallic lustre and black streak. It is brittle, with an irregular fracture and no obvious parting and cleavage. The VHN₂₀ values range from 37 to 50 (mean 42) kg mm⁻² (Mohs hardness 2–2½). In plane-polarized incident light, hansblockite is cream to light grey in colour, weakly bireflectant and weakly pleochroic from greyish cream to cream. Under crossed polars, hansblockite is weakly anisotropic with khaki to pale blue rotation tints. The reflectance values in air for the Commission on Ore Mineralogy (COM) standard wavelengths are: 47.3–48.1 (470 nm), 47.4–49.9 (546 nm), 47.1–49.0 (589 nm) and 46.6–48.5 (650 nm). The mean composition is Cu 9.31, Ag 0.73, Hg 11.43, Pb 3.55, Ni 0.17, Co 0.03, Bi 31.17, Se 34.00, total 100.39 wt.%. The mean empirical formula (based on 4 apfu) is (Cu_{0.68}Hg_{0.27}Ag_{0.03}Ni_{0.01})_{Σ=0.99}(Bi_{0.69}Pb_{0.31})_{Σ=1.00}Se_{2.01}. The simplified formula is (Cu,Hg)(Bi,Pb)Se₂. Hansblockite is monoclinic, space group *P2₁/c*, with *a* = 6.853(1), *b* = 7.635(1), *c* = 7.264(1) Å, β = 97.68(1)°, *V* = 376.66(9) Å³ and *Z* = 4. Density is 8.26 g cm⁻³. The five strongest powder X-ray diffraction lines [*d* in Å (*I*/*I*₀) (*hkl*)] are: 3.97 (90) (111), 3.100 (40) ($\bar{1}$ 21), 2.986 (100) ($\bar{2}$ 11), 2.808 (50) (112) and 2.620 (50) (022). Hansblockite represents the monoclinic polymorph of grundmannite, CuBiSe₂, with Hg and Pb being essential in stabilizing the monoclinic structure via the coupled substitution Cu⁺ + Bi³⁺ ⇌ Hg²⁺ + Pb²⁺. The mineral name is in honour of Hans Block (1881–1953), in recognition of his important role in boosting Bolivian ore mining.

KEYWORDS: hansblockite, new mineral species, chemical composition, crystal structure, selenium, El Dragón, Bolivia.

Introduction

THE Andes of Bolivia host two volumetrically minor, but mineralogically important selenide occurrences: Pacajake, district of Hiaco de Charcas, and El Dragón, Province of Antonio Quijarro, both in the

Department of Potosí. The geology and ore mineralization of the El Dragón mine was first explored in detail by Grundmann *et al.* (1990). Recently, it received renewed attention as the type locality of eldragónite, Cu₆BiSe₄(Se₂) (Paar *et al.*, 2012) and grundmannite, CuBiSe₂ (Förster *et al.*, 2016), and the discovery of the two new Se-bearing secondary species favreaite, PbBiCu₆O₄(SeO₃)₄(OH)·H₂O (Mills *et al.*, 2014) and alfredopetrovite, Al₂(Se⁴⁺O₃)₃·6H₂O (Kampf *et al.*, 2016).

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In addition to the recently described Cu–Bi sulfosalts eldragónite and grundmannite, three unnamed species of the Cu–Hg–Pb–Bi–Se system have been discovered in samples from the El Dragón mine, labelled phases ‘A’, ‘B’ and ‘C’ (cf. Paar *et al.*, 2012; Förster *et al.*, 2016). The new selenium mineral, hansblockite (Cu,Hg)(Bi,Pb)Se₂, described in this paper resembles phase ‘B’, for which initially the ideal formula Cu₂HgPbBi₂Se₆ (normalized to 12 atoms per formula unit, apfu) was proposed (Paar *et al.*, 2012; Förster *et al.*, 2016).

The new species hansblockite and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association, proposal IMA2015-103. The holotype specimen, which is the polished section from which the grain used for crystal-structure determination was obtained, is stored in the collections of the Natural History Museum, London, catalogue number BM 2015, 136. Cotype material, consisting of a hansblockite-bearing section, is deposited within the Mineralogical State Collection Munich (Mineralogische Staatssammlung München, Museum ‘Reich der Kristalle’), inventory number MSM 73573.

The name is in honour of Hans Block (1881–1953), in recognition of his contribution to fostering Bolivian ore mining. Born in Stassfurt, Alemania, Germany, he emigrated to Bolivia in 1904, when he was contracted by the Compañía Huanchaca de Bolivia, the plant operator for the Pulacayo mine. He was later administrator, manager, and owner of several mines, among them the Compañía Minera Gallofa Consolidada de Colquechaca (e.g. Block, 1937; Block and Ahlfeld, 1937). In 1945, Hans Block became a Professor of the Facultad Nacional de Ingeniería in Oruro. In 1952, he was appointed to the Commission for the Nationalization of the Mines.

It is important to note that Herzenberg and Ahlfeld (1935) named a mineral from the lead-silver mine Hiaco, Colquechaca, Bolivia in honour of Hans Block ‘blockite’. Later, Bannister and Hey (1937) demonstrated that ‘blockite’ was identical to penroseite and concluded that the mineral name ‘blockite’ should be discredited. To avoid confusion with two different blockite names in the literature, the name hansblockite was proposed for the present new selenide.

Geological setting

The El Dragón selenide occurrence is situated in southwestern Bolivia, in the Cordillera Oriental,

some 30 km southwest of Cerro Rico de Potosí. The abandoned El Dragón mine (entrance and dump) is located 19°49'23.90" S, 65°55'00.60" W, at an altitude of 4160 m above sea level. The very small longitudinal extension (maximum 15-m-long gallery) of the El Dragón ore vein and its low silver content (averaging to 0.06 wt.% Ag) have probably discouraged further exploitation of the occurrence.

The adit of the El Dragón mine is on the orographic left side of the Rio Jaya Mayu, cutting through a series of thinly-stratified, pyrite-rich black shales and reddish-grey, hematite-bearing siltstones of probably Devonian age, dipping 40° to the north. The almost vertical ore vein is located in the centre of a 1.5-m-wide shear zone (average trend 135 degrees) with shifts of a few cm. In 1988, the selenium mineralization consisted of a single vein, ranging mostly from 0.5–2 cm in thickness.

The El Dragón mineralization is composed of a complex assemblage of primary and secondary minerals, among which Se-bearing phases are most prominent. The full list of minerals recorded from El Dragón is given on mindat.org at <http://www.mindat.org/loc-353.html>. Grundmann *et al.* (1990) and Paar *et al.* (2012) provided detailed descriptions of the entire mineralization.

Appearance and physical properties

Hansblockite typically occurs in lath-shaped thin plates (up to 100 µm long and 10 µm wide) intimately (subparallel) intergrown with unnamed phase ‘A’ (empirical formula Cu₅HgPb₂Bi₃Se₁₀; Paar *et al.*, 2012) and, less frequently, with unnamed phase ‘C’ (empirical formula Cu₄HgBi₄Pb₂Se₁₁; Förster *et al.*, 2016, their figure 2d–e), forming an angular network of tabular hansblockite crystals (Fig. 1). Among these species of the Cu–Hg–Pb–Bi–Se system forming these multi-phase aggregates, phase ‘A’ generally appears to have crystallized earliest in the cores, partially overgrown by hansblockite predominantly forming the rims (Fig. 1). The relatively rare and small grains of phase ‘C’ (max. 20 µm × 20 µm) are the youngest relatively, precipitated in the interstices between the unoriented hansblockite/phase ‘A’ laths, together with Co-rich penroseite (NiSe₂), umangite (Cu₂Se₃), kloekmannite (CuSe), watkinsonite (ideally Cu₂PbBi₄Se₈) and clauthalite (PbSe) (cf. Figs 3, 4). Hansblockite-crystal aggregates cement (usually together with clauthalite, umangite, kloekmannite, eldragónite and co-

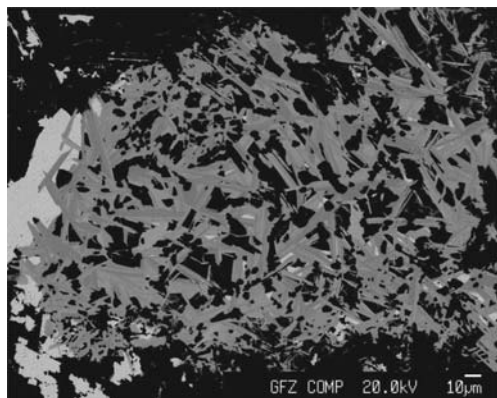


FIG. 1. Back-scattered electron (BSE) image, demonstrating the angular network-like intersetal texture typical for hansblockite-bearing mineral aggregates. Lath-shaped thin plates of hansblockite (light grey) overgrowing elongated plates of unnamed phase 'A' selenide (dark grey), which predate hansblockite and were deposited in the core. The bright mineral represents clausthalite.

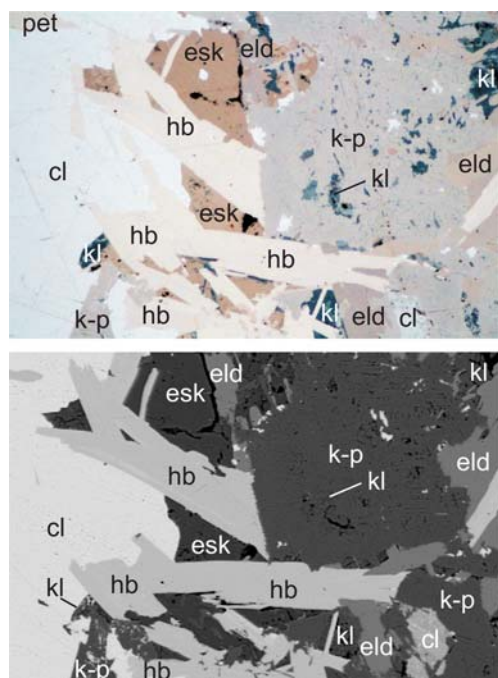


FIG. 2. Reflected light (*upper*) and BSE (*lower*) images of hansblockite (hb) in association with clausthalite (cl), krut'aite-penroseite solid solution (k-p), eskebornite (esk), klockmannite (kl), eldragónite (eld) and petrovicite (pet). Horizontal field of view is $\sim 200 \mu\text{m}$. The crystal used for structural analysis was separated from this area.

rich penroseite) shrinkage cracks or fill interstices in brecciated krut'aite-penroseite ($\text{CuSe}_2\text{-NiSe}_2$) solid solution.

Hansblockite locally forms subhedral to anhedral grains up to $200 \mu\text{m}$ long and $50 \mu\text{m}$ wide, occurring either solitary in the matrix or intergrown with watkinsonite, clausthalite, eldragónite, krut'aite-penroseite solid solution, eskebornite (CuFeSe_2), klockmannite and umangite (Fig. 2). Minerals occasionally found in grain-boundary contact are petrovicite ($\text{Cu}_3\text{HgPbBiSe}_5$), grundmannite (CuBiSe_2) and native gold. Hansblockite partially replaces umangite, klockmannite, eskebornite, and is itself altered by late klockmannite, athabascaite (Cu_5Se_4), and late fracture-filling chalcopyrite and covellite. Secondary minerals adjacent to hansblockite encompass quartz, dolomite, calcite, goethite, lepidocrocite, chalcomenite, molybdomenite, olsacherite, schmiederite, ahlfeldite, favreaite, felsőbányaite and allophane. Berzelianite (Cu_{2-x}Se) and bellidoite (Cu_2Se), previously mentioned by Grundmann *et al.* (1990), were not detected in any samples from El Dragón.

Hansblockite was observed in $\sim 30\%$ out of 180 microscopically studied polished sections from El Dragón, but it only occurred relatively frequently in 10%. Homogenous crystals are rare; typical are intimate intergrowths with phase 'A' down to the nm-scale.

Hansblockite is non-fluorescent, black and opaque with a metallic lustre and black streak. It is brittle, with an irregular fracture and no obvious parting and cleavage. The mean Vickers hardness number (VHN) for a 20 g load is 42 kg mm^{-2} (range 37–50), corresponding to a Mohs hardness of 2–2½. Density could not be measured because of the small grain size. Density calculated on the basis of the mean chemical composition and unit-cell parameters derived from the single-crystal X-ray study is 8.26 g cm^{-3} .

Optical properties

Optical properties of hansblockite are shown in Figs 3 and 4. In plane-polarized incident light, hansblockite is cream to light grey in colour, slightly birefractant and slightly pleochroic from greyish cream to cream. The mineral shows no internal reflections. Under crossed polars, hansblockite is weakly anisotropic, with khaki to pale blue rotation tints. Under crossed polars, the differences in colour are blurred. To see the microstructural properties more clearly, the

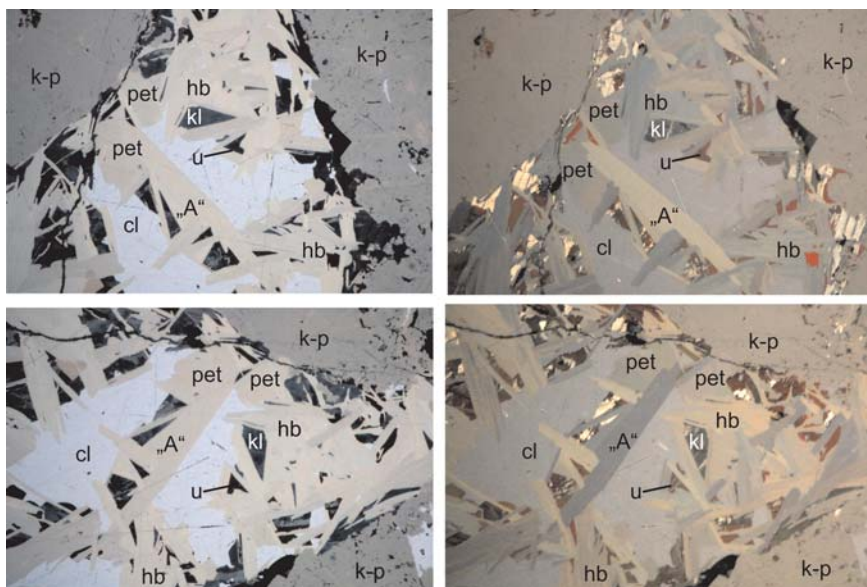


FIG. 3: Reflected light images (each 200 μm wide) of hansblockite and associated minerals. (*Left*) Plane polarized light; (*right*) partly crossed polarizers; (*upper*) and (*lower*) row correspond to different extinction rotations. hb = hansblockite, 'A' = phase 'A', pet = petrovicite, cl = clausenthalite, u = umangite, kl = kloekmannite, k-p = krut'aite-penroseite solid solution. In plane-polarized incident light, hansblockite is cream to light grey in colour, slightly bireflectant and slightly pleochroic from greyish cream to cream. The mineral shows no internal reflections. Under crossed polars, hansblockite is weakly anisotropic with khaki to pale blue rotation tints.

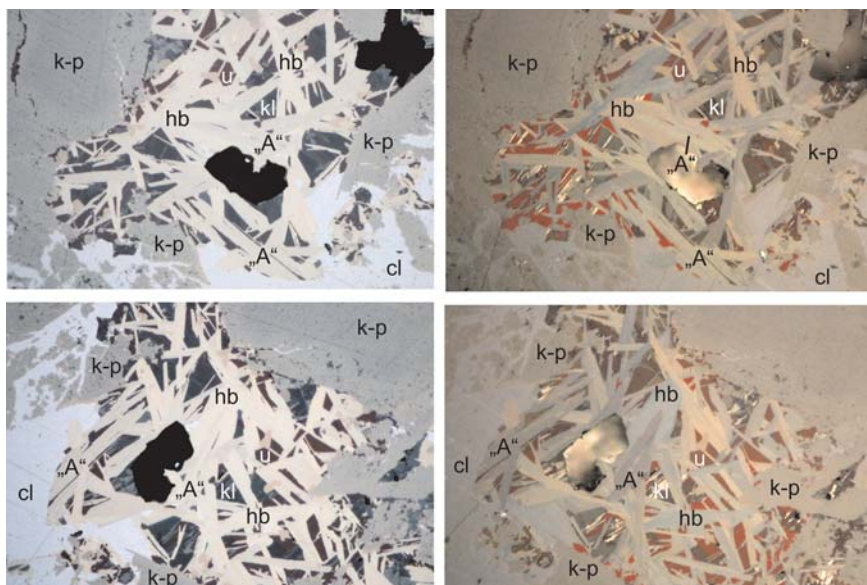


FIG. 4: Reflected light images (each 200 μm wide) of hansblockite and associated minerals. (*Left*) Plane polarized light; (*right*) partly crossed polarizers; (*upper*) and (*lower*) row correspond to different extinction rotations. See Fig. 3 for abbreviations of mineral names. Note the overgrowth of hansblockite on phase 'A' demonstrated well in the right hand side image of the lower row.

respective microphotographs for Figs 3 and 4 were taken under partly crossed polars.

Quantitative reflectance data for hansblockite were obtained in air relative to a Zeiss WTiC standard using a J and M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. Measurements were made on unoriented grains at extinction positions leading to designation of R_1 (minimum) and R_2 (maximum). The results are listed in Table 1 (together with the calculated colour values) and illustrated graphically in Fig. 5.

Chemical composition

All primary minerals from El Dragón were analysed routinely for concentrations of Cu, Ag, Pb, Hg, Fe, Co, Ni, As, Sb, Bi, S and Se. Quantitative chemical analyses were conducted in WDS mode, using a JEOL thermal field-emission-type electron probe X-ray microanalyser (FE-EPMA) JXA-8500F (HYPERPROBE) at Deutsches GeoForschungs Zentrum GFZ, Potsdam, Germany. The probe was operated at 20 kV, 20 nA; the beam size was 1–2 μm . The counting time on peak was 20–40 s,

TABLE 1. Reflectance data and colour values for hansblockite.*

λ (nm)	R_1 (%)	R_2 (%)	λ (nm)	R_1 (%)	R_2 (%)
400	46.7	46.9	560	47.3	49.0
420	46.9	47.1	580	47.2	49.0
440	47.1	47.4	589	47.1	49.0
460	47.3	47.9	600	47.0	48.9
470	47.3	48.1	620	46.9	48.8
480	47.4	48.4	640	46.7	48.6
500	47.4	48.7	650	46.6	48.5
520	47.4	48.9	660	46.5	48.4
540	47.4	49.0	680	46.4	48.2
546	47.4	49.0	700	46.3	48.0

Colour values

	C illuminant		A illuminant	
	R_1	R_2	R_1	R_2
x	0.310	0.312	0.447	0.448
y	0.317	0.320	0.408	0.409
Y (%)	47.2	48.9	47.2	48.9
Δ_d	519	568	511	577
P_c (%)	0.2	1.5	0.2	1.8

*Wavelengths required by the Commission on Ore Mineralogy are given in bold.

with half that time on background on both sites of the peak. The following standards, emission lines and analysing crystals (in parentheses) were used: Cu – synthetic Cu-metal, $K\alpha$ (LIF); Ag – naumannite, $L\alpha$ (PETJ); Pb – clausthalite, $M\alpha$ (PETH); Hg – cinnabar, $L\alpha$ (LIF); Fe – pyrite, $K\alpha$ (LIF); Co – skutterudite, $K\alpha$ (LIF); Ni – pentlandite, $K\alpha$ (LIF); As – skutterudite, $L\alpha$ (TAP); Sb – stibnite, $L\alpha$ (PETJ); Bi – synthetic Bi_2Se_3 , $M\alpha$ (PETH); S – sphalerite, $K\alpha$ (PETJ); and Se – naumannite, $K\alpha$ (LIF). The CITZAF routine in the JEOL software, which is based on the $\phi(\rho Z)$ method (Armstrong, 1995), was used for data processing.

Hansblockite displays only weak variations in composition (Tables 2, 3). In addition to the major cations Cu, Hg, Pb, Bi and Se, the only other omnipresent minor elements are Ag (0.4–1.3 wt.%; probably substituted for monovalent Cu) and Ni, with concentrations between <0.1 and 0.6 wt.%. Trace amounts of Co (<0.1 wt.%) were detected occasionally. Copper and Hg, and Bi and Pb are antipathetically correlated, which argues for operation of the coupled substitution $\text{Hg}^{2+} + \text{Pb}^{2+} \leftrightarrow \text{Cu}^+ + \text{Bi}^{3+}$. The mean empirical formula (based on 4 apfu) of hansblockite is $(\text{Cu}_{0.68}\text{Hg}_{0.27}\text{Ag}_{0.03}\text{Ni}_{0.01})_{\Sigma=0.99}(\text{Bi}_{0.69}\text{Pb}_{0.31})_{\Sigma=1.00}\text{Se}_{2.01}$ ($n = 28$). The ideal formula is $(\text{Cu,Hg})(\text{Bi,Pb})\text{Se}_2$. Table 3 presents a compilation of representative results of electron-microprobe spot analyses of hansblockite and grundmannite, ideally CuBiSe_2 . Compositional data for other Cu–(Pb)–(Hg)–Bi–Se minerals from El Dragón (petrovicite, watkinsonite, eldragónite, unnamed phases ‘A’ and ‘C’) are reported in Förster *et al.* (2016, their table 3). The mean compositions of these phases, together with that of hansblockite, could be displayed, for instance, in the Cu – (Hg + Ag) – Bi ternary diagram (Fig. 6), demonstrating that hansblockite (previously phase ‘B’) is chemically distinct from phases ‘A’ and ‘C’.

Crystal structure

Powder X-ray diffraction data

The observed powder diffraction pattern (Table 4) of the same hansblockite fragment used for the single-crystal study (see below) was collected with a CCD-equipped diffractometer Xcalibur PX Ultra using $\text{CuK}\alpha$ radiation (50 kV and 40 mA – 5 hs exposure time). Crystal-to-detector distance was 7 cm. Data were processed using the *CrysAlis* software package version 1.171.31.2 (Oxford diffraction, 2006) running on the Xcalibur PX control PC. The unit-cell parameters obtained from

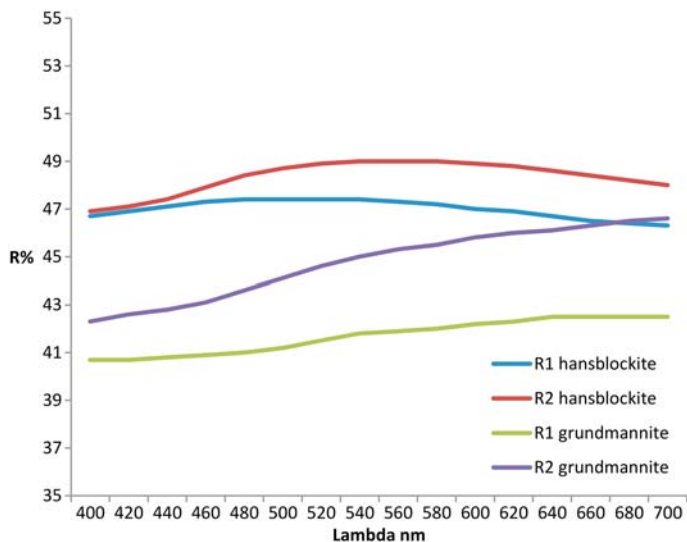


FIG. 5. Reflectance spectra of hansblockite and its orthorhombic dimorph grundmannite (Förster *et al.*, 2016).

powder data (pseudo-Gandolfi mode), using the software *UnitCell* (Holland and Redfern, 1997), are: $a = 6.8529(4)$, $b = 7.6388(5)$, $c = 7.2669(6)$ Å, $\beta = 97.662(5)^\circ$, $V = 377.01(3)$ Å³, in excellent agreement with those obtained from single-crystal data (cf., Table 5).

X-ray single-crystal data

A single hansblockite fragment ($35 \mu\text{m} \times 40 \mu\text{m} \times 55 \mu\text{m}$) was mounted on a 0.005-mm-diameter carbon fibre and checked on a CCD-equipped Oxford Diffraction Xcalibur 3 single-crystal diffractometer, operating with MoK α radiation ($\lambda = 0.71073$ Å). The unit-cell values are: $a = 6.853(1)$, $b = 7.635(1)$, $c = 7.264(1)$ Å, $\beta = 97.68(1)^\circ$, $V = 376.66(9)$ Å³. It showed an excellent diffraction quality and was used for full data collection

(Table 5). Intensity integration and standard Lorentz-polarization corrections were performed with the *CrysAlis RED* (Oxford Diffraction, 2006) software package. The program *ABSPACK* of the *CrysAlis RED* package (Oxford Diffraction, 2006) was used for the absorption correction. Reflection conditions were consistent with space group $P2_1/c$. The full-matrix least-squares program *SHELXL-97* (Sheldrick, 2008), working on F^2 , was used for the refinement of the structure. Given the close stoichiometry and the similarity in the unit-cell values, refinement was performed starting from the atomic coordinates reported for synthetic copper chalcogenides with the formula $LnCuQ_2$ (Ln = rare-earth element, Sc, Y; Q = S, Se, Te; Ijjaali *et al.*, 2004). Site-scattering values were refined using scattering curves for neutral species (Ibers and Hamilton, 1974) as follows: Cu vs. □ (structural vacancy) and Bi vs. □ for the cation sites and

TABLE 2. Composition of hansblockite (wt.%) from El Dragón.

	Cu	Ag	Hg	Pb	Co	Ni	Bi	Se	Total
mean	9.31	0.73	11.43	13.55	0.03	0.17	31.17	34.00	100.39
1 σ	0.43	0.25	0.30	0.24	0.03	0.14	0.26	0.32	0.46
min	8.14	0.42	11.00	13.04	0.00	0.03	30.76	33.53	99.40
max	10.01	1.29	12.23	14.23	0.07	0.65	31.77	34.76	101.77

Notes: 1 σ = 1 σ standard deviation.

TABLE 3. Representative results of electron-microprobe spot analyses of hansblockite and grundmannite from El Dragón.

Mineral:		hansblockite					grundmannite				
Element	d.l. (ppm)	1	2	3	4	5	6	7	8	9	10
Cu (wt.%)	250	8.95	9.80	9.37	9.63	8.52	14.88	14.96	14.78	15.01	14.82
Ag	200	1.29	0.45	0.43	0.49	1.07	0	0	0	0	0
Hg	1100	11.55	11.15	12.23	11.41	11.60	0.24	0	0	0.11	0
Pb	400	13.78	13.35	13.54	13.66	14.23	1.32	1.14	0.99	1.22	1.20
Fe	200	0	0	0	0	0	0	0	0	0	0
Zn	200	0	0	0	0	0	0	0	0	0	0
Co	200	0.06	0.07	0	0	0.04	0	0	0	0	0
Ni	200	0.40	0.65	0.09	0.08	0.05	0	0.18	0	0.22	0.05
As	250	0	0	0	0	0	0	0	0	0	0
Sb	300	0	0	0	0	0	0	0	0	0	0
Bi	300	30.71	30.99	31.12	31.25	30.74	44.71	44.81	45.13	44.65	44.86
S	150	0	0	0	0	0	0	0	0	0	0
Se	800	33.99	33.87	33.52	33.85	33.55	38.77	39.33	38.84	38.78	38.66
Total		100.72	100.34	100.28	100.35	99.79	99.92	100.41	99.74	99.99	99.59
Cu (apfu)		0.65	0.71	0.69	0.71	0.64	0.99	0.98	0.98	0.99	0.99
Ag		0.06	0.02	0.02	0.02	0.05					
Hg		0.27	0.26	0.29	0.27	0.27	0.01				
Pb		0.31	0.30	0.31	0.31	0.33	0.03	0.02	0.02	0.02	0.02
Co			0.01								
Ni		0.03	0.05	0.01	0.01			0.01		0.02	0.00
Bi		0.68	0.68	0.70	0.70	0.70	0.90	0.90	0.91	0.90	0.91
Se		2.00	1.98	1.99	2.00	2.01	2.07	2.08	2.08	2.07	2.07

d.l.: detection limit. 0: sought, but not detected.

Formula proportions were calculated on the basis of 3 apfu.

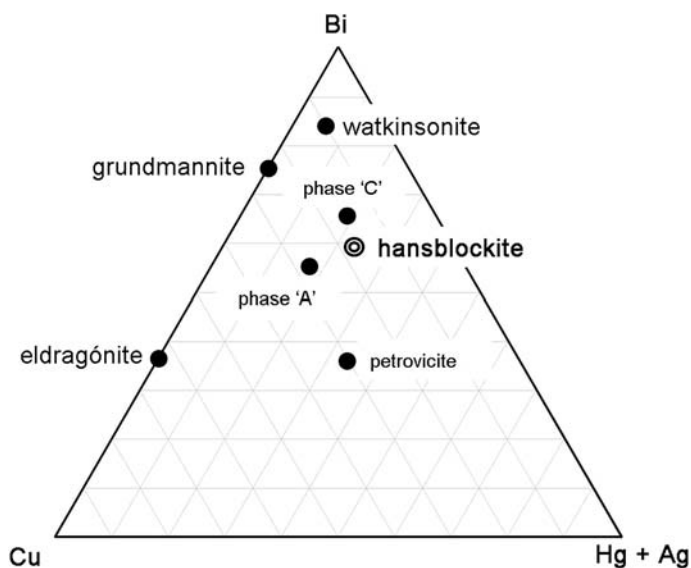


FIG. 6. Cu – (Hg+Ag) – Bi (apfu) ternary diagram showing the mean composition of minerals of the Cu–Hg–Pb–Bi–Se system from El Dragón. Data sources: Förster *et al.* (2016); this work.

TABLE 4. Measured and calculated powder X-ray diffraction data (d in Å) for hansblockite.*

hkl	d_{meas}	I_{obs}	d_{calc}	I_{calc}	hkl	d_{meas}	I_{obs}	d_{calc}	I_{calc}
$\bar{1}11$	4.37	20	4.3575	22	230	–	–	2.0365	6
111	3.97	90	3.9653	90	$\bar{2}13$	2.022	5	2.0214	12
002	–	–	3.5994	6	$\bar{1}23$	2.010	20	2.0098	22
021	–	–	3.3726	8	311	2.008	10	2.0082	16
$\bar{1}02$	3.375	10	3.3723	15	222	–	–	1.9827	6
$\bar{1}21$	3.100	40	3.0990	43	$\bar{3}12$	1.974	10	1.9739	15
$\bar{1}12$	–	–	3.0848	7	320	–	–	1.9472	6
102	–	–	3.0179	10	132	1.946	10	1.9455	12
$\bar{2}11$	2.986	100	2.9849	100	140	1.839	5	1.8376	12
112	2.808	50	2.8066	58	321	1.828	15	1.8275	16
211	2.732	10	2.7307	14	$\bar{3}22$	1.802	15	1.8015	12
$\bar{2}02$	–	–	2.6534	9	004	–	–	1.7997	8
022	2.620	60	2.6189	64	312	–	–	1.7615	6
220	2.534	25	2.5372	28	$\bar{2}04$	1.687	10	1.6862	9
$\bar{1}22$	2.525	20	2.5274	17	223	–	–	1.6625	7
$\bar{2}21$	2.470	10	2.4716	13	$\bar{2}33$	1.618	5	1.6180	9
031	2.400	20	2.3995	19	241	1.600	5	1.5984	9
130	2.385	30	2.3832	36	124	–	–	1.5414	7
202	2.321	20	2.3201	18	313	–	–	1.5159	6
$\bar{1}31$	2.296	25	2.2948	22	$\bar{3}04$	–	–	1.5105	6
013	2.290	35	2.2892	32	$\bar{3}41$	1.455	10	1.4548	12
300	–	–	2.2638	11	015	–	–	1.4148	6
131	–	–	2.2314	5	$\bar{4}32$	–	–	1.3675	7
310	2.171	10	2.1704	11	$\bar{2}52$	–	–	1.3235	8
$\bar{3}11$	–	–	2.1558	8	$\bar{3}34$	–	–	1.2990	5
113	–	–	2.0901	6	450	–	–	1.1354	5

*The calculated diffraction pattern was obtained with the atom coordinates reported in Table 6 (only reflections with $I_{rel} \geq 5$ are listed).

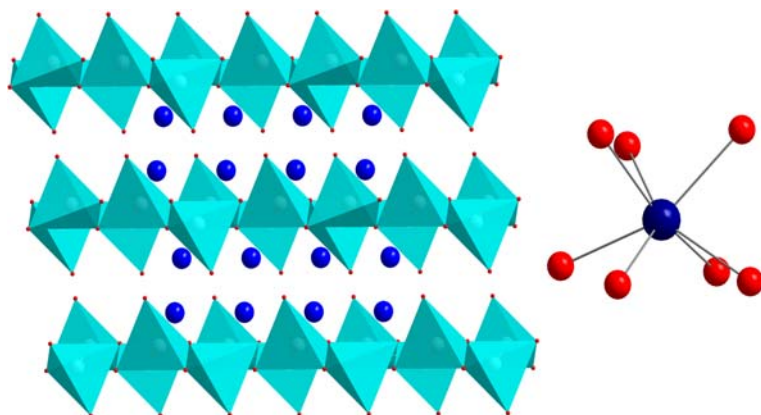


Fig. 7. (Left) The crystal structure of hansblockite projected down [010]. The horizontal direction is the *c* axis. (Cu,Hg) atoms are depicted as light-blue tetrahedra, whereas (Bi,Pb) and Se are given as blue and small red spheres, respectively. (Right) The coordination of the (Bi,Pb) atom.

Se vs. □ for the anion sites. The Se sites were found fully occupied, and the occupancy factors were then fixed to 1.00. The electron density refined at the metal sites (43.8 and 82.7 for the Cu and Bi site, respectively) is in excellent agreement with the electron-microprobe data (Tables 2, 3). Successive cycles were run introducing anisotropic temperature factors for all the atoms leading to $R_1 = 0.0314$ for 713 observed reflections [$F_o > 4\sigma(F_o)$] and $R_1 = 0.0345$ for all 1627 independent reflections. Fractional atomic coordinates and isotropic atomic displacement parameters are reported in Table 6 whereas the bond distances are given in Table 7. Structure factors and a crystallographic information file are deposited with the Principal Editor of *Mineralogical Magazine* at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Results and discussion

Crystal-chemical remarks

The crystal structure of hansblockite (Fig. 7) is topologically identical to that reported for several ternary rare-earth copper chalcogenides $LnCuQ_2$ (Ln = rare-earth element, Sc, Y; Q = S, Se, Te). These compounds show interesting optical, magnetic and thermoelectric properties (e.g. Ijjaali *et al.*, 2004). In the structure, each (Bi,Pb) atom is surrounded by seven Se atoms [3Se(1) + 4Se(2)] to form a monocapped trigonal prism (Fig. 7). These prisms share edges and caps to form double layers that stack perpendicular to the *a* axis. These double

layers are separated by layers of (Cu,Hg) atoms, each atom being tetrahedrally coordinated by four Se atoms [3Se(1) + 1Se(2)]. Alternatively, the structure may be thought of as consisting of [Cu,Hg]Se₂ sheets separated by (Bi,Pb) atoms along the *a* axis.

The mineral chemistry (*cf.*, Tables 2, 3) is in perfect agreement with the results of the structure refinement. The mean bond distance observed for the (Cu,Hg)-tetrahedron (2.536 Å) matches very well that calculated from the weighted bond distance $0.70(\text{Cu}-\text{Se}) + 0.30(\text{Hg}-\text{Se}) = 2.544$ Å [using the ideal (pure) tetrahedral Cu–S and Hg–S distances in grundmannite (Förster *et al.*, 2016) and tiemannite (Wieggers, 1971), respectively]. The 7-fold coordinated (Bi,Pb) site shows a mean bond distance of 3.072 Å, in perfect agreement with the typical environments formed by these cations.

It is noteworthy that the cation coordinations in hansblockite differ from those in the orthorhombic CuBiSe₂ polymorph grundmannite. In the latter, Bi forms BiSe₃ trigonal pyramids (with two additional longer distances), while Cu forms nearly regular CuSe₄ tetrahedra. The mean Cu–Se tetrahedral bond distance in grundmannite is 2.505 Å (Förster *et al.*, 2016), which compares favourably with that observed in hansblockite (2.536 Å).

Hansblockite represents the monoclinic polymorph of CuBiSe₂, after the recently reported orthorhombic grundmannite (Förster *et al.*, 2016). We prefer to propose the hansblockite formula as (Cu,Hg)(Bi,Pb)Se₂ (instead of CuBiSe₂), because Hg and Pb seem fundamental to stabilize the

TABLE 5. Data and experimental details for the selected hansblockite crystal.

Crystal data	
Formula	(Cu,Hg)(Bi,Pb)Se ₂
Crystal size (mm)	0.035 × 0.040 × 0.055
Form	block
Colour	black
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.853(1)
<i>b</i> (Å)	7.635(1)
<i>c</i> (Å)	7.264(1)
β (°)	97.68(1)
<i>V</i> (Å ³)	376.66(9)
<i>Z</i>	4
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	MoKα (λ = 0.71073 Å)
Temperature (K)	293(2)
Detector to sample distance (cm)	5
Number of frames	482
Measuring time (s)	80
Maximum covered 2θ (°)	70.00
Absorption correction	multi-scan (<i>ABSPACK</i> ; Oxford Diffraction, 2006)
Collected reflections	6599
Unique reflections	1627
Reflections with $F_o > 4\sigma(F_o)$	713
R_{int}	0.0308
R_{σ}	0.0431
Range of <i>h, k, l</i>	−11 ≤ <i>h</i> ≤ 11, −12 ≤ <i>k</i> ≤ 12, −11 ≤ <i>l</i> ≤ 11
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0314
Final R_1 (all data)	0.0345
Number of least squares parameters	39
Goodness of fit	0.934
Δρ _{max} (e Å ^{−3})	1.27 (2.11 Å from Bi)
Δρ _{min} (e Å ^{−3})	−1.33 (0.73 Å from Se2)

TABLE 6. Atom coordinates and equivalent isotropic displacement parameters (Å²) for hansblockite.

Atom	Site occupancy	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{iso}/U_{eq}
(Cu,Hg)	Cu _{0.71} Hg _{0.29}	0.0709(2)	0.6630(2)	0.0531(2)	0.0154(4)
(Bi,Pb)	Bi _{0.70} Pb _{0.30}	0.3087(1)	0.05019(9)	0.20049(9)	0.0192(2)
Se1	Se _{1.00}	0.0951(3)	0.3895(3)	0.2764(3)	0.0228(5)
Se2	Se _{1.00}	0.5869(3)	0.2728(3)	0.0010(3)	0.0215(5)

TABLE 7. Selected bond distances (Å) for hansblockite.

Cu–Se2 2.478(3)	Bi–Se2 3.019(2)	Bi–Cu 3.458(2)
Cu–Se1 2.489(2)	Bi–Se1 3.047(2)	Bi–Cu 3.475(2)
Cu–Se1 2.541(3)	Bi–Se1 3.052(2)	
Cu–Se1 2.636(2)	Bi–Se2 3.060(2)	
Cu–Cu 2.745(3)	Bi–Se1 3.062(2)	
	Bi–Se1 3.262(2)	

monoclinic structure via the coupled substitution $\text{Hg}^{2+} + \text{Pb}^{2+} \leftrightarrow \text{Cu}^+ + \text{Bi}^{3+}$.

Origin of hansblockite

Selenium and accompanying elements (Cu, Ag, Co, Ni, Pb, Hg, Bi,...) were most likely to have been mobilized from a *Kupferschiefer*-type reduced black shale rich in framboidal pyrite, copper sulfides and organic material (Förster *et al.*, 2016). The Se-mineralization was deposited in a fault zone at the contact of that shale with a hematite-rich, oxidized siltstone. Transport and deposition of Se and accompanying elements involved a low-*T* hydrothermal fluid and took place during one single event. Hansblockite post-dates the formation of the krut'aite–penroseite solid-solution series that forms the bulk of the Se ore. Deposition of these minerals resulted in enrichment of the ore-forming fluid in elements poorly compatible with their structure, i.e. Hg, Pb and Bi. Hansblockite was deposited from this enriched fluid, together with the bulk of the other Cu–Hg–Pb–Bi–Se minerals. It slightly predates the formation of its orthorhombic polymorph, grundmannite, which is among the youngest primary Se-minerals forming the El Dragón deposit (Förster *et al.*, 2016). As for grundmannite, hansblockite is cogenetic with klockmannite, umangite and clausenthalite, simple selenides for which the thermodynamic properties are well constrained (Simon and Essene, 1996). The absence of berzelianite and bellidoite implies that the selenium fugacity was in a range from below the krut'aite–klockmannite univariant reaction to above the umangite–berzelianite univariant reaction [$\log f_{\text{Se}_2} = -10.5$ to -14.5 for $T = 100^\circ\text{C}$ (cf., Simon and Essene, 1997)]. The presence of hematite/goethite and the absence of chalcopyrite, pyrite and bornite suggest $\log f_{\text{S}_2} < -17$. Thus, hansblockite precipitated at a $f_{\text{Se}_2}/f_{\text{S}_2}$ ratio > 1 , as typifying the environment of formation of

telethermal vein-type selenide mineralization (Simon and Essene, 1997).

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