**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 plates subparallel intergrown with two unnamed Cu–Hg–Pb–Bi–Se species, clausthalite, Co-rich penroseite, and petrovicite. It also forms sub-to anhedral grains up to 150 µm in length and 50 µm in width. Hansblockite is non-fluorescent, black and opaque with a metallic luster 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 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 atoms *pfu*) is $(\text{Cu}_{0.68}\text{Hg}_{0.27}\text{Ag}_{0.03}\text{Ni}_{0.01})_{\Sigma=0.99}(\text{Bi}_{0.69}\text{Pb}_{0.31})_{\Sigma=1.00}\text{Se}_{2.01}$. The simplified formula is $(\text{Cu,Hg})(\text{Bi,Pb})\text{Se}_2$. Hansblockite is monoclinic, space group $P2_1/c$, with a 6.853(1) Å, b 7.635(1) Å, 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 X-ray powder-diffraction lines [d in Å (I/I_0) (hkl)] are: 3.97 (90) (111), 3.100 (40) (-121), 2.986 (100) (-211), 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 $\text{Cu}^+ + \text{Bi}^{3+} \Leftrightarrow \text{Hg}^{2+} + \text{Pb}^{2+}$. The mineral name is in honour of Hans Block (1881–1953), in recognition of his important role in boosting Bolivian ore mining.

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Keywords: hansblockite; new mineral species; chemical composition, crystal structure; selenium; El Dragón, Bolivia

39

40 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 favreauite, $\text{PbBiCu}_6\text{O}_4(\text{SeO}_3)_4(\text{OH}) \cdot \text{H}_2\text{O}$ (Mills *et al.*, 2014), and alfredopetrovite, $\text{Al}_2(\text{Se}^{4+}\text{O}_3)_3 \cdot 6\text{H}_2\text{O}$ (Kampf *et al.*, 2016).

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 $(\text{Cu,Hg})(\text{Bi,Pb})\text{Se}_2$, described in this paper resembles phase “B”, for which initially the ideal formula $\text{Cu}_2\text{HgPbBi}_2\text{Se}_6$ (normalized to 12 *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 IMA, proposal 2015–103. 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 discarded. 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 (latitude), 65° 55' 00.60" W (longitude), 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 center 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 to 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.

97 **Appearance and physical properties**

98 Hansblockite typically occurs in lath-shaped thin plates (up to 100 μm in length and 10 μm in
 99 width) intimately (subparallel) intergrown with unnamed phase "A" (empirical formula
 100 $\text{Cu}_5\text{HgPb}_2\text{Bi}_3\text{Se}_{10}$; Paar *et al.*, 2012) and, less frequently, with unnamed phase "C" (empirical
 101 formula $\text{Cu}_4\text{HgBi}_4\text{Pb}_2\text{Se}_{11}$; Förster *et al.*, 2016, their Figure 2d–e), forming an angular
 102 network of tabular hansblockite crystals (Fig. 1). Among these species of the
 103 Cu–Hg–Pb–Bi–Se system forming these multi-phase aggregates, phase "A" generally appears
 104 to have crystallized earliest in the cores, partially overgrown by hansblockite predominantly
 105 forming the rims (Fig. 1). The relatively rare and small grains of phase "C" (max. 20 x 20 μm)
 106 are the relatively youngest, precipitated in the interstices between the unoriented
 107 hansblockite/phase "A" laths, together with Co-rich penroseite (NiSe_2), umangite (Cu_2Se_3),
 108 klockmannite (CuSe), watkinsonite (ideally $\text{Cu}_2\text{PbBi}_4\text{Se}_8$) and clausthalite (PbSe) (cf. Figs. 3,
 109 4). Hansblockite-crystal aggregates cement (usually together with clausthalite, umangite,
 110 klockmannite, eldragónite and co-rich penroseite) shrinkage cracks or fill interstices in
 111 brecciated krut'aite–penroseite (CuSe_2 – NiSe_2) solid solution.

112 Hansblockite locally forms sub- to anhedral grains up to 200 μm in length and 50 μm
 113 in width, occurring either solitary in the matrix or intergrown with watkinsonite, clausthalite,
 114 eldragónite, krut'aite–penroseite solid solution, eskebornite (CuFeSe_2), klockmannite and
 115 umangite (Fig. 2). Minerals occasionally being in grain-boundary contact are petrovicite
 116 ($\text{Cu}_3\text{HgPbBiSe}_5$), grundmannite (CuBiSe_2), and native gold. Hansblockite partially replaces
 117 umangite, klockmannite, eskebornite, and is itself altered by late klockmannite, athabascaite
 118 (Cu_5Se_4), and late fracture-filling chalcopyrite and covellite. Secondary minerals adjacent to
 119 hansblockite encompass quartz, dolomite, calcite, goethite, lepidocrocite, chalcomenite,
 120 molybdomenite, olsacherite, schmiederite, ahlfeldite, favreaite, felsőbányaite, and allophane.

121 Berzelianite (Cu_{2-x}Se) and bellidoite (Cu_2Se), previously mentioned by Grundmann *et al.*
122 (1990), were not detected in any sample from El Dragón.

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

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

132

133 **Optical properties**

134 Optical properties of hansblockite are shown in Figures 3 and 4. In plane-polarized incident
135 light, hansblockite is cream to light grey in color, slightly bireflectant and slightly pleochroic
136 from greyish cream to cream. The mineral does not show any internal reflections. Under
137 crossed polars, hansblockite is weakly anisotropic, with khaki to pale blue rotation tints.
138 Under crossed polars, the differences in color are blurred. To visualize the microstructural
139 properties more impressively, respective microphotographs 3 and 4 were taken under partly
140 crossed polars.

141 Quantitative reflectance data for hansblockite were obtained in air relative to a Zeiss
142 WTiC standard using a J and M TIDAS diode array spectrometer attached to a Zeiss Axiotron
143 microscope. Measurements were made on unoriented grains at extinction positions leading to

144 designation of R_1 (minimum) and R_2 (maximum). The results are listed in Table 1 (together
145 with the calculated color values) and illustrated graphically in Figure 5.

147 **Chemical Composition**

148 All primary minerals from El Dragón were routinely analyzed for concentrations of Cu, Ag,
149 Pb, Hg, Fe, Co, Ni, As, Sb, Bi, S and Se. Quantitative chemical analyses were conducted in
150 WDS mode, using a JEOL thermal field-emission-type electron probe X-ray microanalyzer
151 (FE-EPMA) JXA-8500F (HYPERPROBE) at Deutsches GeoForschungsZentrum GFZ,
152 Potsdam, Germany. The probe was operated at 20 kV, 20 nA; the beam size was 1–2 μm . The
153 counting time on peak was 20–40 s, with half that time on background on both sites of the
154 peak. The following standards, emission lines and analyzing crystals (in parentheses) were
155 used: Cu – synthetic Cu-metal, $K\alpha$ (LIF); Ag – naumannite, $L\alpha$ (PETJ); Pb – clausthalite, $M\alpha$
156 (PETH); Hg – cinnabar, $L\alpha$ (LIF); Fe – pyrite, $K\alpha$ (LIF); Co – skutterudite, $K\alpha$ (LIF); Ni –
157 pentlandite, $K\alpha$ (LIF); As – skutterudite, $L\alpha$ (TAP); Sb – stibnite, $L\alpha$ (PETJ); Bi – synthetic
158 Bi_2Se_3 , $M\alpha$ (PETH); S – sphalerite, $K\alpha$ (PETJ); Se – naumannite, $K\alpha$ (LIF). The CITZAF
159 routine in the JEOL software, which is based on the $\phi(\rho Z)$ method (Armstrong, 1995), was
160 used for data processing.

161 Hansblockite displays only weak variations in composition (Tables 2, 3). In addition to
162 the major cations Cu, Hg, Pb, Bi and Se, the only other omnipresent minor elements are Ag
163 (0.4 – 1.3 wt.%; likely substituted for monovalent Cu) and Ni, with concentrations between
164 <0.1 and 0.6 wt%. Trace amounts of Co (< 0.1 wt.%) were detected occasionally. Copper and
165 Hg, and Bi and Pb are antipathetically correlated, which argues for operation of the coupled
166 substitution $\text{Hg}^{2+} + \text{Pb}^{2+} \leftrightarrow \text{Cu}^+ + \text{Bi}^{3+}$. The mean empirical formula (based on 4 atoms *pfu*) of
167 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
168 $(\text{Cu,Hg})(\text{Bi,Pb})\text{Se}_2$. 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

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

X-ray single-crystal data

A single hansblockite fragment ($35 \times 40 \times 55 \text{ \mu m}$) was mounted on a 0.005-mm-diameter carbon fiber and checked on a CCD-equipped Oxford Diffraction Xcalibur 3 single-crystal diffractometer, operating with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit-cell values are: $a = 6.853(1) \text{ \AA}$, $b = 7.635(1) \text{ \AA}$, $c = 7.264(1) \text{ \AA}$, $\beta = 97.68(1)^\circ$, $V = 376.66(9) \text{ \AA}^3$. 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 done 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 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 1,627 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 CIF 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 $0.70(\text{Cu-Se}) + 0.30(\text{Hg-Se}) = 2.544 \text{ Å}$ [using the ideal (pure) tetrahedral Cu-S and Hg-S distances in grundmannite (Förster *et al.*, 2016) and tiemannite (Wiegers, 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.

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

242 *Origin of hansblockite*

243 Selenium and accompanying elements (Cu, Ag, Co, Ni, Pb, Hg, Bi,...) were most likely
244 mobilized from a *Kupferschiefer*-type reduced black shale rich in framboidal pyrite, copper
245 sulfides, and organic material (Förster *et al.*, 2016). The Se-mineralization was deposited in a
246 fault zone at the contact of that shale with a hematite-rich, oxidized siltstone. Transport and
247 deposition of Se and accompanying elements involved a low-*T* hydrothermal fluid and took
248 place during one single event. Hansblockite postdates the formation of the
249 krut'aite–penroseite solid-solution series that forms the bulk of the Se ore. Deposition of these
250 minerals resulted in enrichment of the ore-forming fluid in elements poorly compatible with
251 their structure, i.e., Hg, Pb and Bi. Hansblockite was deposited from this enriched fluid,
252 together with the bulk of the other Cu–Hg–Pb–Bi–Se minerals. It little predates the formation
253 of its orthorhombic polymorph, grundmannite, which is among the youngest primary Se-
254 minerals forming the El Dragón deposit (Förster *et al.*, 2016). As for grundmannite,
255 hansblockite is cogenetic with klockmannite, umangite and clausthalite, simple selenides for
256 which the thermodynamic properties are well constrained (Simon and Essene, 1996). The
257 absence of berzelianite and bellidoite implies that the selenium fugacity was in a range from
258 below the krut'aite–klockmannite univariant reaction to above the umangite–berzelianite
259 univariant reaction [$\log f_{\text{Se}_2} = -10.5$ to -14.5 for $T = 100$ °C (*cf.*, Simon and Essene, 1997)].
260 The presence of hematite/goethite and the absence of chalcopyrite, pyrite and bornite suggest
261 $\log f_{\text{S}_2} < -17$. Thus, hansblockite precipitated at a $f_{\text{Se}_2}/f_{\text{S}_2}$ ratio > 1 , as typifying the
262 environment of formation of telethermal vein-type selenide mineralization (Simon and
263 Essene, 1997).

264

265 **Acknowledgements**

Dieter Rhede (formerly Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany) is thanked for his assistance with the electron-microprobe work. CJS acknowledges Natural Environment Research Council grant NE/M010848/1 Tellurium and Selenium Cycling and Supply. The research was partially supported by “progetto d’Ateneo 2013. Università di Firenze” to LB.

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317 Figure captions

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

322 FIG. 2. Reflected light (top) and BSE (bottom) images of hansblockite (hb) in association with
323 clausthalite (cl), krut’aité–penroseite solid solution (k-p), eskebornite (esk), klockmannite (kl),
324 eldragónite (eld), and petrovicite (pet). Horizontal field of view is ~200 µm. The crystal used for
325 structural analysis was separated from this area.

326 FIG. 3: Reflected light images (200 µm width each) of hansblockite and associated minerals. Right
327 hand side with partly crossed polarizers, left hand side without. Top and bottom row correspond to
328 different extinction rotations. hb = hansblockite, “A” = phase “A”, pet = petrovicite, cl = clausthalite, u
329 = umangite, kl = klockmannite, k-p = krut’aité–penroseite solid solution. In plane-polarized incident
330 light, hansblockite is cream to light grey in colour, slightly bireflectant and slightly pleochroic from
331 greyish cream to cream. The mineral does not show any internal reflections. Under crossed polars,
332 hansblockite is weakly anisotropic with khaki to pale blue rotation tints.

333 FIG. 4. Reflected light images (200 µm width each) of hansblockite and associated minerals. Right
334 hand side with partly crossed polarizers, left hand side without. Top and bottom row correspond to
335 different extinction rotations. See Fig. 3 for abbreviations of mineral names. Note the overgrowth of
336 hansblockite on phase “A” nicely demonstrated in the right hand side-image of the bottom row.

337 FIG. 5. Reflectance spectra of hansblockite and its orthorhombic dimorph grundmannite (Förster *et al.*,
338 2016).

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

341 FIG. 7. The crystal structure of hansblockite projected down [010]. The horizontal direction is the *c*-
342 axis. (Cu,Hg) atoms are depicted as light-blue tetrahedral, whereas (Bi,Pb) and Se are given as blue
343 and small red spheres, respectively. The coordination of the (Bi,Pb) atom is shown on the right.

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	640	46.7	48.6
420	46.9	47.1	660	46.5	48.4
440	47.1	47.4	680	46.4	48.2
460	47.3	47.9	700	46.3	48.0
480	47.4	48.4	Commission on Ore Mineralogy wavelengths		
500	47.4	48.7			
520	47.4	48.9			
540	47.4	49.0			
560	47.3	49.0			
580	47.2	49.0	470	47.3	48.1
600	47.0	48.9	546	47.4	49.0
620	46.9	48.8	589	47.1	49.0
			650	46.6	48.5
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_e (%)	0.2	1.5		0.2	1.8

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 element	d.l. (ppm)	hansblockite					grundmannite				
		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 (<i>apfu</i>)		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*.

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

hkl	d_{meas}	I_{obs}	d_{calc}	I_{calc}
-111	4.37	20	4.3575	22
111	3.97	90	3.9653	90
002	-	-	3.5994	6
021	-	-	3.3726	8
-102	3.375	10	3.3723	15
-121	3.100	40	3.0990	43
-112	-	-	3.0848	7
102	-	-	3.0179	10
-211	2.986	100	2.9849	100
112	2.808	50	2.8066	58
211	2.732	10	2.7307	14
-202	-	-	2.6534	9
022	2.620	60	2.6189	64
220	2.534	25	2.5372	28
-122	2.525	20	2.5274	17
-221	2.470	10	2.4716	13
031	2.400	20	2.3995	19
130	2.385	30	2.3832	36
202	2.321	20	2.3201	18
-131	2.296	25	2.2948	22
013	2.290	35	2.2892	32
300	-	-	2.2638	11
131	-	-	2.2314	5
310	2.171	10	2.1704	11
-311	-	-	2.1558	8
113	-	-	2.0901	6
230	-	-	2.0365	6
-213	2.022	5	2.0214	12
-123	2.010	20	2.0098	22
311	2.008	10	2.0082	16
222	-	-	1.9827	6
-312	1.974	10	1.9739	15
320	-	-	1.9472	6
132	1.946	10	1.9455	12
140	1.839	5	1.8376	12
321	1.828	15	1.8275	16
-322	1.802	15	1.8015	12
004	-	-	1.7997	8
312	-	-	1.7615	6
-204	1.687	10	1.6862	9
223	-	-	1.6625	7
-233	1.618	5	1.6180	9

241	1.600	5	1.5984	9
124	-	-	1.5414	7
313	-	-	1.5159	6
-304	-	-	1.5105	6
-341	1.455	10	1.4548	12
015	-	-	1.4148	6
-432	-	-	1.3675	7
-252	-	-	1.3235	8
-334	-	-	1.2990	5
450	-	-	1.1354	5

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

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	MoK α (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</i> , <i>k</i> , <i>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
$\Delta\rho_{\text{max}}$ (e Å ^{−3})	1.27 (2.11 Å from Bi)
$\Delta\rho_{\text{min}}$ (e Å ^{−3})	−1.33 (0.73 Å from Se2)

Table 6. Atom coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for hansblockite.

atom	Site occupancy	x/a	y/b	z/c	$U_{\text{iso}}^*/U_{\text{eq}}$
(Cu,Hg)	$\text{Cu}_{0.71}\text{Hg}_{0.29}$	0.0709(2)	0.6630(2)	0.0531(2)	0.0154(4)
(Bi,Pb)	$\text{Bi}_{0.70}\text{Pb}_{0.30}$	0.3087(1)	0.05019(9)	0.20049(9)	0.0192(2)
Se1	$\text{Se}_{1.00}$	0.0951(3)	0.3895(3)	0.2764(3)	0.0228(5)
Se2	$\text{Se}_{1.00}$	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)

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