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1 **Hansblockite, (Cu,Hg)(Bi,Pb)Se$_2$, the monoclinic polymorph of**

2 **grundmannite: a new mineral from the Se mineralization at El Dragón**

3 **(Bolivia)**

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14 **ABSTRACT:** Hansblockite, ideally (Cu,Hg)(Bi,Pb)Se$_2$, is a new selenide from the El Dragón

15 mine, Bolivia. It typically occurs in thin plates subparallel intergrown with two unnamed

16 Cu−Hg−Pb−Bi−Se species, clausthalite, Co-rich penroseite, and petrovicite. It also forms sub-

17 to anhedral grains up to 150 μm in length and 50 μm in width. Hansblockite is non-

18 fluorescent, black and opaque with a metallic luster and black streak. It is brittle, with an

19 irregular fracture and no obvious parting and cleavage. The VHN$_{20}$ values range from 37 to 50

20 (mean 42) kg mm^{-2} (Mohs hardness 2− 2½). In plane-polarized incident light, hansblockite is

21 cream to light grey in colour, weakly bireflectant and weakly pleochroic from greyish cream

22 to cream. Under crossed polars, hansblockite is weakly anisotropic with khaki to pale blue

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23 rotation tints. The reflectance values in air for the COM standard wavelengths are: 47.3−48.1

24 (470 nm), 47.4−49.9 (546 nm), 47.1−49.0 (589 nm), and 46.6−48.5 (650 nm). The mean

25 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,

26 total 100.39 wt.%. The mean empirical formula (based on 4 atoms *pfu*) is

27 $(Cu_{0.68}Hg_{0.27}Ag_{0.03}Ni_{0.01})_{\Sigma=0.99}(Bi_{0.69}Pb_{0.31})_{\Sigma=1.00}Se_{2.01}$. The simplified formula is

28 $(Cu,Hg)(Bi,Pb)Se_2$. Hansblockite is monoclinic, space group $P2_1/c$, with *a* 6.853(1) Å, *b*

29 7.635(1) Å, *c* 7.264(1) Å, β 97.68(1)°, *V* 376.66(9) Å^3, and *Z* = 4. Density is 8.26 g cm^{-3}.

30 The five strongest X-ray powder-diffraction lines [*d* in Å (*I/I$_0$*) (*hkl*)] are: 3.97 (90) (111),

31 3.100 (40) (-121), 2.986 (100) (-211), 2.808 (50) (112), and 2.620 (50) (022). Hansblockite

32 represents the monoclinic polymorph of grundmannite, $CuBiSe_2$, with Hg and Pb being

33 essential in stabilizing the monoclinic structure via the coupled substitution $Cu^+ + Bi^{3+} \Leftrightarrow$

34 $Hg^{2+} + Pb^{2+}$. The mineral name is in honour of Hans Block (1881−1953), in recognition of his

35 important role in boosting Bolivian ore mining.

36

37 **Keywords**: hansblockite; new mineral species; chemical composition, crystal structure;

38 selenium; El Dragón, Bolivia

39

40 **Introduction**

41 The Andes of Bolivia host two volumetrically minor, but mineralogically important selenide

42 occurrences: Pacajake, district of Hiaco de Charcas, and El Dragón, Province of Antonio

43 Quijarro, both in the Department of Potosí. The geology and ore mineralization of the El

44 Dragón mine was first explored in detail by Grundmann *et al.* (1990). Recently, it received

45 renewed attention as the type locality of eldragónite, $Cu_6BiSe_4(Se_2)$ (Paar *et al.*, 2012), and

46 grundmannite, $CuBiSe_2$ (Förster *et al.*, 2016), and the discovery of the two new Se-bearing

47 secondary species favreauite, $PbBiCu_6O_4(SeO_3)_4(OH) \cdot H_2O$ (Mills *et al*., 2014), and

48 alfredopetrovite, $Al_2(Se^{4+}O_3)_3 \cdot 6H_2O$ (Kampf *et al*., 2016).

49 In addition to the recently described Cu−Bi sulfosalts eldragónite and grundmannite,

50 three unnamed species of the Cu−Hg−Pb−Bi−Se system have been discovered in samples

51 from the El Dragón mine, labelled phases "A", "B", and "C" (*cf.* Paar *et al*., 2012; Förster *et*

52 *al*., 2016). The new selenium mineral, hansblockite $(Cu,Hg)(Bi,Pb)Se_2$, described in this

53 paper resembles phase "B", for which initially the ideal formula $Cu_2HgPbBi_2Se_6$ (normalized

54 to 12 *apfu*) was proposed (Paar *et al*., 2012; Förster *et al*., 2016).

55 The new species hansblockite and its name have been approved by the Commission on

56 New Minerals, Nomenclature and Classification (CNMNC) of the IMA, proposal 2015−103.

57 The holotype specimen, which is the polished section from which the grain used for crystal-

58 structure determination was obtained, is stored in the collections of the Natural History

59 Museum, London, catalogue number BM 2015, 136. Cotype material, consisting of a

60 hansblockite-bearing section, is deposited within the Mineralogical State Collection Munich

61 (Mineralogische Staatssammlung München, Museum "Reich der Kristalle"), inventory

62 number MSM 73573.

63 The name is in honour of Hans Block (1881−1953), in recognition of his contribution

64 to fostering Bolivian ore mining. Born in Stassfurt, Alemania, Germany, he emigrated to

65 Bolivia in 1904, when he was contracted by the Compania Huanchaca de Bolivia, the plant

66 operator for the Pulacayo mine. He was later administrator, manager, and owner of several

67 mines, among them the Compania Minera Gallofa Consolidada de Colquechaca (e.g., Block,

68 1937; Block and Ahlfeld, 1937). In 1945, Hans Block became a Professor of the Facultad

69 Nacional de Ingenieria in Oruro. In 1952, he was appointed to the Commission for the

70 Nationalization of the Mines.

3

71   It is important to note that Herzenberg and Ahlfeld (1935) named a mineral from the

72   lead-silver mine Hiaco, Colquechaca, Bolivia in honour of Hans Block "blockite". Later,

73   Bannister and Hey (1937) demonstrated that "blockite" was identical to penroseite and

74   concluded that the mineral name "blockite" should be discarded. To avoid confusion with two

75   different blockite names in the literature, the name hansblockite was proposed for the present

76   new selenide.

77

78   **Geological setting**

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

80   Oriental, some 30 km southwest of Cerro Rico de Potosí. The abandoned El Dragón mine

81   (entrance and dump) is located 19° 49' 23.90" S (latitude), 65° 55' 00.60" W (longitude), at

82   an altitude of 4160 m above sea level. The very small longitudinal extension (maximum 15-

83   m-long gallery) of the El Dragón ore vein and its low silver content (averaging to 0.06 wt.%

84   Ag) have probably discouraged further exploitation of the occurrence.

85   The adit of the El Dragón mine is on the orographic left side of the Rio Jaya Mayu,

86   cutting through a series of thinly-stratified, pyrite-rich black shales and reddish-grey,

87   hematite-bearing siltstones of probably Devonian age, dipping 40° to the north. The almost

88   vertical ore vein is located in the center of a 1.5-m-wide shear zone (average trend 135

89   degrees) with shifts of a few cm. In 1988, the selenium mineralization consisted of a single

90   vein, ranging mostly from 0.5 to 2 cm in thickness.

91   The El Dragón mineralization is composed of a complex assemblage of primary and

92   secondary minerals, among which Se-bearing phases are most prominent. The full list of

93   minerals recorded from El Dragón is given on mindat.org at http://www.mindat.org/loc-

94   353.html. Grundmann *et al.* (1990) and Paar *et al.* (2012) provided detailed descriptions of

95   the entire mineralization.

4

96

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   $Cu_5HgPb_2Bi_3Se_{10}$; Paar *et al.*, 2012) and, less frequently, with unnamed phase "C" (empirical

101   formula $Cu_4HgBi_4Pb_2Se_{11}$; 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 $Cu_2PbBi_4Se_8$) 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   ($Cu_3HgPbBiSe_5$), 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, favreauite, felsőbányaite, and allophane.

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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 $42 \, kg \cdot mm^{-2}$ (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 $8.26 \, g \cdot cm^{-3}$.

132

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.

146

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 $Hg^{2+} + Pb^{2+} \leftrightarrow Cu^+ + Bi^{3+}$. The mean empirical formula (based on 4 atoms *pfu*) of

167   hansblockite is $(Cu_{0.68}Hg_{0.27}Ag_{0.03}Ni_{0.01})_{\Sigma=0.99}(Bi_{0.69}Pb_{0.31})_{\Sigma=1.00}Se_{2.01}$ (n = 28). The ideal formula is

168    $(Cu,Hg)(Bi,Pb)Se_2$. Table 3 presents a compilation of representative results of electron-

7

169   microprobe spot analyses of hansblockite and grundmannite, ideally CuBiSe$_2$. Compositional

170   data for other Cu−(Pb)−(Hg)−Bi−Se minerals from El Dragón (petrovicite, watkinsonite,

171   eldragónite, unnamed phases "A" and "C") are reported in Förster *et al.*, 2016, their Table 3).

172   The mean compositions of these phases, together with that of hansblockite, could be

173   displayed, for instance, in the Cu – (Hg+Ag) – Bi ternary diagram (Fig. 6), demonstrating that

174   hansblockite (previously phase "B") is chemically distinct from phases "A" and "C".

175

176   **Crystal structure**

177   *X-ray powder-diffraction data*

178   The observed powder diffraction pattern (Table 4) of the same hansblockite fragment used for

179   the single-crystal study (see below) was collected with a CCD-equipped diffractometer

180   Xcalibur PX Ultra using Cu*K*α radiation (50 kV and 40 mA – 5 hs as exposition time).

181   Crystal-to-detector distance was 7 cm. Data were processed using the *CrysAlis* software

182   package version 1.171.31.2 (Oxford diffraction, 2006) running on the Xcalibur PX control

183   PC. The unit-cell parameters obtained from powder data (pseudo-Gandolfi mode), using the

184   software *UnitCell* (Holland and Redfern, 1997), are: $a = 6.8529(4)$ Å, $b = 7.6388(5)$ Å, $c =$

185    $7.2669(6)$ Å, β $97.662(5)°$, $V = 377.01(3)$ Å^3, in excellent agreement with those obtained

186   from single-crystal data (*cf.*, Table 5).

187   *X-ray single-crystal data*

188   A single hansblockite fragment ($35 \times 40 \times 55$ μm) was mounted on a 0.005-mm-diameter

189   carbon fiber and checked on a CCD-equipped Oxford Diffraction Xcalibur 3 single-crystal

190   diffractometer, operating with Mo*K*α radiation ($\lambda = 0.71073$ Å). The unit-cell values are: $a =$

191    $6.853(1)$ Å, $b = 7.635(1)$ Å, $c = 7.264(1)$ Å, $β = 97.68(1)°$, $V = 376.66(9)$ Å^3. It showed an

192   excellent diffraction quality and was used for full data collection (Table 5). Intensity

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193   integration and standard Lorentz-polarization corrections were performed with the *CrysAlis*

194   RED (Oxford Diffraction, 2006) software package. The program ABSPACK of the *CrysAlis*

195   RED package (Oxford Diffraction, 2006) was used for the absorption correction. Reflection

196   conditions were consistent with space group $P2_1/c$. The full-matrix least-squares program

197   SHELXL-97 (Sheldrick, 2008), working on F^2, was used for the refinement of the structure.

198   Given the close stoichiometry and the similarity in the unit-cell values, refinement was done

199   starting from the atomic coordinates reported for synthetic copper chalcogenides with the

200   formula $LnCuQ_2$ (Ln = rare-earth element, Sc, Y; Q = S, Se, Te; Ijjaali *et al.*, 2004). Site-

201   scattering values were refined using scattering curves for neutral species (Ibers and Hamilton,

202   1974) as follows: Cu vs. [] (structural vacancy) and Bi vs. [] for the cation sites, and Se vs. []

203   for the anion sites. The Se sites were found fully occupied, and the occupancy factors were

204   then fixed to 1.00. The electron density refined at the metal sites (43.8 and 82.7 for the Cu and

205   Bi site, respectively) is in excellent agreement with the electron-microprobe data (Tables 2,

206   3). Successive cycles were run introducing anisotropic temperature factors for all the atoms

207   leading to $R_1 = 0.0314$ for 713 observed reflections $[F_o > 4\sigma(F_o)]$ and $R_1 = 0.0345$ for all

208   1,627 independent reflections. Fractional atomic coordinates and isotropic atomic

209   displacement parameters are reported in Table 6 whereas the bond distances are given in

210   Table 7. Structure factors and CIF are deposited with the Principal Editor of Mineralogical

211   Magazine at http://www.minersoc.org/pages/e_journals/dep_mat.html.

212

213   **Results and Discussion**

214   *Crystal-chemical remarks*

215   The crystal structure of hansblockite (Fig. 7) is topologically identical to that reported

216   for several ternary rare-earth copper chalcogenides $LnCuQ_2$ (Ln = rare-earth element, Sc, Y;

217   Q = S, Se, Te). These compounds show interesting optical, magnetic, and thermoelectric

218   properties (e.g., Ijjaali *et al.*, 2004). In the structure, each (Bi,Pb) atom is surrounded by seven

219   Se atoms [3Se(1) + 4Se(2)] to form a monocapped trigonal prism (Fig. 7). These prisms share

220   edges and caps to form double layers that stack perpendicular to the **a**-axis. These double

221   layers are separated by layers of (Cu,Hg) atoms, each atom being tetrahedrally coordinated by

222   four Se atoms [3Se(1) + 1Se(2)]. Alternatively, the structure may be thought of as consisting

223   of [Cu,Hg]Se$_2$ sheets separated by (Bi,Pb) atoms along the **a**-axis.

224   The mineral chemistry (*cf.*, Tables 2, 3) is in perfect agreement with the results of the

225   structure refinement. The mean bond distance observed for the (Cu,Hg)-tetrahedron (2.536 Å)

226   matches very well that calculated from the weighted bond distance 0.70(Cu−Se) +

227   0.30(Hg−Se) = 2.544 Å [using the ideal (pure) tetrahedral Cu−S and Hg−S distances in

228   grundmannite (Förster *et al.*, 2016) and tiemannite (Wiegers, 1971), respectively]. The 7-fold

229   coordinated (Bi,Pb) site shows a mean bond distance of 3.072 Å, in perfect agreement with

230   the typical environments formed by these cations.

231   Noteworthy, the cation coordinations in hansblockite differ from those in the

232   orthorhombic CuBiSe$_2$ polymorph grundmannite. In the latter, Bi forms BiSe$_3$ trigonal

233   pyramids (with two additional longer distances), while Cu forms nearly regular CuSe$_4$

234   tetrahedra. The mean Cu−Se tetrahedral bond distance in grundmannite is 2.505 Å (Förster *et*

235   *al.*, 2016), which compares favorably with that observed in hansblockite (2.536 Å).

236   Hansblockite represents the monoclinic polymorph of CuBiSe$_2$, after the recently

237   reported orthorhombic grundmannite (Förster *et al.*, 2016). We prefer to propose the

238   hansblockite formula as (Cu,Hg)(Bi,Pb)Se$_2$ (instead of CuBiSe$_2$), because Hg and Pb seem

239   fundamental to stabilize the monoclinic structure via the coupled substitution Hg^{2+} + Pb^{2+} ↔

240   Cu^{+} + Bi^{3+}.

241

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$f$Se$_2$ = −10.5 to −14.5 for T = 100 $^{\circ}$C (*cf.,* Simon and Essene, 1997)].

260 The presence of hematite/goethite and the absence of chalcopyrite, pyrite and bornite suggest

261 log$f$S$_2$ < −17. Thus, hansblockite precipitated at a fSe$_2$/fS$_2$ ratio > 1, as typifying the

262 environment of formation of telethermal vein-type selenide mineralization (Simon and

263 Essene, 1997).

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272   **References**

273   Armstrong, J.T. (1995) CITZAF: a package of correction programs for the quantitative electron

274   microbeam X-ray-analysis of thick polished materials, thin films, and particles. *Microbeam*

275   *Analysis*, **4**, 177−200.

276   Bannister, F.A. and Hey, M.H. (1937) The identity of penroseite and blockite. *American Mineralogist*,

277   **22**, 319−324.

278   Block, H. (1937) Das Selenvorkommen von Pacajake in Bolivien. *Erzmetall*, **34**, 237−238.

279   Block, H. and Ahlfeld, F. (1937) Die Selenlagerstätte Pacajake, Bolivia. *Zeitschrift für praktische*

280   *Geologie.*, **45**, 9−14.

281   Förster, H.-J., Bindi, L. and Stanley, C.J. (2016) Grundmannite, $CuBiSe_2$, the Se-analogue of

282   emplectite: a new mineral from the El Dragón mine, Potosí, Bolivia. *European Journal of*

283   *Mineralogy,* doi: 10.1127/ejm/2016/0028-2513.

284   Grundmann, G., Lehrberger, G. and Schnorrer-Köhler, G. (1990) The El Dragón mine, Potosí, Bolivia.

285   *Mineralogical Record*, 21, 133−146.

286   Herzenberg, R. and Ahlfeld, F. (1935) Blockit, ein neues Selenerz aus Bolivien. *Zentralblatt für*

287   *Mineralogie, Geologie und Paläontologie (Abteilung A)*, **9**, 277−279.

288   Holland, T.J.B. and Redfern, S.A.T. (1997) UNITCELL: a nonlinear least-squares program for cell-

289   parameter refinement and implementing regression and deletion diagnostics. *Journal of*

290   *Applied Crystallography*, **30**, 84−84.

291   Ibers, J.A. and Hamilton, W.C. Eds. (1974) *International Tables for X-ray Crystallography*, vol. IV,

292   366p. Kynock, Dordrecht, The Netherlands. $LnCuSe_2$ (Ln = La, Ce, Pr, Nd, Sm).

293   Ijjaali, I., Mitchell, K. and Ibers, J.A. (2004) Preparation and structure of the light rare-earth copper

294   selenides *Ln*CuSe$_2$ (*Ln* = La, Ce, Pr, Nd, Sm). *Journal of Solid State Chemistry*, **177**, 760–764.

295   Kampf, A.R., Mills, S.J., Nash, B.P., Thorne, B. and Favreau, G. (2016) Alfredopetrovicite: a new

296   selenite mineral from the El Dragón mine*. European Journal of Mineralogy,* doi:

297   10.1127/ejm/2015/0027-2506

298   Mills, S. J.,Kampf, A.R., Christy, A.G., Housley, R. M., Thorne, B., Chen, Yu-Sheng and Steele, I. M.

299   (2014) Favreauite, a new selenite mineral from the El Dragón mine, Bolivia*. European

300   Journal of Mineralogy*, **26**, 771−781.

301   Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in *CrysAlis* RED.

302   Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

303   Paar, W.H., Cooper, M.A., Moëlo, Y., Stanley, C.J., Putz, H., Topa, D., Roberts, A.C., Stirling, J.,

304   Raith, J.G. and Rowe, R. (2012) Eldragónite, $Cu_6BiSe_4(Se)_2$, a new mineral species from the

305   El Dragón mine, Potosí, Bolivia, and its crystal structure. *Canadian Minera*logist, **50**,

306   281−294.

307   Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallografica*, **A64**, 112–122.

308   Simon, G. and Essene, E.J. (1996) Phase relations among selenides, sulphides, tellurides, and oxides:

309   I. Thermodynamic properties and calculated equilibria. *Economic Geology,* **91**, 1183−1208.

310   Simon, G. and Essene, E.J. (1997) Phase relations among selenides, sulphides, tellurides, and oxides:

311   II: Applications to selenide-bearing ore deposits. *Economic Geology*, **92**, 468−484.

312   Wiegers, G.A. (1971) The crystal structure of the low-temperature form of silver selenide. *American

313   Mineralogist*, **56**, 1882–1888.

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316

Figure captions

318 Fɪɢ. 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 Fɪɢ. 2. Reflected light (top) and BSE (bottom) images of hansblockite (hb) in association with

323 clausthalite (cl), krut'aite−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 Fɪɢ. 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'aite−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 Fɪɢ. 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 Fɪɢ. 5. Reflectance spectra of hansblockite and its orthorhombic dimorph grundmannite (Förster *et al.*,

338 2016).

339 Fɪɢ. 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.

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341   F<small>IG</small>. 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			
500	47.4	48.7	Commission on Ore Mineralogy		
520	47.4	48.9	wavelengths		
540	47.4	49.0			
560	47.3	49.0	470	47.3	48.1
580	47.2	49.0	546	47.4	49.0
600	47.0	48.9	589	47.1	49.0
620	46.9	48.8	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
1σ	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: 1σ = 1σ 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*.

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 $I_{rel} \geq 5$ 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)	$0.035 \times 0.040 \times 0.055$
Form	block
Colour	black
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	6.853(1)
b (Å)	7.635(1)
c (Å)	7.264(1)
β (°)	97.68(1)
V (Å^3)	376.66(9)
Z	4

Data collection

Instrument	Oxford Diffraction Xcalibur 3
Radiation type	Mo$K\alpha$ (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 (*ABSPACK*; 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 h, k, l	$-11 \leq h \leq 11, -12 \leq k \leq 12, -11 \leq l \leq 11$

Refinement

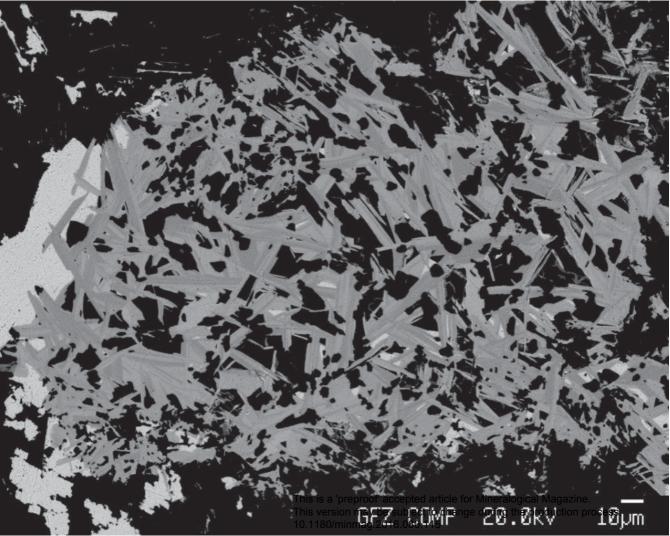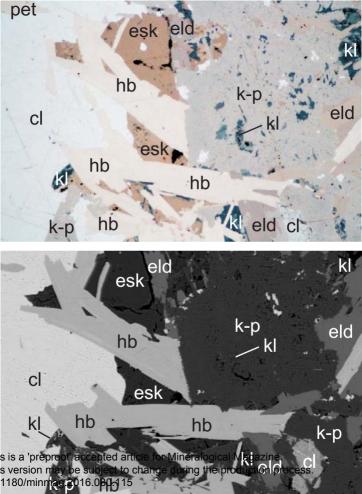|	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0314
Final R_1 (all data)	0.0345
Number of least squares parameters	39
Goodness of Fit	0.934
$\Delta\rho_{max}$ (e Å^{-3})	1.27 (2.11 Å from Bi)
$\Delta\rho_{min}$ (e Å^{-3})	−1.33 (0.73 Å from Se2)

Table 6. Atom coordinates and equivalent isotropic displacement parameters (Å^2) for hansblockite.
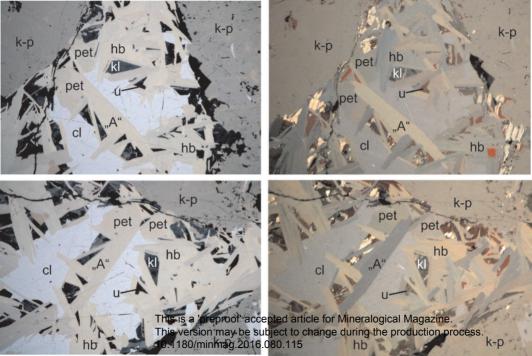
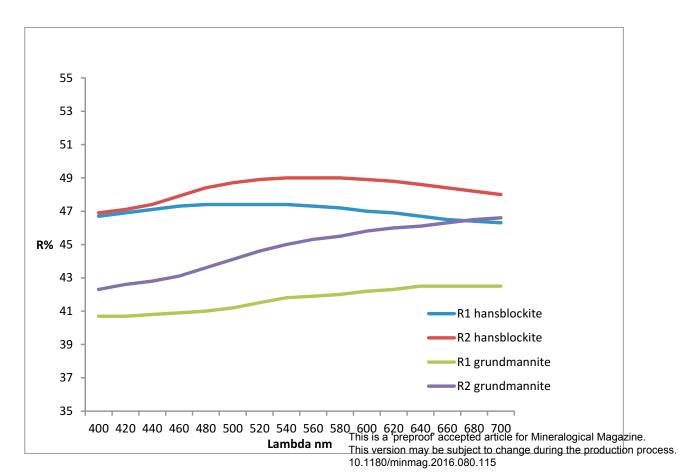| atom	Site occupancy	x/a	y/b	z/c	$U_{iso}*/U_{eq}$
(Cu,Hg)	$Cu_{0.71}Hg_{0.29}$	0.0709(2)	0.6630(2)	0.0531(2)	0.0154(4)
(Bi,Pb)	$Bi_{0.70}Pb_{0.30}$	0.3087(1)	0.05019(9)	0.20049(9)	0.0192(2)
Se1	$Se_{1.00}$	0.0951(3)	0.3895(3)	0.2764(3)	0.0228(5)
Se2	$Se_{1.00}$	0.5869(3)	0.2728(3)	0.0010(3)	0.0215(5)

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)		