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The crystal structure of ramdohrite,

$Pb_{5.9}\ Fe_{0.1}Mn_{0.1}In_{0.1}Cd_{0.2}Ag_{2.8}Sb_{10.8}S_{24}$:

a new refinement

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24 **ABSTRACT**

25

26 The crystal structure of ramdohrite, $Pb_{5.9}Fe_{0.1}Mn_{0.1}In_{0.1}Cd_{0.2}Ag_{2.8}Sb_{10.8}S_{24}$, from the Chocaya

27 mine, Potosí, Bolivia, determined by Makovicky and Mumme from film data in 1983, was refined

28 from single-crystal diffractometer data to the R value 0.060, based on 5230 reflections $[I > 2\sigma(I)]$

29 from a twinned crystal. Lattice parameters are a 8.7348(3) Å, b 13.0543(4) Å, c 19.3117(6) Å and β

30 90.179(2)^{o}, space group $P2_1/n$.

31 Two bicapped trigonal prismatic sites of lead bridge and unite adjacent $(311)_{PbS}$ slabs. These slabs

32 contain five distinct coordination pyramids of Sb with trapezoidal cross-sections, a mixed and

33 disordered Sb-Ag-Cd-(Pb) site, refined as 0.39 Sb + 0.61 Ag, a pure Ag site with a very open,

34 irregular tetrahedral coordination, and an octahedral site occupied by Pb. The $(311)_{PbS}$ slabs contain

35 large lone electron pair micelles formed by four distinct antimony sites in alternation with small

36 such micelles formed by a single Sb site. The geometric arrangement of these slabs is not based on

37 crankshaft chains of short, strong Me-S bonds but on a chess-board arrangement of (predominantly)

38 Sb pairs which share two common S atoms via short bonds. Relationships to, and differenced from,

39 fizelyite and uchucchacuaite are described and discussed.

40

41 **Keywords:** ramdohrite, crystal structure, fizelyite-andorite series, Pb-Ag-Sb sulfosalt.

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44 **INTRODUCTION**

45

46   The andorite – fizelyite substitution series, ideally $Pb_3Sb_2S_6$ – $PbAgSbS_3$, is the $N = 4$ subset of the

47   more general lillianite homologous series. Its internal division into a number of ordered derivatives,

48   structures with incorporation of minor elements and with miscibility gaps between them, contrasts

49   with a relative simplicity of the parallel, bismuth-based lillianite – gustavite series, ideally $Pb_3Bi_2S_6$

50   – $PbAgBiS_3$, with only one composition gap and no need to incorporate other cations in a

51   substantial role.

52

53   Among earlier attempts to organize this complexity we can recall Hellner (1958) and Strunz (1966).

54   By that time, crystal lattice and symmetry studies of museum samples of ramdohrite, fizelyite and

55   andorite were published by Nuffield (1945) but the chemistry data used by him were based on old

56   bulk analyses and the assignment was not quite secure. Donnay and Donnay (1954) studied the

57   complicated superlattices of the highly substituted members of the series, known under a summary

58   name 'andorite'. Kawada and Hellner (1971) determined a 4Å substructure of andorite, and Sawada

59   et al. (1987) described a complete structure of 'andorite VI' which has a six-fold superstructure. A

60   dedicated study by Moëlo, Makovicky and Karup-Møller, published in 1989, investigated a number

61   of specimens from the entire series by means of microprobe analyses, connected with a single-

62   crystal study (a complete crystal lattice and symmetry description) of selected specimens, and for

63   the case of ramdohrite, by a complete crystal structure determination (Makovicky and Mumme

64   1983). The present state of the andorite – fizelyite series was presented by Moëlo et al. (2008). Our

65   knowledge of it, however, was recently enriched by the crystal structure determinations on fizelyite

66    $Ag_{5.94}Pb_{13.74}Sb_{20.84}S_{48}$, uchucchacuaite $AgMnPb_3Sb_5S_{12}$ (Yang et al. 2009, 2011) and menchettiite

67    $AgPb_{2.40}Mn_{1.60}Sb_3As_2S_{12}$ (Bindi et al. 2012).

68

69   Especially because of the results of three latter, modern structure determinations, we decided to re-

70   refine the crystal structure of ramdohrite, with the refinement based on a modern data collection.

71   This refinement makes the results on ramdohrite comparable with the rest of the available crystal

72   chemical data on this group.

73

74

75   EXPERIMENTAL

76

77   The electron microprobe analysis of the studied ramdohrite specimen (apparatus CAMEBAX, at

78   BRGM-CNRS Orléans, operating conditions 25kV and 15nA, counting time 6s, correction using

79   fizelyite from Felsöbanya as internal standard), included in Moëlo et al. (1989), yield 32.9 wt.% Pb,

80   0.16 wt.% Fe, 0.18 wt.% Mn, 0.12 wt.% Sn, 0.22 wt.% In, 0.67 wt.% Cd, 8.1 wt.% Ag, 35.7 wt.%

81   Sb and 21.1 wt% S. No Cu, As and Bi were detected. In *atomic percent of pure cations*, these

82   results indicate 29.3 Pb, 0.5 Fe, 0.6 Mn, 0.2 Sn, 0.4 In, 1.1 Cd, 13.8 Ag and 54.1 Sb. The 'small'

83   cations amount to 2.8 cations *per 100 cations* in this presentation.

84

85   For the X-ray intensity data collection, the same crystal fragment was used as for the first crystal

86   structure determination by Makovicky & Mumme (1983). It was isolated from a sample labeled as

87   'ramdohrite, Colorada Veine' from the Chocaya Mine, Potosí, Bolivia (a type locality of

88   ramdohrite) and kept in the collections of Ecole des Mines de Paris, France. The sample contains a

89   typically twinned ramdohrite, well separated from intimate exsolution intergrowths of andorite and

90   ramdohrite, and owyheeite (Moëlo et al. 1989). Ramdohrite contains widely spaced scarce andorite

91   exsolution on twin composition planes of ramdohrite.

92

93   Single crystal data were collected at the University of Melbourne using an Oxford Diffraction

94   SuperNova diffractometer. Altogether 39479 reflections were collected for the monoclinic cell of a

95   = 8.7348, b = 13.0542, c = 19.3116Å, β = 90.179° chosen by the instrumental software

96   (CRYSALISPRO, 2010). In this orientation the crystal is multiply twinned on (001). Structure

97   refinement was carried out with SHELX97, using as the starting atomic parameters those

98   determined by Makovicky & Mumme (1983), and invoking the TWIN instruction. Details for the

99   data collection are given in Table 1, final atomic parameters in Table 2, and bond lengths and

100   angles in Table 3. Fig. 1 represents the oblique projection of the structure on (100).

101

102   **DESCRIPTION OF THE CRYSTAL STRUCTURE**

103

104   **Crystal lattice**

105   Already the study of 1983 revealed that the reciprocal lattice of ramdohrite is composed of strong

106   ~4 Å levels interspersed by weak ~8 Å levels. The weighted reciprocal lattice and systematic

107   extinctions show that the ~8 Å structure deviates from the orthorhombic symmetry of the parent

108   lillianite structure and, as a consequence, the following lattice description was adopted: a 8.7348(3)

109   Å, b 13.0543(4) Å, c 19.3117(6) Å and β 90.179(2)^o, space group $P2_1/n$. This compares well with

110   the values derived from film data by Makovicky and Mumme (1983) (converted to the current

111   orientation), a 8.73 Å, b 13.08 Å, c 19.24 Å and β 90.28^o. The crystal is twinned – as do all known

112   ramdohrite samples - but the present fragment has a favourable volume ratio of two twin

113   components (7:1 established by a home-designed method in 1989 and 0.76/0.24 in the current

114   refinement; this difference apparently reflects different collection/orientation strategies). It was the

115   best ratio from among the crystal fragments tried by Makovicky and Mumme (1983).

116

117   Unit cell parameters of a related species, Ag-excess fizelyite, $Ag_{5.94}Pb_{13.74}Sb_{20.84}S_{48}$, are (in the

118   above order) c 8.7230(3) Å, b 13.2345(4) Å, a 19.2767(6) Å, and β 90.401(2)° (Yang et al. 2009)

119   whereas those of two related manganese-containing species, uchucchacuaite,

120     $Ag_{0.99}(Mn_{0.92}Pb_{0.03}Sb_{0.02}Bi_{0.01})Pb_{3.00}Sb_{5.00}S_{12.00}$, ideally $AgMnPb_3Sb_5S_{12}$ (Yang et al. 2001), and

121   menchettiite, $AgMn_{1.60}Pb_{2.40}Sb_3As_2S_{12}$ (Bindi et al. 2012), are c 8.7571(6) Å, b 12.7287(8) Å, a

122   19.3645(11) Å, β 90.059(3)°, nd a 19.233(2) Å, b 12.633(3) Å, c 8.476(2) Å, β 90.08(2)°,

123   respectively. Space group symmetry is $P2_1/n$ for both these structures. This confirms that these

124   three structures are isotypic or at least closely homeotypic and the (essential) cation coordination

125   polyhedra are the same in all these structures. The three measurements show values of lattice

126   parameters that appear to be a combination of changes connected with a degree of $2Pb \leftrightarrow Ag + Sb$

127   substitution and with the replacement of Pb by smaller cations – Cd, Mn, Sn. In all three structures,

128   the diagonal glide plane is perpendicular to the ~13 Å axis and the monoclinic angle is comprised

129   by the 8.7 Å axis and the longest, 19.3 Å, axis which is created by stacking of (311) slabs of galena-

130   like arrangement with the homologue order value N = 4.

131

132   **Coordination polyhedra of cations**

133   The crystal structure of ramdohrite is a homeotype of the prototype lillianite structure, with

134   symmetry described by a subgroup, $P2_1/n$, of the aristotype group of symmetry. The latter group is

135   *Cmcm* in the present orientation. The C centration of the 4 x 13 x 19 Å (sub)cell of the lillianite-like

136   aristotype is lost in ramdohrite and replaced by the action of 2_1 axes parallel to the ~13 Å axis. In

137   each 4 Å tier of the ramdohrite structure, the same number of cation and anion sites is present as in

138   the aristotype. Altogether, the complete cell of ramdohrite contains ten independent cation sites and

139   twelve anion sites.

140

141   The Me3 and Me8 sites are bicapped trigonal prismatic sites of lead, bridging and uniting two

142   adjacent $(311)_{PbS}$ slabs. They alternate along the 8.7 Å axis (Figs. 1 and 2). The two lateral caps on

143   the coordination prism of Pb3 are symmetrical, with Pb-S distances respectively equal to 3.002 Å

144   and 3.081 Å. Those on the prism of Pb8 are highly asymmetric, 3.084 Å and 3.497 Å. The 3.081

145   and 3.084 Å caps are on the side where pure Sb polyhedra are attached, the alternation of the 3.002

146   and 3.497 Å caps occurs on the side of alternating cations, Pb and Sb, and Ag and Sb, in the

147   attached octahedra.

148

149   All pure Sb positions in the $(311)_{PbS}$ slabs (Me1, 2, 6, 7, 10) have coordinations which can be

150   described as 'square' coordination pyramids, completed by an additional long distance into an

151   irregular octahedron. The cross-sections of all of them are trapezoidal (Fig. 2) and in a pattern they

152   aggregate *via* straight rows of anions parallel to the 8.7 Å direction and zig-zag rows perpendicular

153   to this direction.

154

155   The purest Sb coordinations are those of Me6, 7 and 10, with three short Sb-S bonds in a range

156   2.42-2.51 Å, two longer distances 3.17-3.30 Å, and a long distance 3.21-3.56 Å which opposes the

157   vertex of the pyramid (Fig. 1).What is of interest, is that in neither of these polyhedra the two short

158   bonds or, alternatively, the two long distances are of the same length. The longer distance of the

159   short set opposes a shorter distance of the longer set, and *vice versa* (Fig. 2). Among the remaining

160   Sb sites, Me1 displays somewhat longer distances (Table 3), whereas Me2 appears more eccentric

161   in the trapezoidal base of the coordination pyramid. Me2 and Me10 have the shortest Sb-S distance,

162   2.42 Å, to the vertex of the pyramid, whereas Me6 has the shortest long distance, below the base of

163   the pyramid; it is equal to 3.21 Å.

164

165 If we compare the *long* Sb-S distances of antimony sites with the data from related structures, in

166 silver-rich fizelyite (Yang et al. 2009) we observe 2 x 3.20 Å and then a range 3.48 – 3.63 Å; in

167 uchucchacuaite (Yang et al. 2011) 3.23 Å and then 3.40 – 3.59 Å. The equivalent distances in the

168 crystal structure of gustavite (Makovicky and Topa 2011) are 3.13 – 3.28 Å, whereas in antimonian

169 gustavite (Pažout and Dušek 2009) 3.18 Å – 3.34 Å. In Ag-and-Sb free lillianite (Pinto et al. 2006)

170 the corresponding distances are 3.02 and 3.28 Å. Thus, the longest Bi-S distances overlap with the

171 shortest Sb-S distances observed, as an expression of a different degree of lone electron pair activity

172 in these homeotypic compounds.

173

174 The Me9 site has an unusual coordination, with four bond lengths rather close to one another

175 (2.749, 2.800, 2.840, 2.937 Å), the perpendicular bonds being 2.721 – 2.910 Å. It apparently is a

176 mixed (and disordered) Sb-Ag-Cd-(Pb) site; the refined occupancy is 0.39 Sb + 0.61 Ag. In the

177 same [100] column, a pure Ag site, Me4, is situated, with a very open, irregular tetrahedral

178 coordination, with two opposing bonds equal to 2.461 and 2.566 Å, and two 'waist' bonds 2.671

179 and 2.815 Å. The two remaining distances are 3.486 and 3.871 Å. The principal Ag site in the

180 related, Ag-surplus fizelyite, named Ag1 (0.75 Ag), has Ag-S bond lengths 2.45, 2.57, 2.73 and

181 2.74 Å, and the Ag site in uchucchacuaite has 2.47, 2.57, 2.68, and 2.80 Å. Both sites are very

182 similar to ramdohrite. This site in gustavite (Makovicky and Topa 2011) has bond distances 2.51,

183 2.69, 2.73, 2.77 Å, and non-bonding distances 3.18 and 3.21 Å. In antimonian gustavite (Pažout and

184 Dušek 2009) the distances are similar, 2.50, 2.61, 2.71, 2.80, 3.31 and 3.36 Å. We can see that the

185 presence of Sb leads to a more eccentric Ag position inside its complete, CN6, coordination

186 polyhedron. Other variations in bond lengths are small, reflecting minute non-systematic shifts of

187 Ag inside its polyhedron.

188

189   The Me5 site in our structure has a lead-like set of interatomic distances (Table 3). The shortest

190   distance, 2.776 Å is at the lower end of Pb-S spectrum. Refinement indicates a Pb position,

191   alternating with Me10 along [100], although an augmented bond-valence sum, 2.24, suggests a

192   possible admixture of smaller cations.

193

194   The special silver site of the structure of *Ag-rich fizelyite*, Ag2, is an irregular tetrahedral site typical

195   for silver in many sulfosalts, with distances 2.35, 2.37, 2.52 and 3.02 Å. It is always positioned

196   between the faces of two adjacent octahedra of the octahedral [100] Ag – Pb column corresponding

197   to our Me5-Me10 column. In this column, the partially occupied Pb site is partly substituted by flat

198   tetrahedral Ag in one 'upper' portion of the coordination octahedron. The alternating octahedra in

199   the [100] Ag – Pb column, however, are partly occupied by Ag1 with a somewhat kinked linear

200   coordination (S-Ag-S angle 154.5°). This coordination is completed to an irregular, open

201   tetrahedron by two bonds, 2.73 and 2.74 Å. A close, partly occupied Ag1' site with an irregular

202   triangular coordination has three bonds 2.48-2.53 Å. We do not know an analogy of this situation in

203   other phases of the lillianite homologous series. However, the tetrahedral sites which are

204   amalgamated to the octahedral column (as the Ag2 site in fizelyite) are a typical feature of copper

205   coordination in pavonite homologues as also are the flat-tetrahedral (copper) sites in the 'upper' and

206   'lower' halves of the coordination octahedra. In these homologues they form the octahedral

207   columns of the thin pavonite layers (e.g., in the structure of dantopaite, Makovicky et al. 2010).

208

209

210   The 'M2' (Yang *et al.* 2009, 2011) site in Ag-rich fizelyite, corresponding to our Me9, is split, with

211   the two partial sites modelled as 0.56Pb+0.10Sb, and 0.33 Ag, respectively. The principal

212   component has bond distances 2.78, 2.87, 2.91, 2.93, 2.99 and 3.03 Å, i.e. a typical set of Pb-S

213   distances, longer than in our structure. In uchucchacuaite, this site was refined as

214   ~$Mn_{0.90}Ag_{0.05}Sb_{0.05}$, with distances 2.58, 2.62/2.64, 2.63, 2.65, 2.66/2.67, 2.76 Å (double values

215   denote results on two distinct uchucchacuaite samples), distinctly below the values obtained in the

216   present refinement. Very similar results were obtained for menchettiite (Bindi et al. 2011): 2.54,

217   2.62, 2.63, 2.65, 2.66, and 2.75 Å. The Mn-S distances in uchucchacuaite and menchettiite are more

218   irregular than the octahedral Mn-S distances in samsonite (2.614 – 2.627 Å; Edenharter and

219   Nowacki 1974) and those of Mn2 in $MnSb_2S_4$ (2.611 – 2.614 Å; Pfitzner and Kurowski 2000), and

220   they resemble more those of Mn1 (2.546-2.643 Å) in the latter structure or the distribution of Mn-S

221   bonds, 2.445 – 2.736 Å in synthetic benavidesite, $MnPb_4Sb_6S_{14}$ (Léone et al. 2003).

222

223   **Modular character**

224   Each $(311)_{PbS}$ slab in the structure of ramdohrite contains one marginal column of alternating Ag

225   (Me4) and mixed-cation Me9, accompanied by an adjacent column with a typical Sb position Me10

226   alternating with a Pb site Me5 (Fig. 2). The rest of the slab is formed by two ribbons of Sb

227   coordination pyramids which share common S-S edges of their bases. The 'framework' created by

228   the Sb positions has been highlighted by Yang et al.(2009) in their description of fizelyite. In the

229   (100) projection (Fig. 1), the pyramids face outwards and together form a large lone electron pair

230   micelle hosting lone electron pairs (LEP) of Sb1, 2, 6 and 7 (Makovicky and Mumme 1983). The

231   lateral pyramids of Me10 are flipped into orientation opposite to the adjacent Me2 and Me7

232   pyramids. On the one hand, they terminate the lone electron pair micelles just defined and on the

233   other hand between themselves they form small Me-10-Me10 lone electron pair micelles

234   (Makovicky and Mumme 1983); the same arrangement was recognized in fizelyite and

235   uchucchacuaite (Yang et al. 2009, 2011). The large and small micelles alternate in an *en echelon*

236   arrangement along [010].

237

238   In the 'andorite' phases, the small lone electron pair micelle is enlarged by an Ag-Sb column

239   situated in the position of our Me4-Me9 column into a large micelle, becoming configurationally

240   fully equivalent to the already present, large micelle (Makovicky and Mumme 1983, Moëlo et al.

241   1989).

242

243   Perpendicular projection of a single $(100)_{PbS}$ layer of cations and anions carved out of the $(311)_{PbS}$

244   slab in the structure of ramdohrite (Fig. 2) reveals that its geometric arrangement is not based on

245   crankshaft chains of short, strong Me-S bonds, but rather on a chess-board arrangement of *Sb- and*

246   *Sb*-mixed cation pairs connected to common S atoms via short bonds. As each of them is situated in

247   a coordination polyhedron with a trapezoidal cross-section, a net of diagonal Me-S-Me-S rows

248   results, with regularly alternating narrower and broader intervals between the rows. The just

249   mentioned Sb pairs form the approximate small squares of the net; the larger interspaces form a sort

250   of 'secondary lone electron pair micelles', accommodating a portion of each LEP cloud. The same

251   bonding scheme is observed in the structure of fizelyite (Yang et al. 2009) whereas the structure of

252   highly substituted andorite-6c (Sawada et al. 1987) is based on a packing of crankshaft chains inside

253   each $(311)_{PbS}$ slab (Moëlo et al. 1989). Combination of two adjacent $(100)_{PbS}$ layers brings about

254   only one new grouping: a pair Sb6-Sb10 connected via short strong Sb-S bonds. Eventually, the

255   Sb1-Sb2 pair can be interconnected via strong bonds of statistically occurring Sb9 with Sb7.

256

257   **DISCUSSION**

258

259   **Comparison of different N=4 homologues with lower degrees of substitution**

260 As an introduction to this comparison, let us compare the position of ramdohrite, fizelyite, and

261 uchucchacuaite on the N = 4 line of the lillianite homologous series. This position defines the

262 degree of $M^{3+} + Ag \leftrightarrow 2$ Pb substitution in these lillianite homologues. The calculation procedure,

263 based on the results of electron microprobe analysis, is outlined in the Appendix. For the studied

264 ramdohrite, the calculated N value is 3.91, close to the structural value of 4.0 (the 4th member of

265 the homologous series), and the percentage of the fully substituted end member, ideally $PbAgSb_3S_6$

266 (see the Appendix), is 46.5 %. The two uchucchacuaite samples analysed by Yang et al. (2011)

267 have N = 3.87 and 54.1 % substitution, and N = 3.93 with 50.6 % substitution. Finally, the Ag-

268 excess fizelyite (Yang et al. 2009) yields a calculated N value of 4.43, which deviates substantially

269 from the expected 4.0 but apparently reflects the presence of excess Ag, not fitting into the basic

270 calculation scheme, and indicates 65.5 % substitution, which apparently reflects the same problem.

271 Menchettiite (Bindi et al. 2011) yields the N value of 3.96 and a substitution percentage equal to

272 50.4. Thus, we are comparing phases in the 46.5 – 65.5 % substitution range. We shall not deal here

273 with andorite varieties which lie at and above 97 % substitution, i.e., after a substantial miscibility

274 gap in the andorite – fizelyite series (Moëlo et al. 1989).

275

276 The principal difference between the crystal structures of ramdohrite and fizelyite is the occupancy

277 of the Me9-Me4 column in ramdohrite, refined as (Ag,Sb)-Ag, which corresponds to the Pb4-

278 Ag2/3 column in silver-rich fizelyite. In fizelyite, with a smaller degree of $2Me^{2+} \leftrightarrow Ag+Sb$

279 substitution (Moëlo et al. 1989), the M9 site was refined as 0.56 Pb+0.10Sb, capped by adjacent

280 0.33Ag. In ramdohrite the M9 site is refined as 0.39Sb+0.61Ag, with the understanding that this

281 may include small amounts of Cd (which makes only about 5% of the atomic percentage of

282 antimony in ramdohrite) and even smaller amounts of Mn, Fe and, perhaps, In. The average atomic

283   number of this mixture is not far from the average atomic number of Ag and Sb in the site, making

284   any further refinement attempts problematic.

285

286   Dimensions (i.e., edges) of the coordination trapezoid of this position in fizelyite are 3.67 Å and

287   4.17 Å along the 8 Å direction, and 4.31 Å and 4.39 Å perpendicular to it. This trapezoid is

288   correspondingly smaller in ramdohrite: 3.61 Å and 4.12 Å, as well as 4.11 Å and 4.14 Å, so that the

289   principal reduction of dimensions is in the direction perpendicular to the 8 Å direction. The

290   horizontal Me-S bonds are reduced from 2.780 Å and 2.990 Å in fizelyite to 2.721 Å and 2.910 Å in

291   ramdohrite. Further reduction takes place in uchucchacuaite: the M9 trapezoid has the dimensions

292   3.47 Å and 3.93 Å along the 8 Å direction and 3.71 Å and 3.73 Å perpendicular to it; the horizontal

293   M9-S bonds are 2.63 Å and 2.76 Å. The presence of As in menchettiite is manifested by a small

294   reduction of the size of the coordination polyhedron of the adjacent Mn site. The vertical trapezoid

295   edges are 3.40 Å and 3.93 Å, the quasi-horizontal ones are 3.67 Å and 3.79 Å; the horizontal Mn-S

296   bonds are 2.63 Å and 2.75 Å.

297

298   Shrinkage of the coordination cross-section of Me9 makes space for extension of the silver Me4

299   site. Its dimensions parallel to the 8 Å axis are 4.62 Å and 5.16 Å in ramdohrite, whereas they are

300   4.56 Å and 5.09 Å in fizelyite. Remarkably, the sums of vertical dimensions of these two

301   coordinations add up to practically the same value, 8.72 versus 8.73 Å, indicating that the rest of the

302   structure is identical and it forces the same bonding scheme for both structures. The closely split

303   silver position Ag2-Ag3 in the refinement by Yang et al. (2009) was modelled by anisotropic

304   displacement parameters of a single site in the present refinement. Uchucchacuaite continues the

305   geometric trend: the vertical edges of its trapezoid are further extended, to 4.83 Å and 5.30 Å,

306   respectively. Their sum results in the unit cell parameter equal to 8.76 Å, i.e., whereas the other

307 dimensions are shrinking, this one is getting marginally longer. The arsenic-containing menchettiite

308 breaks this trend, with this unit cell parameter of only 8.476 Å, composed of the vertical edges of

309 the Mn polyhedron combined with the 4.54 Å and 5.10 Å vertical edges of the Ag polyhedron.

310

311 **Influence on lattice geometry**

312 One of the visible results of the above described uncompensated expansion/contraction of the Me9-

313 Me4 sites in the direction perpendicular to the 8 Å axis is that the most profound difference in unit

314 cell parameters between the three structures we dealing with is not along the 19 Å direction as

315 observed between lillianite and gustavite (Harris and Chen 1975, Makovicky and Karup-Møller

316 1977b) but along the 13 Å axis: 13.23 Å for fizelyite and 13.05 Å for the current ramdohrite. In

317 uchucchacuaite this trend continues, giving 12.73 Å (Yang et al. 2011); Moëlo et al. (1984)

318 indicates 12.67 Å for the latter mineral. Menchettiite has *a* equal to 12.663 Å. This behaviour

319 results from the fact that the oriented expansion of the M9 site, described above, elongates each unit

320 layer of atoms illustrated in Fig. along ~[031] direction of the lillianite scheme, and such shifts,

321 taking place alternatively on both sides of the (001) plane occupied by Pb coordination prisms,

322 extend incrementally the structure along the [010] direction (our orientation). In a more isotropic

323 interpretation, given by Yang et al. (2011), the average bond lengths of the M9 site increase from

324 menchettiite (2.642 Å) and uchucchacuaite (2.654 Å) through ramdohrite (2.826 Å, new data) to

325 fizelyite (2.917 Å), causing the expansion of the structure.

326

327   This situation also reminds one of a 'fizelyite' sample from Kisbanya, in which a parallel

328 superposition of lattices, one with *a* 13.14 Å and another one with *a* 12.62-12.64 Å was observed

329 from single-crystal film data (Nuffield 1945, Moëlo et al. 1989). The 19.23 Å and 8.72 Å

330 parameters were common to both lattices. Microscopic observations at the magnifications of the

331   order of 1250 x revealed extremely fine exsolution lamellae of Fe-Mn ramdohrite (Fe>Mn) in a

332   fizelyite matrix, far below microprobe resolution. This rare example of analyzed exsolution

333   suggests that at least for more extreme occupancies of the M9 site, these two minerals represent

334   distinct species with an exsolution gap between them. Investigation of pure Fe ramdohrite might be

335   of special interest.

336   CONCLUSIONS

337

338   The complexity of chemical compositions of this series, based on a combination of $2Me^{2+} \leftrightarrow Ag+Sb$

339   substitution percentage with the presence of different cation substitutions in the M9 site, has been

340   tabulated and evaluated by Moëlo et al. (1989) although further chemical data exist, scattered in

341   literature which postdates this monograph. In combination with the above quoted recent (2009-

342   2012) structure determinations on the phases of this series, the present paper gives the first insight

343   into the structural reasons and mechanisms of their chemical variability and of the remarkable

344   miscibility gaps among the seemingly very similar phases. Deliberations concerning mineralogical

345   (nomenclatorical) implications of the remarkable cation substitutions in the low-substitution phases

346   of the fizelyite – andorite family are to be found especially in the papers by Moëlo et al. (1989) and

347   by Yang et al. (2011). It appears, however, that we still do not know a sufficiently complete

348   spectrum of compositions and structures offered by nature and laboratory syntheses for constructing

349   a complete picture of the ramdohrite-fizelyite-uchucchacuaite family, which would allow to predict

350   and include further potential phases.

351

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353

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357 Dr. S. Graeser, were appreciated.

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359

360 **APPENDIX**

361

362 The order N of a lillianite homologue with a general formula $Pb_{N-1-2x}Bi_{2+x}Ag_xS_{N+2}$ where 'Pb' also

363 includes other divalent cations, such as Mn, Fe, Cd, Sn, and 'Bi' includes Sb, and rarely also As, is

364 calculated as

365 $N = -1 + 1/(Bi + Pb/2 -1/2)$

366 when the atomic proportions of the above defined 'generalized' cations have first been normalized

367 as $(Ag + Pb + Bi) = 1.0$ (Makovicky and Karup-Møller 1977; Ferraris et al. 2008). For each value

368 of N we can define an Ag-free end member $Pb_{N-1}Bi_2S_{N+2}$ and a '100% substituted end member'

369 $PbBi_{N/2 +1}Ag_{(N-2)/2}S_{N+2}$. Percentage of the fully substituted end member, in which lead remained only

370 in the trigonal prismatic sites, is obtained as

371 mol. $\% = 1 – [(2Bi - Pb - 1)/6(Bi + Pb/2 -5/6)]$ (Makovicky and Karup-Møller 1977).

372 This calculation uses the same normalized 'generalized' cation values as the previous one. The

373 substitution coefficient x in the general formula is then calculated as

374 $x =$ (mol% of the fully substituted end member) x $(N-2)/200$.

375 This calculation should be performed using the calculated N value. Using of the ideal N value for

376 the phase distorts the calculated value.

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490   **TABLE 1.**   Data collection and refinement details for ramdohrite

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Ideal Formula	$Pb_6Sb_{11}Ag_3S_{24}$
Crystal data	
Monoclinic cell	$a = 8.7348(3).$ Å, $b = 13.0542(4)$ Å
parameters	$c = 19.3116(6)$ Å
	$\alpha = 90.0°$, $\beta = 90.179(2)°$, $\gamma = 90.0°$
Z	4
Space group	$P2_1/n$
Calculated density	5.543 g cm^{-3}
Data collection	
Temperature (K)	293
λ (Mo$K\alpha$, Å)	0.71073Å
Crystal size (mm)	0.344 x 0.127 x 0.079
Collection mode	omega scan, $\Delta\omega = 1.0°$

Count time per frame	7.89sec
$2\theta_{max}$ (°)	60.42
No. unique reflections	6155
No. reflections, $I > 2\sigma(I)$	5230
Absorption correction	Multiscan
μ	31.90 mm^{-1}
$Tmin$	0.0537
$Tmax$	1.0
R_{merg} (observed)	0.1819
Refinement	
No. of parameters refined	202
Rw_{obs}, $I > 2\sigma(I)$	0.060
Rw_{obs}, all data	0.103
GOF	2.67
Twin volume fractions	0.759, 0.241(2)
$\Delta\sigma_{min}$, $\Delta\sigma_{max}$ (e/Å^3)	-3.31, +6.4

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496   **TABLE 2.** Fractional positional parameters and esd in ramdohrite

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498 | Atom | Occupancy | x/a | y/b | z/c | UISO(equiv) |
|---|---|---|---|---|---|

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500 | Me1 | Sb | 0.1435(2) | 0.3727(1) | 0.1500(1) | 0.0222(3) |

501	Me2	Sb		0.1227(2)	0.6230(1)	0.0566(1)	0.0221(3)
502	Me3	Pb		0.4026(1)	0.5841(1)	0.2505(1)	0.0327(2)
503	Me4	Ag		0.1179(3)	0.3242(2)	0.3587(1)	0.0567(6)
504	Me5	Pb		0.1313(2)	0.6100(1)	0.4504(1)	0.0314(2)
505	Me6	Sb		0.6199(2)	0.3541(1)	0.1279(1)	0.0217(3)
506	Me7	Sb		0.6377(2)	0.6343(1)	0.0535(1)	0.0223(3)
507	Me8	Pb		0.8931(1)	0.5978(1)	0.2446(1)	0.0336(2)
508	Me9	0.39Sb+0.61Ag	0.6155(2)	0.3513(1)	0.3696(1)	0.0328(6)
509	Me10	Sb		0.6432(2)	0.6219(1)	0.4481(1)	0.0213(6)
510	S1			0.3344(5)	0.4998(4)	0.1046(3)	0.0242(3)
511	S2			0.1541(6)	0.2636(5)	0.9976(3)	0.0344(9)
512	S3			0.1454(6)	0.4545(4)	0.2675(2)	0.0239(11)
513	S4			0.1219(7)	0.7215(4)	0.1627(3)	0.0306(9)
514	S5			0.4348(6)	0.5226(5)	0.3997(3)	0.0317(11)
515	S6			0.0888(5)	0.7410(4)	0.3346(2)	0.0234(11)
516	S7			0.9319(6)	0.4985(4)	0.1008(3)	0.0241(9)
517	S8			0.0673(5)	0.2582(4)	0.4817(2)	0.0249(9)
518	S9			0.6370(6)	0.4393(4)	0.2423(3)	0.0254(10)
519	S10			0.6504(6)	0.7110(5)	0.1678(2)	0.0281(9)
520	S11			0.8461(6)	0.5025(5)	0.4124(3)	0.0330(10)
521	S12			0.6685(5)	0.7311(4)	0.3421(2)	0.0237(11)

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523   ADP harmonic parameters in ramdohrite

524		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
525	Me1	0.0214(6)	0.0259(6)	0.0194(6)	-0.0005(5)	0.0023(5)	0.0022(5)
526	Me2	0.0261(6)	0.0260(6)	0.0142(5)	-0.0046(5)	0.0030(5)	-0.0016(4)
527	Me3	0.0352(4)	0.0309(4)	0.0320(4)	-0.0021(3)	0.0050(4)	-0.0042(3)
528	Me4	0.0717(2)	0.0574(12)	0.0411(11)	0.0035(12)	0.0179(10)	0.0245(10)
529	Me5	0.0306(4)	0.0386(4)	0.0250(4)	0.0013(4)	0.0013(3)	0.0025(3)
530	Me6	0.0218(6)	0.0254(6)	0.0179(5)	-0.0010(5)	-0.0002(5)	0.0009(4)

531	Me7	0.0219(6)	0.0290(6)	0.0159(5)	-0.0013(5)	0.0014(5)	0.0006(5)
532	Me8	0.0283(4)	0.0405(4)	0.0321(4)	0.0042(3)	-0.0029(4)	-0.0117(4)
533	Me9	0.0449(10)	0.0237(8)	0.0299(8)	0.0013(6)	-0.0077(7)	-0.0007(5)
534	Me10	0.0201(6)	0.0295(6)	0.0143(5)	-0.0042(5)	-0.0004(5)	-0.0010(5)
535	S1	0.0170(20)	0.0310(23)	0.0246(23)	-0.0016(17)	-0.0002(16)	0.0045(18)
536	S2	0.0196(22)	0.0570(34)	0.0266(25)	-0.0029(23)	0.0022(20)	0.0131(24)
537	S3	0.0254(22)	0.0299(22)	0.0164(20)	0.0032(18)	0.0021(16)	0.0032(17)
538	S4	0.0343(27)	0.0392(27)	0.0182(23)	-0.0125(23)	0.0055(20)	-0.0093(19)
539	S5	0.0239(24)	0.0516(34)	0.0197(23)	-0.0097(22)	0.0018(18)	-0.0084(22)
540	S6	0.0210(21)	0.0321(24)	0.0170(21)	0.0025(18)	-0.0012(16)	-0.0013(17)
541	S7	0.0212(21)	0.0299(23)	0.0213(22)	-0.0023(18)	0.0028(17)	-0.0021(18)
542	S8	0.0175(20)	0.0414(27)	0.0159(21)	0.0003(18)	0.0009(16)	0.0018(19)
543	S9	0.0282(22)	0.0268(21)	0.0212(22)	-0.0003(17)	-0.0016(19)	-0.0057(18)
544	S10	0.0259(23)	0.0479(29)	0.0103(19)	0.0096(22)	-0.0035(17)	-0.0025(18)
545	S11	0.0268(25)	0.0352(26)	0.0369(28)	0.0076(21)	0.0009(22)	0.0019(22)
546	S12	0.0220(21)	0.0302(23)	0.0189(22)	0.0005(17)	-0.0009(17)	-0.0010(18)
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553 **TABLE 3.** Bond lengths, bond angles and their esd's in ramdohrite

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Me1-S1	2.512(5)	Me4-S3	2.461(5)	Me7-S1	3.330(6)
Me1-S2	3.271(6)	Me4-S4	2.671(6)	Me7-S2	2.464(5)
Me1-S3	2.508(5)	Me4-S8	2.566(5)	Me7-S7	3.251(6)
Me1-S6	2.917(5)	Me4-S10	2.815(6)	Me7-S8	2.505(5)
Me1-S7	2.646(5)	Me4-S11	3.486(6)	Me7-S10	2.426(5)
Me1-S12	3.297(6)	Me4-S5	3.871(6)	Me7-S1'	3.530(6)
Me2-S1	2.619(5)	Me5-S2	2.920(6)	Me8-S3	2.923(5)
Me2-S2	3.020(5)	Me5-S5	3.050(6)	Me8-S4	3.021(5)
Me2-S4	2.418(5)	Me5-S6	2.837(6)	Me8-S6	3.070(5)
Me2-S7	2.482(5)	Me5-S8	2.776(6)	Me8-S7	3.084(5)
Me2-S7	3.460(6)	Me5-S11	2.950(6)	Me8-S9	3.047(9)
Me2-S8	3.317(6)	Me5-S11	3.036(6)	Me8-S10	2.977(5)
				Me8-S11	3.497(6)
Me3-S1	3.081(5)			Me8-S12	3.233(6)
Me3-S3	2.8325)				
Me3-S4	3.476(6)	Me6-S1	3.167(6)		
Me3-S5	3.002(5)	Me6-S6	2.457(5)	Me9-S2	2.910(6)
Me3-S9	2.7925)	Me6-S7	3.356(6)	Me9-S4	2.749(6)
Me3-S10	3.163(6)	Me6-S8	3.213(6)	Me9-S5	2.800(6)
Me3-S12	3.490(6)	Me6-S9	2.477(5)	Me9-S9	2.721(5)
Me3-S6	3.791(6)	Me6-S12	2.514(5)	Me9-S10	2.840(6)
				Me9-S11	2.937(6)

		Me10-S2 3.358(6)
		Me10-S5 2.421(5)
		Me10-S8 3.265(6)
		Me10-S11 2.460(5)
		Me10-S12 2.505(5)
		Me10-S5 3.561(6)

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S3 - Me1 - S1 91.8(2)	S9 - Me6 - S6 92.8(2)
S3 - Me1 - S7 93.6(2)	S9 - Me6 - S12 92.2(2)
S1 - Me1 - S7 85.9(2)	S6 - Me6 - S12 95.4(2)
S3 - Me1 - S6 99.0(2)	S9 - Me6 - S1 84.4(2)
S3 - Me1 - S12 101.5(2)	S9 - Me6 - S7 80.8(2)
S6 - Me1 - S12 109.1(2)	S1 - Me6 - S7 106.3(2)
S4 - Me2 - S1 91.7(2)	S10- Me7 - S1 89.0(2)
S4 - Me2 - S7 93.0(2)	S10- Me7 - S7 86.3(2)
S1 - Me2 - S7 97.3(2)	S1 - Me7 - S7 104.9(3)
S4 - Me2 - S2 91.6(2)	S10- Me7 - S2 96.3(2)
S4 - Me2 - S8 84.9(2)	S10- Me7 - S8 90.6(2)
S2 - Me2 - S8 108.4(2)	S2 - Me7 - S8 94.0(2)
S3 - Me3 - S6 72.4(2)	S3 - Me8 - S6 83.4(2)
S3 - Me3 - S4 78.8(2)	S3 - Me8 - S4 85.5(2)
S4 - Me3 - S6 54.6(2)	S4 - Me8 - S6 66.6(2)
S9 - Me3 - S10 79.8(2)	S9 - Me8 - S12 85.8(2)
S9 - Me3 - S12 85.1(2)	S9 - Me8 - S10 79.0(2)
S10- Me3 - S12 60.8(2)	S10- Me8 - S12 65.8(2)
S3 - Me3 – S9 100.6(2)	S3 - Me8 - S9 96.9(2)
S6 - Me3 – S12 88.1(2)	S6 - Me8 - S12 71.3(2)
S4 - Me3 – S10 88.0(2)	S4 - Me8 - S10 86.8(2)

S3 - Me4 - S8 155.8(2)	S9 - Me9 - S4 96.3(2)
S3 - Me4 - S4 98.7(2)	S9 - Me9 - S10 89.5(2)
S3 - Me4 - S10 108.4(2)	S9 - Me9 - S5 83.7(2)
S8 - Me4 - S4 97.1(2)	S9 - Me9 - S11 85.5(2)
S8 - Me4 - S10 81.2(2)	S4 - Me9 - S10 95.1(2)
S4 - Me4 - S10 114.6(2)	S5 - Me9 - S11 78.0(2)
	S2 - Me9 - S4 87.7(2)
S11'- Me5 - S2 89.5(3)	S2 - Me9 - S10 78.6(2)
S11'- Me5 - S8 83.3(3)	S2 - Me9 - S5 107.4(2)
S2 - Me5 - S8 79.2(3)	S2 - Me9 - S11 91.7(2)
S11'- Me5 - S5 92.6(3)	S2 - Me9 - S9 167.7(2)
S11'- Me5 - S11 92.2(3)	
S5 - Me5 - S11 92.6(3)	S12- Me10 - S5 93.3(4)
S6 - Me5 - S2 118.5(3)	S12- Me10 - S11 93.8(4)
S6 - Me5 - S8 85.3(3)	S5 - Me10 - S11 95.4(3)
S6 - Me5 - S5 94.8(3)	S12- Me10 - S2 90.7(3)
S6 -Me5 - S11 89.0(3)	S12- Me10 - S8 89.8(3)
S6 -Me5 - S11 170.8(3)	S2 - Me10 - S8 101.8(3)

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562 Bond-valence totals for cations: Sb1 2.78, Sb2 3.02, Pb3 1.90, Ag4 1.19,

563 Pb5 2.24, Sb6 3.11, Sb7 2.78, Pb8 1.95, (Ag,Sb)9 1.47, Sb10 3.16

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FIGURE CAPTIONS

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Figure 1.   Oblique projection of the crystal structure of ramdohrite onto the (100) plane. *b* axis is pointing down, *c* axis to the right. In the order of decreasing size, spheres indicate S, Pb (grey), mixed cation positions, Ag (black) and Sb (void). Lone electron pair micelles are located at (y,z) equal to (1/2,0), (0,1/2) as well as (0,0) and (1/2,1/2).

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Figure 2.   Perpendicular projection of a single $(100)_{PbS}$ plane from the $(311)_{PbS}$ slab in the structure of ramdohrite. Trapezoidal cross-sections of coordination polyhedra are indicated by S-S joins. *a* axis is vertical. Short Sb-S bonds are indicated by grey colouring.

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