1 **Structural and compositional variations of basic Cu(II) chlorides in the herbertsmithite**

2 **and gillardite structure field**

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18
19 **Abstract**

20   Natural samples of the substituted basic Cu(II) chloride series, $Cu_{4-x}M^{2+}_x(OH)_6Cl_2$ (M

21 = Zn, Ni, or Mg) were investigated by single-crystal X-ray diffraction in order to elucidate

22 compositional boundaries associated with paratacamite and its congeners. The compositional

23 ranges examined are $Cu_{3.65}Zn_{0.35}(OH)_6Cl_2$ – $Cu_{3.36}Zn_{0.64}(OH)_6Cl_2$ and $Cu_{3.61}Ni_{0.39}(OH)_6Cl_2$ –

24 $Cu_{3.13}Ni_{0.87}(OH)_6Cl_2$, along with a single Mg-bearing phase. The majority of samples studied

25 have trigonal symmetry ($R\overline{3}m$) analogous to that of herbertsmithite (Zn) and gillardite (Ni),

26 with $a \approx 6.8$, $c \approx 14.0$ Å. Crystallographic variations for these samples caused by composition

27 are compared with both published and new data for the $R\overline{3}m$ sub-cell of paratacamite,

28 paratacamite-(Mg) and paratacamite-(Ni). The observed trends suggest that the composition

29 of end-members associated with the paratacamite congeners depend upon the nature of the

30 substituting cation.

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32 Key words: Paratacamite; Paratacamite-(Mg), Paratacamite-(Ni); Herbertsmithite; Gillardite;

33 Compositional boundary; Crystal structure

34

Introduction

Paratacamite, $Cu_3(Cu,Zn)(OH)_6Cl_2$, trigonal, space group $R\bar{3}$ (Smith 1906; Frondel 1950; Fleet 1975; Welch *et al*., 2014), is a member of the substituted basic Cu(II) chloride group of minerals. Two newly described paratacamite congeners, paratacamite-(Ni), $Cu_3(Ni,Cu)(OH)_6Cl_2$ (Sciberras *et al*., 2013) and paratacamite-(Mg), $Cu_3(Mg,Cu)(OH)_6Cl_2$ (Kampf *et al*., 2013a), are characterised by extensive substitution for Cu in the interlayer sites. Jambor *et al*. (1996) reported that clinoatacamite, $Cu_2(OH)_3Cl$, monoclinic, space group $P2_1/n$, structurally transforms to a trigonal phase, assumed to be paratacamite, when 2-3 wt% Zn or Ni occupies its structure. The associated solid-solution series is apparently continuous and extends to the minerals herbertsmithite, $Cu_3Zn(OH)_6Cl_2$ (Braithwaite *et al*., 2004), gillardite, $Cu_3Ni(OH)_6Cl_2$ (Colchester *et al*., 2007; Clissold *et al*., 2007), leverettite, $Cu_3Co(OH)_6Cl_2$ (Kampf *et al*., 2013b) and tondiite, $Cu_3Mg(OH)_6Cl_2$ (Malcherek *et al*., 2014) (isostructural, trigonal, space group $R\bar{3}m$), depending upon the nature of the dominant substituting cation. This $R\bar{3}m$ structure corresponds to a pronounced substructure inherent in paratacamite (Fleet, 1975; Kampf *et al*., 2013a; Sciberras *et al*., 2013; Welch *et al*., 2014) and may be considered as the aristotype model for the group of basic Cu(II) chlorides (Malcherek and Schlüter, 2009). This group has received much attention in recent years due to their structure induced magnetic properties, as they are so-called "frustrated antiferromagnets" (Schores *et al*., 2005; Helton *et al*., 2007; Freedman *et al*., 2010; Chu *et al*., 2010; Han *et al*., 2011, 2012; Li and Zhang, 2013).

Malcherek and Schlüter (2009) suggested that the sequence of compositionally related structural transformations that lead to herbertsmithite can be described by the space group chain $P\bar{1} \rightarrow P2_1/c\ (P2_1/n) \rightarrow R\bar{3}m$. However, the triclinic phase originally attributed to the series, known as "anatacamite", has recently been discredited by the Commission on New Minerals Nomenclature and Classification of the International Mineralogical Association (Hålenius *et al*., 2015). Welch *et al*. (2014) reported a reversible structural transformation from paratacamite $R\bar{3}$ to herbertsmithite $R\bar{3}m$ structures that occurs at 353–393 K. This transformation is in line with the predicted space group chain associated with the paratacamite phase, $P\bar{1} \rightarrow R\bar{3} \rightarrow R\bar{3}m$ (Malcherek and Schlüter, 2009). The boundary between the $R\bar{3}$ and $R\bar{3}m$ phases is difficult to quantify due to the very similar powder X-ray diffraction patterns of the minerals (Jambor *et al*., 1996; Braithwaite *et al*., 2004; Kampf *et al*., 2013a; Sciberras *et al*., 2013). The superstructure reflections of paratacamite may only be

67 quantifiable using single-crystal diffraction methods (Kampf *et al*., 2013a; Sciberras *et al*.,

68 2013; Welch *et al*., 2014).

69   Braithwaite *et al*. (2004) suggested an upper compositional limit for the stability of

70 paratacamite of *ca* 50% interlayer occupancy of Zn, which implies a destabilisation of the

71 herbertsmithite structure below this threshold. Paratacamite from the type material (British

72 Museum specimen BM86958) was reported by Welch *et al*. (2014) as having the composition

73 $Cu_{3.71}Zn_{0.29}(OH)_6Cl_2$, which is in line with the observations made by Braithwaite *et al*. (2004)

74 and Jambor *et al*. (1996). However, recent reports of paratacamite-(Mg) (Kampf *et al*.,

75 2013a) and paratacamite-(Ni) (Sciberras *et al*., 2013) both with a composition significantly

76 greater than 50% occupancy of the interlayer by the substituting cation has indicated that the

77 compositional stability fields of paratacamite and herbertsmithite congeners may be

78 significantly different from those of these two minerals.

79   This crystallographic investigation of naturally occurring samples from the series was

80 carried out to elucidate the compositional boundary between the $R\bar{3}$ and $R\bar{3}m$ structures in

81 terms of Zn and Ni substitution.

82

83 **Experimental**

84 *Samples and analysis*

85   Specimens of the basic Cu(II) chlorides were obtained from the Mineralogical

86 Museum, Hamburg, Germany, and from several private collections for compositional and

87 crystallographic analysis. The authors analysed samples of paratacamite from the British

88 Museum, London, UK (specimen BM86958), paratacamite-(Mg) from the Natural History

89 Museum of Los Angeles County, USA (specimen 64041), and paratacamite-(Ni) from the

90 Western Australian Museum, Western Australia, Australia (specimen WAM M365.2003), in

91 this study, but full data of the analyses appear in the separate publications Welch *et al*.,

92 (2014), Kampf *et al*. (2013a), and Sciberras *et al*. (2013), respectively. Additional analyses of

93 these samples are included in this paper. The remainder of samples and their localities are

94 reported in Table 1.

95   Two different electron microprobes were used, a JEOL 8600 electron microprobe for

96 samples originating from 132N nickel mine, Widgiemooltha, Western Australia, and a

97 Cameca SX 100 electron microprobe for the remaining samples. Both microprobes were

98 operated in WDS mode with an accelerating voltage of 15 kV, a specimen current of 20 nA

99 and focussed beam. Table 1 also lists the empirical formulae determined from these analyses.

100 The simplified formula, based on Σ(cations) = 4, for each sample was used in the structural

101 refinement and is reported as follows: CB03, $Cu_{3.61}Ni_{0.39}(OH)_6Cl_2$;

102 CB07, $Cu_{3.51}Ni_{0.49}(OH)_6Cl_2$; G8502, $Cu_{3.12}Ni_{0.88}(OH)_6Cl_2$; G8568,

103 $Cu_{3.11}Ni_{0.88}Co_{0.01}(OH)_6Cl_2$; G7751, $Cu_{3.09}Ni_{0.90}Co_{0.01}(OH)_6Cl_2$; MD166-3,

104 $Cu_{3.65}Zn_{0.35}(OH)_6Cl_2$; MM02, $Cu_{3.61}Zn_{0.39}(OH)_6Cl_2$ and MD166-2, $Cu_{3.36}Zn_{0.64}(OH)_6Cl_2$.

105

106 *Crystallographic measurements*

107 Crystals of Ni-bearing specimens from the 132 N deposit G8502, G8568, and G7751,

108 were measured at 293(2) K using a Bruker Smart 1000 CCD diffractometer with graphite-

109 monochromated Mo$K\alpha$ radiation. The remaining samples from the Carr Boyd Rocks mine,

110 the Murrin Murrin mine, and the San Francisco mine, CB03, CB07, MM02, MD166-2 and

111 MD166-3 were analysed at 294(2) K on a Nonius Kappa CCD diffractometer with Mo$K\alpha$

112 radiation. Final unit-cell dimensions were determined by a least-squares refinement of the full

113 data sets and all structure refinements were made using SHELXL (Sheldrick, 2008) based on

114 atom coordinates reported for analogous phases (Braithwaite *et al.*, 2004; Clissold *et al.*,

115 2007).

116 Special attention was given to the identification of weak reflections at half integer

117 positions of *h* and *k*, which correspond to the paratacamite super-structure. Pseudo-precession

118 diffraction patterns reconstructed from the full data collections for each sample indicated the

119 $R\bar{3}m$ substructure (Table 2), $2a^*$ superlattice reflections being absent.

120 Samples containing Ni as the substituting cation have unit-cell dimensions analogous

121 to those of gillardite ($a \sim 6.8$, $c \sim 13.9$ Å). Along the compositional series studied, the *c* axis

122 showed the greatest variation, decreasing from 13.936(2) to 13.848(2) Å as Cu is replaced by

123 Ni. The cell dimensions of sample G7751 are $a = 6.8421(8)$ and $c = 13.848(2)$ Å, and the

124 composition $Cu_3(Ni_{0.90}Cu_{0.09}Co_{0.01})(OH)_6Cl_2$, compare well with the unit cell reported for

125 holotype gillardite, $a = 6.8364(1)$ and $c = 13.8459(4)$ Å,

126 $Cu_3(Ni_{0.903}Cu_{0.081}Co_{0.012}Fe_{0.004})(OH)_6Cl_2$, by Clissold *et al.* (2007).

127 Similarly, Zn-bearing samples exhibited unit cell parameters related to herbertsmithite

128 ($a \sim 6.8$, $c \sim 14.1$ Å). The range detected expressed the varying contribution of Zn content,

129 increasing from 14.046(9) to 14.062(4) Å, as Zn content increases. The reported unit cell for

130 herbertsmithite is $a = 6.834$, $c = 14.075$ Å for material of end-member composition

131 $Cu_3Zn(OH)_6Cl_2$ (Braithwaite *et al.*, 2004) and is in line with the composition versus unit cell

132 relationship determined here. These results are also in accord with the variation in cell

133 parameters reported for synthetic trigonal Zn-bearing members of the basic Cu(II) chlorides

134 by Jambor *et al.* (1996).

135   Due to the absence of any super-lattice reflections and the similarity of these unit cells

136   with those reported for herbertsmithite and gillardite, structural refinements were made in

137   space group $R\bar{3}m$ for all data sets. All structures were refined based on the atom coordinates

138   established by Braithwaite et al. (2004) and Clissold et al. (2007) for herbertsmithite and

139   gillardite, respectively, and converged to acceptable residuals and anisotropic thermal

140   parameters. Structure refinement details can be found in Table 2. Selected crystallographic

141   data are given in Table 3.

142   The paratacamite $R\bar{3}m$ sub-cell structure is an average representation of the full $R\bar{3}$

143   super-cell structure (Fleet 1975; Welch et al., 2014). Crystallographic data for the

144   substructures of samples identified as paratacamite (BM86958) (Welch et al., 2014),

145   paratacamite-(Mg) (64041) (Kampf et al., 2013a) and paratacamite-(Ni) (WAM M365.2003)

146   (Sciberras et al., 2013), were refined in space group $R\bar{3}m$ after data reduction of the full set of

147   structure factors to include only the sublattice reflections. Selected crystallographic data for

148   the sub-cell structure of these paratacamite samples is given in Table 3.

149

150   **Description of the structures**

151   The $R\bar{3}m$ structure is characterised by layers of (4+2) Jahn-Teller distorted octahedra

152   of composition $[CuCl_2(OH)_4]$ (centred at the $M(2)$ site), which are linked together in the

153   interlayer $M(1)$ site by an $M^{2+}O_6$ octahedron. This interlayer metal position is bonded to six

154   symmetry equivalent O atoms and exhibits a slight angular distortion. While the $M(2)$ site is

155   completely composed of Cu^{2+}, the $M(1)$ site bears the extent of Cu substitution by other

156   divalent cations with similar ionic radius. This is the same scheme of metal distribution

157   adopted for the related $R\bar{3}m$ phases herbertsmithite (Braithwaite et al., 2004), gillardite

158   (Clissold et al., 2007), leverettite (Kampf et al., 2013b), and tondiite (Malcherek et al., 2014).

159   The $R\bar{3}$ structure of paratacamite, published in full in Welch et al. (2014), Kampf et al.

160   (2013a), and Sciberras et al. (2013), is composed of similar layers of $[CuCl_2(OH)_4]$ ($M(3)$ and

161    $M(4)$ sites), which also exhibit typical (4+2) Jahn-Teller distortion. The interlayer is

162   composed of two metal positions ($M(1)$ and $M(2)$ sites), which link the sheets together via

163   common O atoms. The $M(1)$ site is octahedrally coordinated to six symmetry equivalent O

164   atoms, similar to the $M(1)O_6$ octahedron of the $R\bar{3}m$ structure. The $M(2)$ site is bonded to

165   three symmetry equivalent O atoms ($trans$), in an apparent (2+2+2) Jahn-Teller distorted

166   octahedron. Similarly, the interlayer metal positions of the $R\bar{3}$ structure were assigned the full

167   extent of Cu substitution.

168

Results and discussion

The compositional range determined for Zn- and Ni-bearing single-crystals, $Cu_{3.65}Zn_{0.35}(OH)_6Cl_2$– $Cu_{3.36}Zn_{0.64}(OH)_6Cl_2$ and $Cu_{3.61}Ni_{0.39}(OH)_6Cl_2$ – $Cu_{3.13}Ni_{0.87}(OH)_6Cl_2$, respectively, indicates that the $R\bar{3}m$ structure can exist down to the monoclinic – trigonal transition zone determined by Jambor *et al*. (1996), between *ca* $Cu_{3.75}Zn_{0.25}(OH)_6Cl_2$ to $Cu_{3.66}Zn_{0.34}(OH)_6Cl_2$. Schores *et al*. (2005) reported X-ray structural data for synthetic single-crystals of Zn-bearing paratacamite, produced by hydrothermal methods. Although, all structure refinements by these authors were made on the $R\bar{3}m$ sub-cell, the authors did not mention the presence of any super-lattice reflections and their data are in complete agreement with those for herbertsmithite. The range of compositions studied by these authors is $Cu_{3.67}Zn_{0.33}(OH)_6Cl_2$ – $Cu_3Zn(OH)_6Cl_2$, and supports these observations.

It is important to note that the $R\bar{3}m$ structure shared by herbertsmithite, gillardite, leverettite and tondiite, is topologically, but not crystallographically, identical to that of paratacamite ($R\bar{3}$) and its congeners. The former minerals, *sensu stricto*, are defined as having an interlayer site that is dominated by Zn, Ni, Co or Mg respectively (Braithwaite *et al*., 2004; Clissold *et al*., 2007; Kampf *et al*., 2013b; Malcherek *et al*., 2014). Guidelines for nomenclature of topologically identical phases defer to the "dominant-constituent rule" (Hatert and Burke, 2008). Therefore, those samples exhibiting the $R\bar{3}m$ structure but with Cu dominance in the interlayer, represent a separate species that deserves a unique name. This issue will be addressed in a future manuscript.

An examination of selected crystallographic data (Table 3) for samples containing Zn^{2+} as the primary substituting cation shows that *a* and *c* axes decrease towards the monoclinic–trigonal transformation boundary, in line with the observations of powdered material in Jambor *et al*. (1996). There is a small contraction of *M*–O bond lengths for both metal sites with decreasing Zn content. All *cis*∠O–*M*–O show a corresponding increase along the series, of which the most pronounced increase is associated with the $M(1)O_6$ octahedron. The trends are generally reversed when Ni^{2+} is the dominant substituting cation. The *c* axis length increases by ~ 0.1 Å with decreasing Ni content. Along the same compositional trend *cis* ∠O–*M*–O of both *M*(1)- and *M*(2)-centred octahedra gradually increase, with the most pronounced change existing in the *cis*∠O–*M*(1)–O.

For Zn-bearing samples, there is no significant change in the O···Cl distance with changes in composition. The Ni-bearing samples show only a minor decrease in the O···Cl

201 distance with increasing Ni-content. Data from the paratacamite $R\bar{3}m$ structure are generally

202 consistent with trends observed for herbertsmithite and gillardite ($R\bar{3}m$) samples.

203   There is no significant difference between the paratacamite-(Mg) sub-cell structure

204 and tondiite, which only differ in composition by a small amount, where x(Mg) = 0.60 in

205 paratacamite-(Mg) (Kampf $et\ al.$, 2013a) and x(Mg) = ca 0.70 in tondiite (Malcherek $et\ al.$,

206 2014) for the formula $Cu_{4-x}Mg_x(OH)_6Cl_2$. The average sub-cell structure of paratacamite-

207 (Mg) appears consistent with variation attributed to the difference in ionic radius of the

208 cations. The effective ionic radius of [6]Mg^{2+} (0.72 Å) is only marginally less than that of

209 [6]Cu^{2+} and [6]Zn^{2+} (0.73 Å and 0.74 Å, respectively), but is larger than [6]Ni^{2+} (0.69 Å)

210 (Shannon, 1976). The leverettite (Co-end member) sample has a relatively large unit cell

211 which would be influenced to some degree by the presence of [6]Mn^{2+} (0.83 Å) which is

212 significantly larger than [6]Co^{2+} (0.745 Å), in a six-coordinate environment (Shannon, 1976).

213   The lattice strain induced by composition was calculated by determining the

214 corresponding strain tensor of the aristotype unit cell as well as the transformed paratacamite

215 sub-cell for samples listed in Table 3. The strain tensors were then used to calculate the scalar

216 strain. According to the crystallographic data in Table 3, the paratacamite substructure offers

217 a good comparison with samples exhibiting the aristotype structure ($sensu\ stricto$). Therefore,

218 the corresponding unit cell strain observed for this substructure should also be comparable

219 with the compositional trends observed for the aristotype structure. The tensor components

220 for the hexagonal setting can be determined from the following equations:

221

222 $$e_{11} = e_{22} = \frac{a}{a_o} - 1 \qquad\qquad\qquad (1)$$

223 $$e_{33} = \frac{c}{c_o} - 1 \qquad\qquad\qquad (2)$$

224 $$e_{23} = e_{13} = e_{12} = 0 \qquad\qquad\qquad (3)$$

225

226   The above equations are from Carpenter $et\ al.$ (1998) and are discussed in the context

227 of this mineral series by Malcherek and Schlüter (2009). The unit cell reported by

228 Braithwaite $et\ al.$ (2004) for herbertsmithite was used for reference values in the calculation

229 giving a_o = 6.834 and c_o = 14.075 Å. The reference unit cell for gillardite, a_o = 6.8364 and

230 c_o = 13.8459 Å, was taken from Clissold $et\ al.$ (2007) for material of composition

231 $(Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004})(OH)_6Cl_2$. This material is not ideal as a reference for the lattice

232 parameters expected for pure $Cu_3Ni(OH)_6Cl_2$, but was retained here because it exhibits the

233 smallest lattice volume and highest substitution of the available gillardites in the literature

234 and this study. Calculations were made using the unit cell parameters in Table 3 for all Zn-

235 and Ni-bearing samples. The trace amount of Co present in some of the gillardite samples is

236 not expected to contribute significantly to the unit cell volume. The scalar strain and

237 calculated tensor components can be found in Table 4 in the final column.

238   The distortion of the aristotype unit cell increases towards the trigonal→monoclinic

239 transformation as the critical interlayer Cu content is approached. The strain for both

240 chemical systems is small across the entire series, but increases much more rapidly for Ni-

241 bearing samples. This might be due to the greater difference in ionic radius between $^{[6]}Cu^{2+}$

242 and $^{[6]}Ni^{2+}$, versus $^{[6]}Zn^{2+}$. Figure 1 displays the strain tensor e_{33} plot against composition.

243 The sub-cell of paratacamite (BM86958) shows the greatest strain of all Zn-bearing samples.

244 The upper compositional limit proposed for the stability of clinoatacamite, at $x \sim 0.33$,

245 appears to be a critical composition in terms of the aristotype unit-cell strain. Extrapolation of

246 the trend for Zn-bearing samples indicates that the Zn composition of holotype paratacamite

247 examined by Fleet (1975), with a scalar strain of 0.0028 associated with the sub-cell, is

248 between ca $Cu_{3.70}Zn_{0.30}(OH)_6Cl_2$ and $Cu_{3.67}Zn_{0.33}(OH)_6Cl_2$.

249   The distortion of the $M(1)$ octahedron in the $R\overline{3}m$ aristotype structure was calculated

250 for Zn- and Ni-bearing material in this study using the formulation for quadratic elongation

251 (QE) and bond-angle variance (BAV) of Robinson $et\ al.$ (1971), as implemented in the

252 program VESTA (Momma and Izumi, 2008). The data are displayed in Figure 2. Both the QE

253 and BAV values for herbertsmithite and gillardite samples show significant changes that can

254 be related to composition. The single representative QE and BAV value determined from the

255 paratacamite (BM86958) $R\overline{3}m$ structure, with a composition of $Cu_{3.71}Zn_{0.29}(OH)_6Cl_2$ (Welch

256 $et\ al.$, 2014), has the highest distortion of all Zn-bearing samples. With increasing Zn content,

257 both QE and BAV values decrease to a minimum for compositions above $x \sim 0.6$ and are

258 unaffected by increased Zn content. Similarly, gillardite samples show a significant and

259 reproducible decrease for both QE and BAV values with excess Ni content. However, the

260 decrease in these values appears to be sharper and occurs at a composition $x > 0.7$. The $R\overline{3}m$

261 structure of paratacamite-(Ni) gives comparable QE and BAV values with samples having

262 lower Ni contents.

263   The holotype paratacamite of Fleet (1975) has QE and BAV values associated with

264 the interlayer octahedron of the average sub-cell structure of 1.053 and 207.64 deg^2,

265 respectively. Extrapolation of the trends in Figure 2 indicate a compositional range in

266 agreement with that suggested from the scalar strain results described above.

267

268

Conclusions

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270   The difference in trend evolution of QE and BAV values between the Zn- or Ni-
271   bearing aristotype structure may be attributed to the difference in crystal-chemical behaviour
272   of these cations. These results show that the distortion exhibited by the $M(1)O_6$ octahedron
273   varies with changes in composition in the aristotype structure. It may be inferred that the
274   analogous interlayer position in the paratacamite superstructure at $M(1)$, which is invariant
275   with temperature (Welch *et al*., 2014), varies with composition. Therefore, it is likely that the
276   Zn- and Ni-bearing samples of paratacamite would have a different set of end-members. This
277   could also be true of other paratacamite congeners. However, the end-members associated
278   with Zn or Ni substitution in paratacamite could not be identified from this study.

279   Both paratacamite-(Ni) and paratacamite-(Mg) examined here have greater than 50%
280   interlayer occupancy of the substituting cation. This may indicate that the $R\bar{3}$ super-cell may
281   also exist across much of the substitution series. One must consider also the multitude of
282   structural refinements for the $R\bar{3}m$ aristotype structure with end-member or near end-member
283   stoichiometry from the literature (Clissold *et al*., 2007; Braithwaite *et al*., 2004; Chu *et al*.,
284   2011; Chu *et al*., 2010; Han *et al*., 2011; Chu, 2011; Wulferding *et al*., 2010; Schores *et al*.,
285   2005). The aristotype structure appears to be thermodynamically stable near the end-member
286   composition $Cu_3M(OH)_6Cl_2$. As the presence of Cu^{2+} becomes significant in the interlayer the
287    $R\bar{3}$ structure may become metastable. Based on the quantifiable distortion of the interlayer
288   position in the aristotype structure, the substituting cation defines the range of stability (or
289   metastability) for the phase. This implies that under the right conditions paratacamite
290   congeners would crystallise before their corresponding aristotype phase, herbertsmithite or
291   gillardite for Zn and Ni, respectively, and by extension tondiite and leverettite for Mg and Co,
292   respectively, described by the Ostwald step rule (Ostwald, 1897). The particular conditions
293   which promote the nucleation and growth of the aristotype structure may serve to inhibit the
294   nucleation and growth of $R\bar{3}$ domains.

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Table 1. Electron microprobe analyses of material in this study.

Sample	Spots	CuO	ZnO	NiO	MgO	CoO	MnO	Cl	H_2O**	O≡Cl	Total	Empirical formula
		*Average (above), range (below) (wt%)										
CB03	100	67.29(0.93)	-	6.75(0.69)	-	-	0.01(0.02)	16.12(0.14)	12.59	-3.64	102.76	$(Cu_{3.63}Ni_{0.39})_{\Sigma4.02}Cl_{1.95}(OH)_{6.00}$
		65.64-70.59		4.54-7.70			0-0.05	15.78-16.42				
CB07	8	65.79(2.29)	-	8.71(1.63)	-	-	0.07(0.04)	16.70(0.13)	12.77	-3.77	100.27	$(Cu_{3.50}Ni_{0.49})_{\Sigma3.99}Cl_{2.00}(OH)_{6.00}$
		62.99-69.65		5.17-10.12			0-0.12	16.44-16.84				
G8502	8	60.81(0.41)	-	16.19(0.96)	0.06(0.05)	0.15(0.07)	-	17.23(12)	13.28	-3.89	103.83	$(Cu_{3.11}Ni_{0.88})_{\Sigma3.99}Cl_{1.98}(OH)_{6.00}$
		59.92-61.16		14.93-17.45	0-0.14	0.06-0.24		17.04-17.46				
G8568	12	60.25(1.98)	-	16.01(1.40)	0.02(0.03)	0.25(0.07)	-	17.40(0.26)	13.20	-3.93	103.20	$(Cu_{3.10}Ni_{0.88}Co_{0.01})_{\Sigma3.99}Cl_{2.01}(OH)_{6.00}$
		56.60-64.86		13.92-18.49	0-0.11	0.12-0.40		17.09-17.95				
G7751	16	59.11(2.21)	-	16.32(1.33)	0.02(0.03)	0.24(0.10)	-	17.58(0.22)	13.10	-3.97	102.40	$(Cu_{3.07}Ni_{0.90}Co_{0.01})_{\Sigma3.98}Cl_{2.05}(OH)_{6.00}$
		55.96-62.27		14.74-19.05	0-0.10	0.11-0.49		17.24-18.00				
MD166-3	15	68.10(0.52)	6.65(0.11)	-	-	-	-	16.27(0.21)	12.63	-3.68	99.97	$(Cu_{3.67}Zn_{0.35})_{\Sigma4.02}Cl_{1.97}(OH)_{6.00}$
		67.39-69.27	6.44-6.80					15.98-16.85				
MM02	100	66.76(2.41)	7.32(1.67)	-	-	-	-	16.66(0.26)	12.59	-3.77	99.56	$(Cu_{3.61}Zn_{0.39})_{\Sigma4.00}Cl_{2.02}(OH)_{6.00}$
		62.03-71.94	4.56-11.29					16.17-17.51				
MD166-2	40	61.42(0.86)	11.93(0.83)	-	-	-	-	16.57(0.26)	12.46	-3.74	98.64	$(Cu_{3.35}Zn_{0.64})_{\Sigma3.99}Cl_{2.03}(OH)_{6.00}$
		59.96-64.91	9.57-13.84					16.23-17.34				

*Fields with a dash (-) represent elements not detected. **H_2O content was calculated based on 8 anions *pfu*.

CB03	Carr Boyd Rocks Mine, Western Australia, Australia
CB07	Carr Boyd Rocks Mine, Western Australia, Australia
G8502	132N nickel mine, Widgiemoothla, Western Australia, Australia
G8568	132N nickel mine, Widgiemoothla, Western Australia, Australia
G7751	132N nickel mine, Widgiemoothla, Western Australia, Australia
MD166-3	San Francisco Mine, Sierra Gorda, Chile
MM02	Murrin Murrin mine, Western Australia, Australia
MD166-2	San Francisco Mine, Sierra Gorda, Chile

425	Table 2. Crystal data and structure refinements of samples in this study			
426	Sample	MD166-3	MM02	MD166-2
427	Normalised formula[a]	$Cu_{3.65}Zn_{0.35}Cl_2O_6H_6$	$Cu_{3.61}Zn_{0.39}Cl_2O_6H_6$	$Cu_{3.36}Zn_{0.64}Cl_2O_6H_6$
428	Formula weight	427.75	427.82	428.28
429	Temperature (K)	294(2)	294(2)	294(2)
430	Wavelength (Å)	0.71073	0.71073	0.71073
431	Crystal system	trigonal	trigonal	trigonal
432	Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
433	Unit cell dimensions a(Å)	6.835(4)	6.839(7)	6.8347(9)
434	c (Å)	14.046(9)	14.052(4)	14.062(4)
435	Volume (Å^3)	568.3(6)	569.2(8)	568.87(19)
436	Z, Calculated density (g cm^{-3})	3, 3.750	3, 3.744	3, 3.750
437	Absorption coefficient (mm^{-1})	11.885	11.880	11.976
438	$F(000)$	613	613	614
439	Crystal size (mm)	0.11 x 0.09 x 0.08	0.24 x 0.20 x 0.16	0.25 x 0.20 x 0.15
440	Theta range for data	3.74 to 34.98°	3.73 to 34.95°	3.73 to 34.98°
441	Limiting indices	$-10 \le h \le 10$	$-10 \le h \le 10$	$-10 \le h \le 9$
442		$-11 \le k \le 11$	$-10 \le k \le 10$	$-10 \le k \le 11$
443		$-21 \le l \le 22$	$-22 \le l \le 22$	$-22 \le l \le 22$
444	Reflections/unique	3714/339	4024/340	3797/340
445	R_{int}	0.0369	0.0290	0.0289
446	Completeness to theta	34.98° 99.7 %	34.95° 100.0 %	34.97° 100.0 %
447	Refinement method	Full-matrix	Full-matrix	Full-matrix
448		least-squares on F^2	least-squares on F^2	least-squares on F^2
449	Data/restraints/parameters	339/1/18	340/1/19	340/1/19
450	Goodness-of-fit on F^2	1.326	1.322	1.415
451	Final R indices[$I>2\sigma(I)$] R_1	0.0153	0.0191	0.0192
452	wR_2	0.0337	0.0491	0.0466
453	R indices (all data) R_1	0.0172	0.0204	0.0197
454	wR_2	0.0340	0.0495	0.0469
455	$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e.Å^{-3})	0.818 and -0.636	0.555 and -0.525	0.495 and -1.274

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Table 2. *Continued*

Sample	CB03	CB07	G8502	G8568	G7751
Normalised formula[a]	$Cu_{3.61}Ni_{0.39}Cl_2O_6H_6$	$Cu_{3.51}Ni_{0.49}Cl_2O_6H_6$	$Cu_{3.12}Ni_{0.88}Cl_2O_6H_6$	$Cu_{3.11}Ni_{0.88}Co_{0.01}Cl_2O_6H_6$	$Cu_{3.09}Ni_{0.90}Co_{0.01}Cl_2O_6H_6$
Formula weight	425.24	424.74	422.91	422.81	422.71
Temperature (K)	294(2)	294(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
Unit cell dimensions a (Å)	6.8376(8)	6.841(4)	6.8403(8)	6.8407(9)	6.8421(8)
c (Å)	13.936(2)	13.944(5)	13.852(2)	13.846(2)	13.848(2)
Volume ($Å^3$)	564.27(11)	565.1(5)	561.30(12)	561.10(17)	561.42(11)
Z, Calculated density (g cm^{-3})	3, 3.754	3, 3.744	3, 3.753	3, 3.754	3, 3.751
Absorption coefficient (mm^{-1})	11.717	11.666	11.622	11.616	11.603
$F(000)$	611	611	609	609	609
Crystal size (mm)	0.22 x 0.18 x 0.15	0.15 x 0.11 x 0.08	0.18 x 0.20 x 0.20	0.08 x 0.10 x 0.10	0.10 x 0.10 x 0.14
Theta range for data	3.74 to 34.97°	3.74 to 34.99 °	3.74 to 28.16°	3.74 to 28.23°	3.74 to 28.27°
Limiting indices	$-10 \leq h \leq 10$	$-10 \leq h \leq 11$	$-9 \leq h \leq 8$	$-8 \leq h \leq 8$	$-8 \leq h \leq 9$
	$-10 \leq k \leq 10$	$-11 \leq k \leq 11$	$-8 \leq k \leq 8$	$-8 \leq k \leq 8$	$-8 \leq k \leq 7$
	$-22 \leq l \leq 22$	$-22 \leq l \leq 21$	$-17 \leq l \leq 17$	$-15 \leq l \leq 17$	$-18 \leq l \leq 18$
Reflections/unique	8365/336	3755/338	1462/186	1481/187	1450/189
R_{int}	0.0343	0.0290	0.0254	0.0202	0.0218
Completeness to theta	34.97° 99.7%	34.99° 100.0%	28.16° 96.9 %	28.23° 96.4 %	28.27° 95.9%
Refinement method	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2
Data/restraints/parameters	336/1/18	338/1/19	186/1/19	187/1/19	189/1/19
Goodness-of-fit on F^2	1.279	1.221	1.394	1.325	1.290
Final R indices [$I>2\sigma(I)$] R_1	0.0159	0.0139	0.0297	0.0221	0.0231
wR_2	0.0385	0.0327	0.0786	0.0569	0.0568
R indices (all data) R_1	0.0166	0.0151	0.0297	0.0222	0.0234
wR_2	0.0387	0.0330	0.0786	0.0570	0.0571
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e.$Å^{-3}$)	0.558 and -0.759	0.444 and -0.611	0.609 and -2.449	0.467 and -1.741	0.576 and -1.5810

[a]The normalised formula used in the structure refinements was made to $\sum$(cations) = 4.

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Table 3. Unit cell data and selected bond lengths, distances and angles of the paratacamite substructure in space group $R\bar{3}m$.

Sample	Interlayer cations	$M(x)$	a(Å)	c(Å)	$M(1)$–O (Å)	O–$M(1)$–O cis (°)	$M(2)$–O (Å)	$M(2)$–Cl (Å)	O–$M(2)$–O cis (°)	O–$M(2)$–Cl cis (°)	O···Cl (Å)
[1]Paratacamite*	Cu > Zn[#]	(-)	6.827(5)	14.041(6)	2.11	(-)	1.98	2.78	(-)	(-)	3.07
[2]BM86958*	Cu > Zn	0.29	6.8247(1)	14.0298(4)	2.102(2)	103.99(7)	1.9774(9)	2.7774(6)	98.25(11)	97.59(7)	3.072(1)
[3]MD166-3	Cu > Zn	0.35	6.835(4)	14.046(9)	2.112(2)	103.77(7)	1.982(1)	2.778(1)	97.77(8)	97.59(5)	3.073(2)
[3]MM02	Cu > Zn	0.39	6.839(7)	14.052(4)	2.109(2)	103.78(6)	1.983(2)	2.781(2)	97.94(9)	97.56(5)	3.074(2)
[3]MD166-2	Zn > Cu	0.64	6.8347(9)	14.062(4)	2.114(1)	103.67(5)	1.9838(6)	2.7778(6)	97.62(7)	97.49(3)	3.072(1)
[4]Herbertsmithite	Zn > Cu	1	6.834(1)	14.075(2)	2.119(1)	(-)	1.985(1)	2.779(1)	(-)	(-)	3.071
[3]CB03	Cu > Ni	0.39	6.8376(6)	13.936(2)	2.088(1)	103.31(5)	1.9827(6)	2.7735(5)	98.42(8)	97.66(3)	3.060(1)
[3]CB07	Cu > Ni	0.49	6.841(4)	13.944(5)	2.089(1)	103.36(5)	1.983(1)	2.775(1)	98.46(7)	97.69(4)	3.063(2)
[5]Paratacamite-(Ni)*	Ni > Cu[§]	0.73	6.843(1)	13.935(3)	2.088(2)	103.39(9)	1.982(1)	2.775(8)	98.48(13)	97.75(5)	3.064(2)
[3]G8502	Ni > Cu	0.88	6.8403(8)	13.852(2)	2.077(3)	102.93(14)	1.983(2)	2.768(1)	98.48(19)	97.80(8)	3.051(3)
[3]G8568	Ni > Cu[§]	0.89	6.8407(9)	13.846(2)	2.079(2)	102.99(10)	1.981(1)	2.7673(9)	98.43(14)	97.89(6)	3.053(2)
[3]G7751	Ni > Cu[§]	0.91	6.8421(8)	13.848(2)	2.077(2)	102.94(10)	1.983(1)	2.7676(9)	98.53(14)	97.85(6)	3.053(2)
[6]Gillardite	Ni > Cu	0.90	6.8364(1)	13.8459(4)	2.0791(8)	102.93(3)	1.9812(4)	2.7665(3)	98.34(5)	97.81(2)	3.049(8)
[7]Paratacamite-(Mg)*	Mg > Cu	0.60	6.8441(8)	14.025(1)	2.104(3)	103.33(10)	1.988(1)	2.7764(9)	97.96(15)	97.49(6)	3.069(2)
[8]Tondiite	Mg > Cu	0.70	6.8345(2)	14.0022(7)	2.0971(7)	103.33(6)	1.9855(6)	2.7716(4)	98.15(6)	97.49(5)	3.0659(8)
[9]Leverettite	Co > Cu[¥]	0.67	6.8436(6)	14.064(1)	2.114(3)	103.92(11)	1.983(1)	2.782(1)	97.87(17)	97.67(7)	3.079(2)

The composition (x) corresponds to the formula $Cu_{4-x}M_x(OH)_6Cl_2$; (-) not given. [1]Average distances with respect to split sites in space group $R\bar{3}m$ of the paratacamite substructure from Fleet (1975); [2]Paratacamite from the type specimen at 300 K examined in Welch *et al.* (2014); [3]This study; [4]Braithwaite *et al.* (2004); [5]Sciberras *et al.* (2013); [6]Clissold *et al.* (2007); [7]Kampf *et al.* (2013a); [8]Malcherek *et al.* (2014); [9]Kampf *et al.* (2013b). [#]True composition must be considered unknown. [¥]Also contains a small amount of Mn and trace Ni and Mg. [§]Also contains trace Co.   Contains minor Co and trace Fe. *$R\bar{3}$ super-structure is considered to be the true structure.

Sample	$Zn_x^{\#}$	e_{11}	e_{22}	e_{33}	$\sqrt{\Sigma e_{ij}^2}$
Paratacamite*	(-)	-0.0010	-0.0010	-0.0024	0.0028
BM86958*	0.29	-0.0014	-0.0014	-0.0032	0.0037
MD166-3	0.35	0.0001	0.0001	-0.0021	0.0021
MM02	0.39	0.0007	0.0007	-0.0016	0.0019
MD166-2	0.64	0.0001	0.0001	-0.0009	0.0009

Sample	$Ni_x^{\#}$	e_{11}	e_{22}	e_{33}	$\sqrt{\Sigma e_{ij}^2}$
CB03	0.39	0.0002	0.0002	0.0065	0.0065
CB07	0.49	0.0007	0.0007	0.0071	0.0071
[5]Paratacamite-(Ni)*	0.71	0.0010	0.0010	0.0064	0.0066
G8502	0.88	0.0006	0.0006	0.0004	0.0009
G8568	0.89	0.0006	0.0006	0.0	0.0009
G7751	0.91	0.0008	0.0008	0.0002	0.0012

517 Table 4. Scalar strain and strain tensor components for the aristotype unit-cell

*The true unit-cell is the paratacamite super-cell. [#]The composition relates to the formula $Cu_{4-x}M_x(OH)_6Cl_2$; (-) not known.

535

536   Figure 1. The paratacamite sub-cell strain tensor e_{33} of samples used in this study. The
537   composition x applies to the formula $Cu_{4-x}M_x(OH)_6Cl_2$ where M = Zn (blue triangles) or Ni
538   (red squares). Filled markers are samples of the paratacamite congeners and open markers are
539   either herbertsmithite, gillardite or their Cu-rich congeners. The dotted lines mark the
540   proposed compositional transformation zone between monoclinic and trigonal members
541   determined by Jambor *et al*. (1996).
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546   Figure 2. Quadratic elongation (QE) and bond-angle variance (BAV) of $M(1)$ interlayer
547   octahedron of herbertsmithite, gillardite and their Cu-rich congerns (open shapes) and in the
548   paratacamite $R\bar{3}m$ substructure (filled shapes). Compositional error bars are smaller than the
549   size of the symbol.
550