

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, $\text{Cu}_{4-x}\text{M}^{2+}_x(\text{OH})_6\text{Cl}_2$ (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 $\text{Cu}_{3.65}\text{Zn}_{0.35}(\text{OH})_6\text{Cl}_2 - \text{Cu}_{3.36}\text{Zn}_{0.64}(\text{OH})_6\text{Cl}_2$ and $\text{Cu}_{3.61}\text{Ni}_{0.39}(\text{OH})_6\text{Cl}_2 -$
24 $\text{Cu}_{3.13}\text{Ni}_{0.87}(\text{OH})_6\text{Cl}_2$, along with a single Mg-bearing phase. The majority of samples studied
25 have trigonal symmetry ($R\bar{3}m$) 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 $R\bar{3}m$ 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

35 Introduction

36 Paratacamite, $\text{Cu}_3(\text{Cu,Zn})(\text{OH})_6\text{Cl}_2$, trigonal, space group $R\bar{3}$ (Smith 1906; Frondel
37 1950; Fleet 1975; Welch *et al.*, 2014), is a member of the substituted basic Cu(II) chloride
38 group of minerals. Two newly described paratacamite congeners, paratacamite-(Ni),
39 $\text{Cu}_3(\text{Ni,Cu})(\text{OH})_6\text{Cl}_2$ (Sciberras *et al.*, 2013) and paratacamite-(Mg), $\text{Cu}_3(\text{Mg,Cu})(\text{OH})_6\text{Cl}_2$
40 (Kampf *et al.*, 2013a), are characterised by extensive substitution for Cu in the interlayer
41 sites. Jambor *et al.* (1996) reported that clinoatacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, monoclinic, space group
42 $P2_1/n$, structurally transforms to a trigonal phase, assumed to be paratacamite, when 2-3 wt%
43 Zn or Ni occupies its structure. The associated solid-solution series is apparently continuous
44 and extends to the minerals herbertsmithite, $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ (Braithwaite *et al.*, 2004),
45 gillardite, $\text{Cu}_3\text{Ni}(\text{OH})_6\text{Cl}_2$ (Colchester *et al.*, 2007; Clissold *et al.*, 2007), leverettite,
46 $\text{Cu}_3\text{Co}(\text{OH})_6\text{Cl}_2$ (Kampf *et al.*, 2013b) and tondiite, $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Cl}_2$ (Malcherek *et al.*, 2014)
47 (isostructural, trigonal, space group $R\bar{3}m$), depending upon the nature of the dominant
48 substituting cation. This $R\bar{3}m$ structure corresponds to a pronounced substructure inherent in
49 paratacamite (Fleet, 1975; Kampf *et al.*, 2013a; Sciberras *et al.*, 2013; Welch *et al.*, 2014) and
50 may be considered as the aristotype model for the group of basic Cu(II) chlorides (Malcherek
51 and Schlüter, 2009). This group has received much attention in recent years due to their
52 structure induced magnetic properties, as they are so-called “frustrated antiferromagnets”
53 (Schores *et al.*, 2005; Helton *et al.*, 2007; Freedman *et al.*, 2010; Chu *et al.*, 2010; Han *et al.*,
54 2011, 2012; Li and Zhang, 2013).

55 Malcherek and Schlüter (2009) suggested that the sequence of compositionally related
56 structural transformations that lead to herbertsmithite can be described by the space group
57 chain $P\bar{1} \rightarrow P2_1/c (P2_1/n) \rightarrow R\bar{3}m$. However, the triclinic phase originally attributed to the
58 series, known as "anatacamite", has recently been discredited by the Commission on New
59 Minerals Nomenclature and Classification of the International Mineralogical Association
60 (Hålenius *et al.*, 2015). Welch *et al.* (2014) reported a reversible structural transformation
61 from paratacamite $R\bar{3}$ to herbertsmithite $R\bar{3}m$ structures that occurs at 353–393 K. This
62 transformation is in line with the predicted space group chain associated with the
63 paratacamite phase, $P\bar{1} \rightarrow R\bar{3} \rightarrow R\bar{3}m$ (Malcherek and Schlüter, 2009). The boundary
64 between the $R\bar{3}$ and $R\bar{3}m$ phases is difficult to quantify due to the very similar powder X-ray
65 diffraction patterns of the minerals (Jambor *et al.*, 1996; Braithwaite *et al.*, 2004; Kampf *et*
66 *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 $\text{Cu}_{3.71}\text{Zn}_{0.29}(\text{OH})_6\text{Cl}_2$, 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 $\Sigma(\text{cations}) = 4$, for each sample was used in the structural

101 refinement and is reported as follows: CB03, $\text{Cu}_{3.61}\text{Ni}_{0.39}(\text{OH})_6\text{Cl}_2$;
102 CB07, $\text{Cu}_{3.51}\text{Ni}_{0.49}(\text{OH})_6\text{Cl}_2$; G8502, $\text{Cu}_{3.12}\text{Ni}_{0.88}(\text{OH})_6\text{Cl}_2$; G8568,
103 $\text{Cu}_{3.11}\text{Ni}_{0.88}\text{Co}_{0.01}(\text{OH})_6\text{Cl}_2$; G7751, $\text{Cu}_{3.09}\text{Ni}_{0.90}\text{Co}_{0.01}(\text{OH})_6\text{Cl}_2$; MD166-3,
104 $\text{Cu}_{3.65}\text{Zn}_{0.35}(\text{OH})_6\text{Cl}_2$; MM02, $\text{Cu}_{3.61}\text{Zn}_{0.39}(\text{OH})_6\text{Cl}_2$ and MD166-2, $\text{Cu}_{3.36}\text{Zn}_{0.64}(\text{OH})_6\text{Cl}_2$.

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 $\text{MoK}\alpha$ 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 $\text{MoK}\alpha$
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 $\text{Cu}_3(\text{Ni}_{0.90}\text{Cu}_{0.09}\text{Co}_{0.01})(\text{OH})_6\text{Cl}_2$, compare well with the unit cell reported for
125 holotype gillardite, $a = 6.8364(1)$ and $c = 13.8459(4)$ Å,
126 $\text{Cu}_3(\text{Ni}_{0.903}\text{Cu}_{0.081}\text{Co}_{0.012}\text{Fe}_{0.004})(\text{OH})_6\text{Cl}_2$, 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 $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ (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 $[\text{CuCl}_2(\text{OH})_4]$ (centred at the $M(2)$ site), which are linked together in the
153 interlayer $M(1)$ site by an $M^{2+}\text{O}_6$ 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 $[\text{CuCl}_2(\text{OH})_4]$ ($M(3)$ 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 $M(1)\text{O}_6$ 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

169 **Results and discussion**

170 The compositional range determined for Zn- and Ni-bearing single-crystals,
171 $\text{Cu}_{3.65}\text{Zn}_{0.35}(\text{OH})_6\text{Cl}_2$ – $\text{Cu}_{3.36}\text{Zn}_{0.64}(\text{OH})_6\text{Cl}_2$ and $\text{Cu}_{3.61}\text{Ni}_{0.39}(\text{OH})_6\text{Cl}_2$ – $\text{Cu}_{3.13}\text{Ni}_{0.87}(\text{OH})_6\text{Cl}_2$,
172 respectively, indicates that the $R\bar{3}m$ structure can exist down to the monoclinic – trigonal
173 transition zone determined by Jambor *et al.* (1996), between *ca* $\text{Cu}_{3.75}\text{Zn}_{0.25}(\text{OH})_6\text{Cl}_2$ to
174 $\text{Cu}_{3.66}\text{Zn}_{0.34}(\text{OH})_6\text{Cl}_2$. Schores *et al.* (2005) reported X-ray structural data for synthetic single-
175 crystals of Zn-bearing paratacamite, produced by hydrothermal methods. Although, all
176 structure refinements by these authors were made on the $R\bar{3}m$ sub-cell, the authors did not
177 mention the presence of any super-lattice reflections and their data are in complete agreement
178 with those for herbertsmithite. The range of compositions studied by these authors is
179 $\text{Cu}_{3.67}\text{Zn}_{0.33}(\text{OH})_6\text{Cl}_2$ – $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, and supports these observations.

180 It is important to note that the $R\bar{3}m$ structure shared by herbertsmithite, gillardite,
181 leverettite and tonidite, is topologically, but not crystallographically, identical to that of
182 paratacamite ($R\bar{3}$) and its congeners. The former minerals, *sensu stricto*, are defined as
183 having an interlayer site that is dominated by Zn, Ni, Co or Mg respectively (Braithwaite *et al.*,
184 2004; Clissold *et al.*, 2007; Kampf *et al.*, 2013b; Malcherek *et al.*, 2014). Guidelines for
185 nomenclature of topologically identical phases defer to the “dominant-constituent rule”
186 (Hatert and Burke, 2008). Therefore, those samples exhibiting the $R\bar{3}m$ structure but with Cu
187 dominance in the interlayer, represent a separate species that deserves a unique name. This
188 issue will be addressed in a future manuscript.

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

199 For Zn-bearing samples, there is no significant change in the O⋯Cl distance with
200 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 tonidiite, which only differ in composition by a small amount, where $x(\text{Mg}) = 0.60$ in
205 paratacamite-(Mg) (Kampf *et al.*, 2013a) and $x(\text{Mg}) = ca\ 0.70$ in tonidiite (Malcherek *et al.*,
206 2014) for the formula $\text{Cu}_{4-x}\text{Mg}_x(\text{OH})_6\text{Cl}_2$. 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 $^{[6]}\text{Mg}^{2+}$ (0.72 Å) is only marginally less than that of
209 $^{[6]}\text{Cu}^{2+}$ and $^{[6]}\text{Zn}^{2+}$ (0.73 Å and 0.74 Å, respectively), but is larger than $^{[6]}\text{Ni}^{2+}$ (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 $^{[6]}\text{Mn}^{2+}$ (0.83 Å) which is
212 significantly larger than $^{[6]}\text{Co}^{2+}$ (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

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

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

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

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 $(\text{Cu}_{3.081}\text{Ni}_{0.903}\text{Co}_{0.012}\text{Fe}_{0.004})(\text{OH})_6\text{Cl}_2$. This material is not ideal as a reference for the lattice
232 parameters expected for pure $\text{Cu}_3\text{Ni}(\text{OH})_6\text{Cl}_2$, 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 $^{[6]}\text{Cu}^{2+}$
242 and $^{[6]}\text{Ni}^{2+}$, versus $^{[6]}\text{Zn}^{2+}$. 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* $\text{Cu}_{3.70}\text{Zn}_{0.30}(\text{OH})_6\text{Cl}_2$ and $\text{Cu}_{3.67}\text{Zn}_{0.33}(\text{OH})_6\text{Cl}_2$.

249 The distortion of the $M(1)$ octahedron in the $R\bar{3}m$ 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) $R\bar{3}m$ structure, with a composition of $\text{Cu}_{3.71}\text{Zn}_{0.29}(\text{OH})_6\text{Cl}_2$ (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 $R\bar{3}m$
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

269 **Conclusions**

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.

295

296 **Acknowledgements**

297 The author MJS acknowledges financial support from the Western Sydney University for a
298 post-graduate studies grant and a scholarship from the Deutscher Akademischer Austausch

299 Dienst (DAAD) in the program Research Grant for Doctoral Candidates and Young
300 Academics and Scientists A/11/93939.

301

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

Sample	Spots	*Average (above), range (below) (wt%)										Total	Empirical formula
		CuO	ZnO	NiO	MgO	CoO	MnO	Cl	H ₂ O**	O≡Cl			
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}) _{Σ4.02} 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}) _{Σ3.99} 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}) _{Σ3.99} 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}) _{Σ3.99} 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}) _{Σ3.98} 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}) _{Σ4.02} 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}) _{Σ4.00} 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}) _{Σ3.99} Cl _{2.03} (OH) _{6.00}	
		59.96-64.91	9.57-13.84					16.23-17.34					

415 *Fields with a dash (-) represent elements not detected. **H₂O content was calculated based on 8 anions *pfu*.

416		
417	CB03	Carr Boyd Rocks Mine, Western Australia, Australia
418	CB07	Carr Boyd Rocks Mine, Western Australia, Australia
419	G8502	132N nickel mine, Widgiemoothla, Western Australia, Australia
420	G8568	132N nickel mine, Widgiemoothla, Western Australia, Australia
421	G7751	132N nickel mine, Widgiemoothla, Western Australia, Australia
422	MD166-3	San Francisco Mine, Sierra Gorda, Chile
423	MM02	Murrin Murrin mine, Western Australia, Australia
424	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 ₂ O ₆ H ₆	Cu _{3.61} Zn _{0.39} Cl ₂ O ₆ H ₆	Cu _{3.36} Zn _{0.64} Cl ₂ O ₆ H 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 ≤ h ≤ 10	-10 ≤ h ≤ 10	-10 ≤ h ≤ 9	
442		-11 ≤ k ≤ 11	-10 ≤ k ≤ 10	-10 ≤ k ≤ 11	
443		-21 ≤ l ≤ 22	-22 ≤ l ≤ 22	-22 ≤ l ≤ 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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458 Table 2. *Continued*

459	Sample	CB03	CB07	G8502	G8568	G7751
460	Normalised formula ^a	Cu _{3.61} Ni _{0.39} Cl ₂ O ₆ H ₆	Cu _{3.51} Ni _{0.49} Cl ₂ O ₆ H ₆	Cu _{3.12} Ni _{0.88} Cl ₂ O ₆ H ₆	Cu _{3.11} Ni _{0.88} Co _{0.01} Cl ₂ O ₆ H ₆	Cu _{3.09} Ni _{0.90} Co _{0.01} Cl ₂ O ₆ H ₆
461	Formula weight	425.24	424.74	422.91	422.81	422.71
462	Temperature (K)	294(2)	294(2)	293(2)	293(2)	293(2)
463	Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
464	Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal
465	Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
466	Unit cell dimensions	a (Å) 6.8376(8)	6.841(4)	6.8403(8)	6.8407(9)	6.8421(8)
467		c (Å) 13.936(2)	13.944(5)	13.852(2)	13.846(2)	13.848(2)
468	Volume (Å ³)	564.27(11)	565.1(5)	561.30(12)	561.10(17)	561.42(11)
469	Z, Calculated density (g cm ⁻³)	3, 3.754	3, 3.744	3, 3.753	3, 3.754	3, 3.751
470	Absorption coefficient (mm ⁻¹)	11.717	11.666	11.622	11.616	11.603
471	$F(000)$	611	611	609	609	609
472	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
473	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°
474	Limiting indices	-10 ≤ h ≤ 10	-10 ≤ h ≤ 11	-9 ≤ h ≤ 8	-8 ≤ h ≤ 8	-8 ≤ h ≤ 9
475		-10 ≤ k ≤ 10	-11 ≤ k ≤ 11	-8 ≤ k ≤ 8	-8 ≤ k ≤ 8	-8 ≤ k ≤ 7
476		-22 ≤ l ≤ 22	-22 ≤ l ≤ 21	-17 ≤ l ≤ 17	-15 ≤ l ≤ 17	-18 ≤ l ≤ 18
477	Reflections/unique	8365/336	3755/338	1462/186	1481/187	1450/189
478	R_{int}	0.0343	0.0290	0.0254	0.0202	0.0218
479	Completeness to theta	34.97° 99.7%	34.99° 100.0%	28.16° 96.9%	28.23° 96.4%	28.27° 95.9%
480	Refinement method	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix
481		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
482	Data/restraints/parameters	336/1/18	338/1/19	186/1/19	187/1/19	189/1/19
483	Goodness-of-fit on F^2	1.279	1.221	1.394	1.325	1.290
484	Final R indices [$I > 2\sigma(I)$]	R_1 0.0159	0.0139	0.0297	0.0221	0.0231
485		wR_2 0.0385	0.0327	0.0786	0.0569	0.0568
486	R indices (all data)	R_1 0.0166	0.0151	0.0297	0.0222	0.0234
487		wR_2 0.0387	0.0330	0.0786	0.0570	0.0571
488	$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (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

489 ^aThe normalised formula used in the structure refinements was made to $\sum(\text{cations}) = 4$.

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

491	Interlayer		Unit cell parameters		$M(1)-O$	$O-M(1)-O$	$M(2)-O$	$M(2)-Cl$	$O-M(2)-O$	$O-M(2)-Cl$	$O...Cl$	
492	Sample	cations	$M(x)$	$a(\text{Å})$	$c(\text{Å})$	(Å)	cis (°)	(Å)	(Å)	cis (°)	cis (°)	(Å)
493	¹ Paratacamite*	Cu > Zn [#]	(-)	6.827(5)	14.041(6)	2.11	(-)	1.98	2.78	(-)	(-)	3.07
494	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)
495	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)
496	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)
497	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)
498	⁴ Herbertsmithite	Zn > Cu	1	6.834(1)	14.075(2)	2.119(1)	(-)	1.985(1)	2.779(1)	(-)	(-)	3.071
499												
500	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)
501	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)
502	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)
503	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)
504	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)
505	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)
506	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)
507												
508	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)
509	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)
510												
511	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)

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

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

518	Sample	Zn _x [#]	e_{11}	e_{22}	e_{33}	$\sqrt{\sum e_{ij}^2}$
519	Paratacamite*	(-)	-0.0010	-0.0010	-0.0024	0.0028
520	BM86958*	0.29	-0.0014	-0.0014	-0.0032	0.0037
521	MD166-3	0.35	0.0001	0.0001	-0.0021	0.0021
522	MM02	0.39	0.0007	0.0007	-0.0016	0.0019
523	MD166-2	0.64	0.0001	0.0001	-0.0009	0.0009
524						
525	Sample	Ni _x [#]	e_{11}	e_{22}	e_{33}	$\sqrt{\sum e_{ij}^2}$
526	CB03	0.39	0.0002	0.0002	0.0065	0.0065
527	CB07	0.49	0.0007	0.0007	0.0071	0.0071
528	⁵ Paratacamite-(Ni)*	0.71	0.0010	0.0010	0.0064	0.0066
529	G8502	0.88	0.0006	0.0006	0.0004	0.0009
530	G8568	0.89	0.0006	0.0006	0.0	0.0009
531	G7751	0.91	0.0008	0.0008	0.0002	0.0012

532 *The true unit-cell is the paratacamite super-cell. [#]The composition relates to the formula
533 Cu_{4-x}M_x(OH)₆Cl₂; (-) not known.

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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 $\text{Cu}_{4-x}\text{M}_x(\text{OH})_6\text{Cl}_2$ where $M = \text{Zn}$ (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 congeners (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



