Structural and compositional variations of basic Cu(II) chlorides in the herbertsmithite and gillardite structure field

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[Received 12 November 2015; Accepted 27 January 2016; Associate Editor: G. Diego Gatta]

Natural samples of the substituted basic Cu(II) chloride series, Cu4-xMx+(OH)6Cl2 (M = Zn, Ni, or Mg) were investigated by single-crystal X-ray diffraction in order to elucidate compositional boundaries associated with paratacamite and its congeners. The compositional ranges examined are Cu3.65Zn0.35(OH)6Cl2 – Cu3.36Zn0.64(OH)6Cl2 and Cu3.61Ni0.39(OH)6Cl2 – Cu3.13Ni0.87(OH)6Cl2, along with a single Mg-bearing phase. The majority of samples studied have trigonal symmetry (R3m) analogous to that of herbertsmithite (Zn) and gillardite (Ni), with a ≈ 6.8, c ≈ 14.0 Å. Crystallographic variations for these samples caused by composition are compared with both published and new data for the R3m sub-cell of paratacamite, paratacamite-(Mg) and paratacamite-(Ni). The observed trends suggest that the composition of end-members associated with the paratacamite congeners depend upon the nature of the substituting cation.

KEYWORDS: paratacamite, paratacamite-(Mg), paratacamite-(Ni), herbertsmithite, gillardite, compositional boundary, crystal structure.

Introduction

PARATACAMITE, Cu4(Cu,Zn)(OH)6Cl2, trigonal, space group R3 (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), Cu4(Ni,Cu)(OH)6Cl2 (Seiberras et al., 2013) and paratacamite-(Mg), Cu4(Mg,Cu)(OH)6Cl2 (Kampf et al., 2013a), are characterized by extensive substitution for Cu in the interlayer sites. Jambor et al. (1996) reported that clinoatacamite, Cu2(OH)3Cl, monoclinic, space group P21/n, transforms structurally 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, Cu3Zn(OH)6Cl2 (Braithwaite et al., 2004), gillardite, Cu3Ni(OH)6Cl2 (Colchester et al., 2007; Clissold et al., 2007), leverettite, Cu3Co(OH)6Cl2 (Kampf et al., 2013b) and tondiite, Cu3Mg(OH)6Cl2 (Malcherek et al., 2014) (isostructural, trigonal, space group R3m), depending upon the nature of the dominant substituting cation. This R3m structure corresponds to a pronounced substructure inherent in paratacamite (Fleet, 1975; Kampf et al., 2013a; Seiberras 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, 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 $P1 \rightarrow P2_1/c (P2_1/n) \rightarrow R3m$. 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 $R3 \rightarrow$ herbertsmithite $R3m$ structures that occurs at 353–393 K. This transformation is in line with the predicted space group chain associated with the paratacamite phase, $P1 \rightarrow R3 \rightarrow R3m$ (Malcherek and Schlüter, 2009). The boundary between the $R3$ and $R3m$ 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 quantifiable using single-crystal diffraction methods (Kampf et al., 2013a; Sciberras et al., 2013; Welch et al., 2014).

Braithwaite et al. (2004) suggested an upper compositional limit for the stability of paratacamite of ~50% interlayer occupancy of Zn, which implies a destabilization of the herbertsmithite structure below this threshold. Paratacamite from the type material (British Museum specimen BM86958) was reported by Welch et al. (2014) as having the composition $\text{Cu}_{3.71}\text{Zn}_{0.29}(\text{OH})_6\text{Cl}_2$, which is in line with the observations made by Braithwaite et al. (2004) and Jambor et al. (1996). However, recent reports of paratacamite-(Mg) (Kampf et al., 2013a) and paratacamite-(Ni) (Sciberras et al., 2013) both with a composition significantly >50% occupancy of the interlayer by the substituting cation has indicated that the compositional stability fields of paratacamite and herbertsmithite congeners may be significantly different from those of these two minerals.

This crystallographic investigation of naturally occurring samples from the series was carried out to elucidate the compositional boundary between the $R3$ and $R3m$ structures in terms of Zn and Ni substitution.

### Experimental

#### Samples and analysis

Specimens of the basic Cu(II) chlorides were obtained from the Mineralogical Museum, Hamburg, Germany, and from several private collections for compositional and crystallographic analysis. The authors analysed samples of paratacamite from the British Museum, London, UK (specimen BM86958), paratacamite-(Mg) from the Natural History Museum of Los Angeles County, USA (specimen 64041) and paratacamite-(Ni) from the Western Australian Museum, Western Australia, Australia (specimen WAM M365.2003), in this study, but full data of the analyses appear in the separate publications Welch et al. (2014), Kampf et al. (2013a) and Sciberras et al. (2013), respectively. Additional analyses of these samples are included in this paper. The remainder of samples and their localities are reported in Table 1.

Two different electron microprobes were used, a JEOL 8600 electron microprobe for samples originating from 132N nickel mine, Widgiemooltha, Western Australia, and a Cameca SX 100 electron microprobe for the remaining samples. Both microprobes were operated in wavelength dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA and focused beam. Table 1 also lists the empirical formulae determined from these analyses. The simplified formula, based on $\Sigma$ (cations) = 4, for each sample was used in the structural refinement and is reported as follows: CB03, $\text{Cu}_{3.61}\text{Ni}_{0.39}(\text{OH})_6\text{Cl}_2$; 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, $\text{Cu}_{3.11}\text{Ni}_{0.88}\text{Co}_{0.01}(\text{OH})_6\text{Cl}_2$; G7751, $\text{Cu}_{3.09}\text{Ni}_{0.09}\text{Co}_{0.01}(\text{OH})_6\text{Cl}_2$; MD166-3, $\text{Cu}_{2.65}\text{Zn}_{0.35}(\text{OH})_6\text{Cl}_2$; MM02, $\text{Cu}_{3.61}\text{Zn}_{0.39}(\text{OH})_6\text{Cl}_2$ and MD166-2, $\text{Cu}_{3.36}\text{Zn}_{0.64}(\text{OH})_6\text{Cl}_2$.

#### Crystallographic measurements

Crystals of Ni-bearing specimens from the 132 N deposit G8502, G8568 and G7751, were measured at 293(2) K using a Bruker Smart 1000 CCD diffractometer with graphite-monochromated MoKα radiation. The remaining samples from the Carr Boyd Rocks mine, the Murrin Murrin mine and the San Francisco mine, CB03, CB07, MM02, MD166-2 and MD166-3 were analysed at 294(2) K on a Nonius Kappa CCD diffractometer with MoKα radiation. Final unit-cell dimensions were determined by a least-squares refinement of the full data sets and all structure refinements were made.
| Sample | Spots | CuO      | ZnO      | NiO      | MgO      | CoO      | MnO      | Cl       | H$_2$O** | O≡Cl | Total | Empirical formula |
|--------|-------|----------|----------|----------|----------|----------|----------|----------|----------|-------|-------|------------------|
| 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$_{0.39}$)$_{24.02}$Cl$_{1.95}$(OH)$_{6.00}$ |
|        |       | 65.64–70.59 | 5.17–10.12 | 0–0.12 | 16.44–16.84 |       |      |         |         |       |       |                   |
| 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$_{0.49}$)$_{23.99}$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) | 0.15(0.07) | 17.23(12) | 13.28 | 3.99 | 103.83 | (Cu$_{3.11}$Ni$_{0.88}$)$_{23.99}$Cl$_{1.95}$(OH)$_{6.00}$ |
|        |       | 59.92–61.16 | 14.93–17.45 | 0–0.14 | 17.04–17.46 |       |      |         |         |       |       |                   |
| G8568  | 12    | 60.25(1.98) | 16.01(1.40) | 0.25(0.07) | 17.40(0.26) | 13.20 | 3.93 | 103.20 | (Cu$_{3.10}$Ni$_{0.88}$Co$_{0.01}$)$_{23.99}$Cl$_{2.01}$(OH)$_{6.00}$ |
|        |       | 56.60–64.86 | 13.92–18.49 | 0–0.11 | 17.91–17.95 |       |      |         |         |       |       |                   |
| G7751  | 16    | 59.11(2.21) | 16.32(1.33) | 0.24(0.10) | 17.58(0.22) | 13.10 | 3.97 | 102.40 | (Cu$_{3.07}$Ni$_{0.90}$Co$_{0.01}$)$_{23.98}$Cl$_{2.03}$(OH)$_{6.00}$ |
|        |       | 55.96–62.27 | 14.74–19.05 | 0–0.10 | 17.24–18.00 |       |      |         |         |       |       |                   |
| MD166-3| 15    | 68.10(0.52) | 6.65(0.11) | 0.06(0.05) | 16.27(0.21) | 12.63 | 3.68 | 99.97  | (Cu$_{1.67}$Zn$_{0.33}$)$_{24.02}$Cl$_{1.95}$(OH)$_{6.00}$ |
|        |       | 67.39–69.27 | 6.44–6.80  | 0–0.14 | 15.98–16.85 |       |      |         |         |       |       |                   |
| MM02   | 100   | 66.76(2.41) | 7.32(1.67) | 0.02(0.03) | 16.66(0.26) | 12.59 | 3.77 | 99.56  | (Cu$_{3.61}$Zn$_{0.39}$)$_{24.00}$Cl$_{2.03}$(OH)$_{6.00}$ |
|        |       | 62.03–71.94 | 4.56–11.29 | 0–0.11 | 16.17–17.51 |       |      |         |         |       |       |                   |
| MD166-2| 40    | 61.42(0.86) | 11.93(0.83) | 0.24(0.10) | 16.57(0.26) | 12.46 | 3.74 | 98.64  | (Cu$_{3.35}$Zn$_{0.62}$)$_{23.99}$Cl$_{2.03}$(OH)$_{6.00}$ |
|        |       | 59.96–64.91 | 9.57–13.84 | 0–0.10 | 16.23–17.34 |       |      |         |         |       |       |                   |

*Fields with a dash (−) represent elements not detected. **H$_2$O 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.
using SHELXL (Sheldrick, 2008) based on atom coordinates reported for analogous phases (Braithwaite et al., 2004; Clissold et al., 2007).

Special attention was given to the identification of weak reflections at half integer positions of $h$ and $k$, which correspond to the paratacamite superstructure. Pseudo-precession diffraction patterns reconstructed from the full data collections for each sample indicated the $R\bar{3}m$ substructure (Table 2), $2a^*$ superlattice reflections being absent.

Samples containing Ni as the substituting cation have unit-cell dimensions analogous to those of gillardite ($a \approx 6.8$, $c \approx 13.9\, \text{Å}$). Along the compositional series studied, the $c$ axis showed the greatest variation, decreasing from $13.936(2)$ to $13.848(2)\, \text{Å}$ as Cu is replaced by Ni. The cell dimensions of sample G7751 are $a = 6.8421(8)$ and $c = 13.848(2)\, \text{Å}$, and the 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 holotype gillardite, $a = 6.8364(1)$ and $c = 13.8459(4)\, \text{Å}$. $\text{Cu}_3(\text{Ni}_{0.93}\text{Cu}_{0.08}\text{Co}_{0.012}\text{Fe}_{0.004})(\text{OH})_6\text{Cl}_2$, by Clissold et al. (2007).

Similarly, Zn-bearing samples exhibited unit-cell parameters related to herbertsmithite ($a \approx 6.8$, $c \approx 14.1\, \text{Å}$). The range detected expressed the varying contribution of Zn content, increasing from $14.046(9)$ to $14.062(4)\, \text{Å}$, as Zn content increases. The reported unit cell for herbertsmithite is $a = 6.834, c = 14.075\, \text{Å}$ for material of end-member composition $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ (Braithwaite et al., 2004) and is in line with the composition vs. unit-cell relationship determined here. These results are also in accord with the variation in cell parameters reported for synthetic trigonal Zn-bearing members of the basic Cu(II) chlorides by Jambor et al. (1996).

Due to the absence of any super-lattice reflections and the similarity of these unit cells with those reported for herbertsmithite and gillardite, structural refinements were made in space group $R\bar{3}m$ for all data sets. All structures were refined based on the atom coordinates established by Braithwaite et al. (2004) and Clissold et al. (2007) for herbertsmithite and gillardite, respectively, and converged to acceptable residuals and anisotropic thermal parameters. Structure refinement details can be found in Table 2. Selected crystallographic data are given in Table 3.

The paratacamite $R\bar{3}m$ sub-cell structure is an average representation of the full $R\bar{3}$ super-cell structure (Fleet 1975; Welch et al., 2014). Crystallographic data for the substructures of samples identified as paratacamite (BM69858) (Welch et al., 2014), paratacamite-(Mg) (64041) (Kampf et al., 2013a) and paratacamite-(Ni) (WAM M365.2003) (Sciberras et al., 2013), were refined in space group $R\bar{3}m$ after data reduction of the full set of structure factors to include only the sublattice reflections. Selected crystallographic data for the sub-cell structure of these paratacamite samples is given in Table 3.

### Description of the structures

The $R\bar{3}m$ structure is characterized by layers of $(4+2)$ Jahn-Teller distorted octahedra of composition $[\text{CuCl}_2(\text{OH})_4]$ (centred at the $M(2)$ site), which are linked together in the interlayer $M(1)$ site by an $M^{2+}\text{O}_6$ octahedron. This interlayer metal position is bonded to six symmetry equivalent O atoms and exhibits a slight angular distortion. While the $M(2)$ site is completely composed of Cu$^{2+}$, the $M(1)$ site bears the extent of Cu substitution by other divalent cations with similar ionic radius. This is the same scheme of metal distribution adopted for the related $R\bar{3}m$ phases herbertsmithite (Braithwaite et al., 2004), gillardite (Clissold et al., 2007), leverettite (Kampf et al., 2013b) and tondiite (Malcherek et al., 2014). The $R\bar{3}$ structure of paratacamite, published in full in Welch et al. (2014), Kampf et al. (2013a) and Sciberras et al. (2013), is composed of similar layers of $[\text{CuCl}_2(\text{OH})_4]$ ($M(3)$ and $M(4)$ sites), which also exhibit typical $(4+2)$ Jahn-Teller distortion. The interlayer is composed of two metal positions ($M(1)$ and $M(2)$ sites), which link the sheets together via common O atoms. The $M(1)$ site is octahedrally coordinated to six symmetry equivalent O atoms, similar to the $M(1)\text{O}_6$ octahedron of the $R\bar{3}m$ structure. The $M(2)$ site is bonded to three symmetry equivalent O atoms (trans), in an apparent $(2+2+2)$ Jahn-Teller distorted octahedron. Similarly, the interlayer metal positions of the $R\bar{3}$ structure were assigned the full extent of Cu substitution.

### Results and discussion

The compositional range determined for Zn- and Ni-bearing single-crystals, 

$$\text{Cu}_{3.65}\text{Zn}_{0.35}(\text{OH})_6\text{Cl}_2 - \text{Cu}_{3.36}\text{Zn}_{0.34}(\text{OH})_6\text{Cl}_2$$

and 

$$\text{Cu}_{3.61}\text{Ni}_{0.39}(\text{OH})_6\text{Cl}_2 - \text{Cu}_{3.13}\text{Ni}_{0.87}(\text{OH})_6\text{Cl}_2,$$

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 $c$. $\text{Cu}_{3.75}\text{Zn}_{0.25}(\text{OH})_6\text{Cl}_2$ to $\text{Cu}_{3.66}\text{Zn}_{0.34}(\text{OH})_6\text{Cl}_2$. Schores et al. (2005) reported X-ray structural data
Table 2. Crystal data and structure refinements of samples in this study.

| Sample     | MD166-3          | MM02           | MD166-2          | CB03           |
|------------|------------------|----------------|------------------|----------------|
| Normalized 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$_6$ | Cu$_{3.61}$Ni$_{0.39}$Cl$_2$O$_6$H$_6$ |
| Formula weight | 427.75           | 427.82         | 428.28           | 425.24         |
| Temperature (K) | 294(2)          | 294(2)         | 294(2)           | 294(2)         |
| Wavelength (Å) | 0.71073         | 0.71073        | 0.71073          | 0.71073        |
| Crystal system  | trigonal      | trigonal       | trigonal         | trigonal       |
| Space group    | $R3m$           | $R3m$          | $R3m$            | $R3m$          |
| Unit-cell dimensions $a$(Å), | $6.835(4)$ | $6.839(7)$ | $6.8347(9)$ | $6.8347(9)$ |
| c (Å) | 14.046(9) | 14.052(4) | 14.062(4) | 13.936(2) |
| Volume ($Å^3$) | 568.3(6) | 569.2(8) | 568.87(19) | 564.27(11) |
| Z, Calculated density (g cm$^{-3}$) | 3 | 3.750 | 3 | 3.750 |
| Absorption coefficient (mm$^{-1}$) | 11.885 | 11.880 | 11.976 | 11.717 |
| F(000) | 613            | 613            | 614              | 611            |
| Crystal size (mm) | $0.11 \times 0.09 \times 0.08$ | $0.24 \times 0.20 \times 0.16$ | $0.25 \times 0.20 \times 0.15$ | $0.22 \times 0.18 \times 0.15$ |
| Theta range for data | 3.74 to 34.98° | 3.73 to 34.95° | 3.73 to 34.98° | 3.74 to 34.97° |
| Limiting indices | $-10 \leq h \leq 10$ | $-10 \leq h \leq 10$ | $-10 \leq h \leq 9$ | $-10 \leq h \leq 10$ |
| $-11 \leq k \leq 11$ | $-10 \leq k \leq 10$ | $-10 \leq k \leq 11$ | $-10 \leq k \leq 10$ | $-10 \leq k \leq 10$ |
| $-21 \leq l \leq 22$ | $-22 \leq l \leq 22$ | $-22 \leq l \leq 22$ | $-22 \leq l \leq 22$ | $-22 \leq l \leq 22$ |
| Reflections/unique | 3714/339 | 4024/340 | 3797/340 | 8365/336 |
| $R_{int}$ | 0.0369 | 0.0290 | 0.0289 | 0.0343 |
| Completeness to theta | 34.98° 99.7% | 34.95° 100.0% | 34.97° 100.0% | 34.97° 99.7% |
| Refinement method | Full-matrix | Full-matrix | Full-matrix | Full-matrix |
| Data/restraints/parameters | least-squares on $F^2$ | least-squares on $F^2$ | least-squares on $F^2$ | least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 339/1/18 | 340/1/19 | 340/1/19 | 336/1/18 |
| Final $R$ indices [i>2σ(|F|)] $R_1$, $wR_2$ | 0.0153, 0.0337 | 0.0191, 0.0491 | 0.0192, 0.0466 | 0.0159, 0.0385 |
| $R$ indices (all data) $R_1$, $wR_2$ | 0.0172, 0.0340 | 0.0204, 0.0495 | 0.0197, 0.0469 | 0.0166, 0.0387 |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e.Å$^{-3}$) | 0.818 and 0.0066 | 0.555 and 0.0066 | 0.495 and 0.0066 | 0.558 and 0.0066 |
| Sample | CB07 | G8502 | G8568 | G7751 |
|--------|------|-------|-------|-------|
| Normalized formula | 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$_6$ |
| Formula weight | 424.74 | 422.91 | 422.81 | 422.71 |
| Temperature (K) | 294(2) | 293(2) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | trigonal | trigonal | trigonal | trigonal |
| Space group | R$_3$ | R$_3$ | R$_3$ | R$_3$ |
| Unit-cell dimensions | | | | |
| $a$ (Å) | 6.841(4) | 6.8403(8) | 6.8407(9) | 6.8421(8) |
| $c$ (Å) | 13.944(5) | 13.852(2) | 13.846(2) | 13.848(2) |
| Volume (Å$^3$) | 565.71(12) | 561.30(12) | 561.10(17) | 561.42(11) |
| Z | 3, 3, 3, 3 | 3, 3, 3, 3 | 3, 3, 3, 3 | 3, 3, 3, 3 |
| Calculated density (g cm$^{-3}$) | 3.744 | 3.753 | 3.754 | 3.751 |
| Absorption coefficient (mm$^{-1}$) | 0.080(9) | 0.080(9) | 0.080(9) | 0.080(9) |
| $F$(000) | 600 | 600 | 600 | 600 |
| Crystal size (mm) | 0.15×0.11×0.08 | 0.18×0.20×0.20 | 0.08×0.10×0.10 | 0.10×0.10×0.14 |
| Theta range for data | 3.74 to 34.99° | 3.74 to 28.16° | 3.74 to 28.23° | 3.74 to 28.27° |
| Limiting indices | $-10 \leq h \leq 11$ | $-9 \leq h \leq 8$ | $-8 \leq h \leq 7$ | $-7 \leq h \leq 6$ |
| $-11 \leq k \leq 11$ | $-8 \leq k \leq 8$ | $-7 \leq k \leq 7$ | $-6 \leq k \leq 6$ |
| $-22 \leq l \leq 22$ | $-17 \leq l \leq 17$ | $-15 \leq l \leq 15$ | $-14 \leq l \leq 14$ |
| $3.74 \leq 2\theta \leq 28.23°$ | $3.74 \leq 2\theta \leq 28.23°$ | $3.74 \leq 2\theta \leq 28.23°$ | $3.74 \leq 2\theta \leq 28.23°$ |
| Reflections/unique | 3755/338 | 1462/186 | 1481/187 | 1450/189 |
| $R_{int}$ | 0.0290 | 0.0254 | 0.0254 | 0.0254 |
| Completeness to theta | 34.99° | 34.99° | 34.99° | 34.99° |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 338/1/19 | 186/1/19 | 187/1/19 | 189/1/19 |
| Goodness-of-fit on $F^2$ | 1.221 | 1.290 | 1.325 | 1.394 |
| $R$ indices (all data) | 0.0139, 0.0327 | 0.0297, 0.0786 | 0.0297, 0.0569 | 0.0297, 0.0571 |
| $R$ indices (all data) | 0.0144, 0.0330 | 0.0297, 0.0569 | 0.0297, 0.0571 | 0.0297, 0.0571 |
| $\Delta \rho_{max}$ ($e$.Å$^{-3}$) | 0.444 and -0.611 | 0.444 and -0.611 | 0.444 and -0.611 | 0.444 and -0.611 |
| $\Delta \rho_{min}$ ($e$.Å$^{-3}$) | 0.467 and -1.741 | 0.467 and -1.741 | 0.467 and -1.741 | 0.467 and -1.741 |

The normalized formula used in the structure refinements was made to $\sum$(cations) = 4.
Table 3. Unit-cell data and selected bond lengths, distances and angles of the paratacamite substructure in space group R3\textbar m.

| Sample          | Interlayer | Cations     | M(1)–O | O–M(1)–O | M(2)–O | O–M(2)–O | O–M(2)–Cl | cis (°) | cis (°) | cis (°) |
|-----------------|------------|-------------|---------|-----------|---------|-----------|------------|---------|---------|---------|
| 1 Paratacamite* | Cu > Zn    | (x)         | 6.827(5)| 14.041(6)| 2.11    | –         | 1.98       | 2.78    | 98.25(11)| 97.59(7)| 3.072(1) |
| 2 BM86958*      | Cu > Zn    | 0.29        | 6.8247(1)| 14.0298(4)| 2.102(2)| 103.99(7)| 1.9774(9) | 2.7774(6)| 97.77(8)| 97.59(5)| 3.073(2) |
| 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) | 97.94(9)| 97.56(5)| 3.074(2) |
| 4 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) |
| 5 MD166-2       | Zn > Cu    | 0.64        | 6.8347(9)| 14.062(4)| 2.114(1)| 103.67(5)| 1.9838(6) | 2.778(6) | 97.62(7)| 97.49(3)| 3.072(1) |
| 6 Herbertsmithite | Zn > Cu  | 1           | 6.834(1)| 14.075(2)| 2.119(1)| –         | 1.985(1)  | 2.779(1) | –       | –       | 3.071   |
| 7 CB03          | Cu > Ni    | 0.39        | 6.8376(6)| 13.936(2)| 2.088(1)| 103.31(5)| 1.9827(6) | 2.773(5) | 98.42(8)| 97.66(3)| 3.060(1) |
| 8 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) |
| 9 Paratacamite-(Ni)* | Ni > Cu  | 0.73        | 6.843(1)| 13.933(3)| 2.088(2)| 103.39(9)| 1.982(1)  | 2.775(8) | 98.48(13)| 97.75(5)| 3.064(2) |
| 10 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) |
| 11 G8568        | Ni > Cu    | 0.89        | 6.8407(9)| 13.846(2)| 2.079(2)| 102.99(10)| 1.981(1)  | 2.767(9)| 98.43(14)| 97.89(6)| 3.053(2) |
| 12 G7751        | Ni > Cu    | 0.91        | 6.8421(8)| 13.848(2)| 2.071(2)| 102.94(10)| 1.983(1)  | 2.767(9)| 98.53(14)| 97.85(6)| 3.053(2) |
| 13 Gillardite   | Ni > Cu    | 0.90        | 6.8364(1)| 13.8459(4)| 2.079(1)| 102.93(3)| 1.9812(4) | 2.766(3)| 98.34(5)| 97.81(2)| 3.049(8) |
| 14 Paratacamite-(Mg)* | Mg > Cu  | 0.60        | 6.8441(8)| 14.025(1)| 2.104(3)| 103.33(10)| 1.988(1)  | 2.776(4)| 97.96(15)| 97.49(6)| 3.069(2) |
| 15 Tondiite     | Mg > Cu    | 0.70        | 6.8345(2)| 14.002(7)| 2.097(1)| 103.33(6)| 1.9855(6) | 2.771(4)| 98.15(6)| 97.49(5)| 3.065(8) |
| 16 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 R3\textbar m of the paratacamite substructure from Fleet (1975); paratacamite from the type specimen at 300 K examined in Welch et al. (2014); this study; Braithwaite et al. (2004); Sciberras et al. (2013); Clissold et al. (2007); Kampf et al. (2013a); Malcherek et al. (2014); 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. R3 super-structure is considered to be the true structure.
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 $Cu_{3.67}Zn_{0.33}(OH)_6Cl_2$ – $Cu_2Zn(OH)_6Cl_2$, 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 ($R3$) 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 refer 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 cisZO–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 $\sim$0.1 Å with decreasing Ni content. Along the same compositional trend cisZO–M–O of both $M(1)$- and $M(2)$-centred octahedra gradually increase, with the most pronounced change existing in the cisZO–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 distance with increasing Ni-content. Data from the paratacamite $R\bar{3}m$ structure are generally consistent with trends observed for herbertsmithite and gillardite ($R\bar{3}m$) samples.

There is no significant difference between the paratacamite-(Mg) sub-cell structure and tondiite, which only differ in composition by a small amount, where $x$(Mg) = 0.60 in paratacamite-(Mg) (Kampf et al., 2013a) and $x$(Mg) = $\approx$0.70 in tondiite (Malcherek et al., 2014) for the formula $Cu_{x=3}Mg_{x=5}(OH)_6Cl_2$. The average sub-cell structure of paratacamite-(Mg) appears consistent with variation attributed to the difference in ionic radius of the cations. The effective ionic radius of $[6]$Mg$^{2+}$ (0.72 Å) is only marginally less than that of $[6]$Cu$^{2+}$ and $[6]$Zn$^{2+}$ (0.73 Å and 0.74 Å, respectively), but is larger than $[6]$Ni$^{2+}$ (0.69 Å) (Shannon, 1976). The leverettite (Co end-member) sample has a relatively large unit cell which would be influenced to some degree by the presence of $[6]$Mn$^{2+}$ (0.83 Å) which is significantly larger than $[6]$Co$^{2+}$ (0.745 Å), in a six-coordinate environment (Shannon, 1976).

The lattice strain induced by composition was calculated by determining the corresponding strain tensor of the aristotype unit cell as well as the transformed paratacamite sub-cell for samples listed in Table 3. The strain tensors were then used to calculate the scalar strain. According to the crystallographic data in Table 3, the paratacamite substructure offers a good comparison with samples exhibiting the aristotype structure (sensu stricto). Therefore, the corresponding unit-cell strain observed for this substructure should also be comparable with the compositional trends observed for the aristotype structure. The tensor components for the hexagonal setting can be determined from the following equations:

\[ e_{11} = e_{22} = \frac{a}{a_o} - 1 \quad (1) \]
\[ e_{33} = \frac{C}{C_o} - 1 \quad (2) \]
\[ e_{23} = e_{13} = e_{12} = 0 \quad (3) \]

The above equations are from Carpenter et al. (1998) and are discussed in the context of this mineral series by Malcherek and Schlüter (2009). The unit cell reported by Braithwaite et al. (2004) for herbertsmithite was used for reference values in the calculation giving $a_o = 6.834$ and $c_o = 14.075$ Å. The reference unit cell for gillardite, $a_o = 6.8364$ and $c_o = 13.8459$ Å, was taken from Clissold et al. (2007) for material of composition ($Cu_{3.081}Ni_{0.903}Co_{0.012}Fe_{0.004}(OH)_6Cl_2$. This material is not ideal as a reference for the lattice parameters expected for pure $Cu_3Ni(OH)_6Cl_2$, but was retained here because it exhibits the smallest lattice volume and highest substitution of the available gillardites in the literature of this study.
Calculations were made using the unit-cell parameters in Table 3 for all Zn- and Ni-bearing samples. The trace amount of Co present in some of the gillardite samples is not expected to contribute significantly to the unit cell volume. The scalar strain and calculated tensor components can be found in Table 4 in the final column.

The distortion of the aristotype unit cell increases towards the trigonal→monoclinic transformation as the critical interlayer Cu content is approached. The

**TABLE 4. Scalar strain and strain tensor components for the aristotype unit-cell.**

| Sample         | Zn\(^x\) | \(e_{11}\)     | \(e_{22}\)     | \(e_{33}\)     | \(\sqrt{\sum e_{ij}^2}\) |
|----------------|----------|----------------|----------------|----------------|-------------------------|
| 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\(^x\) | \(e_{11}\)     | \(e_{22}\)     | \(e_{33}\)     | \(\sqrt{\sum e_{ij}^2}\) |
|----------------|----------|----------------|----------------|----------------|-------------------------|
| CB03           | 0.39     | 0.0002         | 0.0002         | 0.0065         | 0.0065                  |
| CB07           | 0.49     | 0.0007         | 0.0007         | 0.0071         | 0.0071                  |
| 5Paratacamite-(Ni)* | 0.71  | 0.0010         | 0.0010         | 0.0064         | 0.0066                  |
| G8502          | 0.88     | 0.0006         | 0.0006         | 0.0004         | 0.0009                  |
| G85068         | 0.89     | 0.0006         | 0.0006         | 0.012          | 0.0009                  |
| G7751          | 0.91     | 0.0008         | 0.0008         | 0.0002         | 0.0012                  |

*The true unit-cell is the paratacamite super-cell. \(^x\)The composition relates to the formula \(\text{Cu}_{4-x}M_x(\text{OH})_6\text{Cl}_2\).  

**FIG. 1.** The paratacamite sub-cell strain tensor \(e_{33}\) of samples used in this study. The composition \(x\) applies to the formula \(\text{Cu}_{4-x}M_x(\text{OH})_6\text{Cl}_2\) where \(M = \text{Zn}\) (blue triangles) or Ni (red squares). Filled markers are samples of the paratacamite congeners and open markers are either herbertsmithite, gillardite or their Cu-rich congeners. The dotted lines mark the proposed compositional transformation zone between monoclinic and trigonal members determined by Jambor et al. (1996).
strain for both chemical systems is small across the entire series, but increases much more rapidly for Ni-bearing samples. This might be due to the greater difference in ionic radius between $^{60}$Cu$^{2+}$ and $^{60}$Ni$^{2+}$, versus $^{60}$Zn$^{2+}$. The strain tensor $e_{33}$ plot against composition is displayed in Fig. 1. The sub-cell of paratacamite (BM86958) shows the greatest strain of all Zn-bearing samples. The upper compositional limit proposed for the stability of clinoatacamite, at $x \approx 0.33$, appears to be a critical composition in terms of the aristotype unit-cell strain. Extrapolation of the trend for Zn-bearing samples indicates that the Zn composition of holotype paratacamite examined by Fleet (1975), with a scalar strain of 0.0028 associated with the sub-cell, is between $\text{Cu}_{3.70}\text{Zn}_{0.30}(\text{OH})_6\text{Cl}_2$ and $\text{Cu}_{3.67}\text{Zn}_{0.33}(\text{OH})_6\text{Cl}_2$.

The distortion of the $M(1)$ octahedron in the $R3m$ aristotype structure was calculated for Zn- and Ni-bearing material in this study using the formulation for quadratic elongation (QE) and bond-angle variance (BAV) of Robinson et al. (1971), as implemented in the program VESTA (Momma and Izumi, 2008). The data are displayed in Fig. 2. Both the QE and BAV values determined from the paratacamite (BM86958) $R3m$ structure, with a composition of $\text{Cu}_{3.71}\text{Zn}_{0.29}(\text{OH})_6\text{Cl}_2$ (Welch et al., 2014), has the highest distortion of all Zn-bearing samples. With increasing Zn content, both QE and BAV values decrease to a minimum for compositions above $x \approx 0.6$ and are unaffected by increased Zn content. Similarly, gillardite samples show a significant and reproducible decrease for both QE and BAV values with excess Ni content. However, the decrease in these values appears to be sharper and occurs at a composition $x > 0.7$. The $R3m$ structure of paratacamite-(Ni) gives comparable QE and BAV values with samples having lower Ni contents.

The holotype paratacamite of Fleet (1975) has QE and BAV values associated with the interlayer octahedron of the average sub-cell structure of 1.053 and 207.64 deg$^2$, respectively. Extrapolation of the trends in Fig. 2 indicate a compositional range in agreement with that suggested from the scalar strain results described above.

**Conclusions**

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

Both paratacamite-(Ni) and paratacamite-(Mg) examined here have >50% interlayer occupancy of the substituting cation. This may indicate that the $R3$ super-cell may also exist across much of the substitution series. One must consider also the multitude of structural refinements for the $R3m$ aristotype structure with end-member or near end-member stoichiometry from the literature (Clissold et al., 2007; Braithwaite et al., 2004; Chu et al., 2010, 2011; Han et al., 2011; Chu, 2011; Wulfirding et al., 2010; Schores et al., 2005). The aristotype structure appears to be thermodynamically stable near the end-member composition Cu$_3$M(OH)$_6$Cl$_2$. As the presence of Cu$^{2+}$ becomes significant in the interlayer the $R3$ structure may become metastable. Based on the quantifiable distortion of the interlayer position in the aristotype structure, the substituting cation defines the range of stability (or metastability) for the phase. This implies that under the right conditions paratacamite congeners would crystallize before their corresponding aristotype phase, herbertsmithite or gillardite for Zn and Ni, respectively, and by extension tondite and leverettite for Mg and Co, respectively, described by the Ostwald step rule (Ostwald, 1897). The particular conditions which promote the nucleation and growth of the aristotype structure may serve to inhibit the nucleation and growth of $R3$ domains.

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