

Paratacamite-(Mg), $\text{Cu}_3(\text{Mg,Cu})\text{Cl}_2(\text{OH})_6$; a new substituted basic copper chloride mineral from Camerones, Chile

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ABSTRACT

Paratacamite-(Mg) (IMA 2013-014), $\text{Cu}_3(\text{Mg,Cu})\text{Cl}_2(\text{OH})_6$, is the new Mg-analogue of paratacamite. It was found near the village of Cuya in the Camarones Valley, Arica Province, Chile. The mineral is a supergene secondary phase occurring in association with anhydrite, atacamite, chalcophyrite, copiapite, dolomite, epsomite, haydeite, hematite, magnesite and quartz. Paratacamite-(Mg) crystals are rhombs and thick to thin prisms up to 0.3 mm in size exhibiting the forms {201} and {001}. Twinning by reflection on {10 $\bar{1}$ } is common. The mineral is transparent with a vitreous lustre, with medium to deep-green colour and light-green streak. Mohs hardness is 3–3½, the tenacity is brittle and the fracture is conchoidal. Paratacamite-(Mg) has one perfect cleavage on {201}. The measured and calculated densities are 3.50(2) and 3.551 g cm⁻³, respectively. The mineral is optically uniaxial (–) with $\varepsilon = 1.785(5)$ and $\omega > 1.8$ and slight pleochroism: *O* (bluish green) > *E* (green). Electron-microprobe analyses provided the empirical formula $\text{Cu}_3(\text{Mg}_{0.60}\text{Cu}_{0.38}\text{Ni}_{0.01}\text{Mn}_{0.01})\text{Cl}_2(\text{OH})_6$. The mineral is easily soluble in dilute HCl. Paratacamite-(Mg) is trigonal, $R\bar{3}$, with cell parameters $a = 13.689(1)$, $c = 14.025(1)$ Å, $V = 2275.8(3)$ Å³ and $Z = 12$. There is a pronounced sub-cell corresponding to $d' \approx \frac{1}{2}a$, $c' \approx c$ in space group $R\bar{3}m$. The eight strongest lines in the X-ray powder diffraction pattern are [d_{obs} Å(hkl)]: 5.469(87)(021), 4.686(26)(003), 2.904(34)(401), 2.762(100)(22 $\bar{3}$,042), 2.265(81)(404), 1.819(26)(603), 1.710 (34)(440) and 1.380(19)(446). The structure was refined to $R_1 = 0.039$ for 480 $F_o > 4\sigma F$ reflections. Refinement using interlayer Mg-Cu site scattering factors indicated that Mg is distributed statistically between both interlayer octahedra $M1\text{O}_6$ and $M2\text{O}_6$. A comparison of the distortions associated with $M1\text{O}_6$ and $M2\text{O}_6$ octahedra suggest that the sample is near the upper compositional limit for stability of the $R\bar{3}$ phase.

KEYWORDS: paratacamite, new mineral, basic copper chloride, Chile.

Introduction

EARLY in 2012, one of the authors (AAMD) collected specimens, in the Camarones Valley of Chile's Arica Province, which contained green crystals resembling the atacamite-group basic

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copper chloride minerals clinoatacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$ (Jambor *et al.*, 1996), herbertsmithite, $\text{Cu}_3\text{ZnCl}_2(\text{OH})_6$ (Braithwaite *et al.*, 2004), gillardite, $\text{Cu}_3\text{NiCl}_2(\text{OH})_6$ (Colchester *et al.*, 2007; Clissold *et al.*, 2007) and paratacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ (Smith, 1906; Frondel, 1950). Chemical analyses revealed these crystals to be a basic copper chloride of composition $(\text{Cu}_{3.38}\text{Mg}_{0.60}\text{Ni}_{0.01}\text{Mn}_{0.01})(\text{OH})_6\text{Cl}_2$. Single-crystal X-ray diffraction (XRD) studies indicated trigonal symmetry with a hexagonal unit cell of $a = 13.689(1)$ and $c = 14.025(1)$ Å, in space group $R\bar{3}$. The structure is confirmed as being analogous to that of paratacamite, originally determined by Fleet (1975) and recently confirmed by Welch *et al.* (2013) using material from the BM86958 type specimen of composition $\text{Cu}_{3.71}\text{Zn}_{0.29}\text{Cl}_2(\text{OH})_6$.

Holotype paratacamite was reported in space group $R\bar{3}$ (Fleet, 1975) with a hexagonal super-cell of dimensions a 13.654(5) and c 14.041(6) Å, and a pronounced sub-cell corresponding to $a' = \frac{1}{2}a$, $c' = c$ in space group $R\bar{3}m$, for material assumed to be of composition $\text{Cu}_2\text{Cl}(\text{OH})_3$. More recent analyses of the paratacamite type specimen revealed the presence of a significant amount of Zn (Kracher and Pertlik, 1983). Braithwaite *et al.* (2004) reported electron microprobe analyses from the type specimen containing 0.32–4.78 wt.% Zn. In line with these analyses, Jambor *et al.* (1996) determined from synthetic studies that the rhombohedral structure type is stabilized by the presence of some Zn or Ni (2–3 wt.%). Welch *et al.* (2013) determined the structure of paratacamite in $R\bar{3}$ and reported electron microprobe analytical data on the same crystal as that used in the single-crystal study, for which a formula $\text{Cu}_{3.71}\text{Zn}_{0.29}(\text{OH})_6\text{Cl}_2$ was obtained. Based on these results, it is now recognized that paratacamite is an intermediate phase in a composition-induced transformation series from clinoatacamite [$\text{Cu}_2\text{Cl}(\text{OH})_3$, monoclinic, $P2_1/n$] to herbertsmithite [ideally $\text{Cu}_3\text{ZnCl}_2(\text{OH})_6$, rhombohedral, $R\bar{3}m$], when Zn is the dominant substituting cation (Jambor *et al.*, 1996; Braithwaite *et al.*, 2004). Similar series are recognized which involve Cu substitution by Ni and Co, leading respectively to the herbertsmithite analogues gillardite [ideally $\text{Cu}_3\text{NiCl}_2(\text{OH})_6$] (Colchester *et al.*, 2007; Clissold *et al.*, 2007) and leverettite [ideally $\text{Cu}_3\text{CoCl}_2(\text{OH})_6$] (IMA 2013-011; Kampf *et al.*, 2013b). The minerals of the atacamite group have received much attention in recent years due to their magnetic properties (Helton *et al.*, 2007; Chu *et al.*, 2011).

The new mineral paratacamite-(Mg) has been approved by the International Mineralogical Association (IMA 2013-014), on the basis of the Dominant Constituent Rule (Hatert and Burke, 2008). The suffix-based system of nomenclature is adopted here, and in the case of the new mineral paratacamite-(Ni) (Sciberras *et al.*, 2013), to describe the nature of the dominant interlayer cation. The holotype and two co-type specimens (catalogue numbers 64041, 64042 and 64043, respectively) have been deposited in the collections of the Natural History Museum of Los Angeles County, USA. Paratacamite-(Mg) is the first reported example of a naturally occurring paratacamite congener.

Occurrence

Paratacamite-(Mg) occurs at a small deposit 5 km NE of the village of Cuya in the Camarones Valley, Arica Province, Chile (approximately 19°08'14"S 70°08'49"W). This deposit does not have a formal name, so we have designated it the Cuya NE5 chloride occurrence. Using this same approach, the site of the sulfate deposit ~9 km NE of Cuya in which the recently approved new mineral camaronesite (IMA 2012-094, Kampf *et al.*, 2013a) was found has been designated the Cuya NE9 sulfate occurrence and a nearby deposit containing several potentially new arsenite minerals (currently under study) is designated the Cuya NE9 arsenite occurrence.

At the Cuya NE5 chloride occurrence paratacamite-(Mg) is found in association with anhydrite, atacamite, chalcopyrite, copiapite, dolomite, epsomite, haydeite, hematite, magnesite and quartz. Note that paratacamite-(Mg) is always found in intimate association with haydeite, and layers of haydeite crystals are found overgrowing layers of paratacamite-(Mg) crystals on the type specimens.

Recent studies of the formation of atacamite and paratacamite in the deposits of the Atacama Desert (e.g. Cameron *et al.*, 2007; Reich *et al.*, 2008, 2009) relate to the large-scale Cu deposits in the region. These studies suggest that supergene Cu enrichment, in the form of secondary Cu sulfides, oxides and hydroxides, occurred as the result of weathering of hypogene sulfide mineralization by circulating meteoric water over a long period of time, from ~45 Ma to 9–5 Ma. The formation of Cu chlorides took place in a second step during more arid conditions as the result of the upward circulation of deep saline waters, which reacted

with the supergene Cu sulfides, oxides and hydroxides. The solubility of atacamite and paratacamite dictates that existing samples date to the current period of hyperaridity in the region that began ~1.5 Ma ago. This two-step process does not seem to have been responsible for the mineralization in the much smaller and more localized deposits in the Camarones Valley area.

Information on the geology and mineralogy of the Camarones Valley area is very limited. The most pertinent studies are those by Salas (1964, 1965) and Thomas (1971), which indicate that the rocks in this area consist principally of andesite and metamorphosed lavas, lithic tuffs and marine sediments. Sulfide accumulations (mostly pyrite, but also locally chalcopyrite and/or arsenopyrite) are present in the marine shales; deposits of secondary sulfates, arsenates, arsenites, chlorides, etc. appear to be directly related to the near-surface, low-temperature oxidation of those deposits under increasingly arid conditions. At the Cuya NE5 chloride occurrence, the close association of the Cu chlorides with chalcopyrite supports this interpretation.

In a study of modern sea floor gossans, Hannington (1993) noted that exposed surfaces of sulfide deposits undergo rapid oxidation when cold seawater infiltrates the porous sulfide matrix. Strongly acidic fluids are produced by sulfide-oxidation reactions and these fluids dissolve sulfides, such as chalcopyrite, releasing Cu^{2+} and cuprous chloride complexes. Atacamite and paratacamite are reprecipitated when the solutions come in contact with normal seawater of near-neutral pH. Hannington (1993) provides an Eh–pH diagram for the system Cu–O–H–S–Cl in seawater at 25°C, which shows the atacamite and paratacamite stability field to correspond to moderately high Eh and near-neutral (6–8) pH.

The mechanism of the atacamite-paratacamite formation process described by Hannington (1993) seems applicable to the much smaller-scale process by which paratacamite-(Mg) formed at the Cuya NE5 chloride occurrence. The sulfide accumulations in the marine shales of the Camarones Valley were altered by saline fluids, which mobilized Cu under locally acidic conditions. As these fluids migrated away from the sulfide accumulations, they became less acidic and paratacamite-(Mg) was precipitated. It is not clear whether the saline nature of the fluids was derived from the dissolution of chlorides in the surrounding sediments or whether the fluids had a more distant, possibly deeper source.

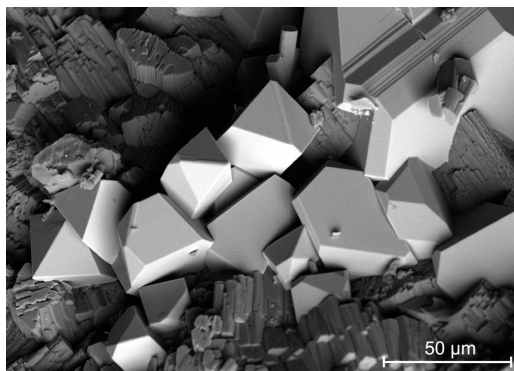


FIG. 1. SEM image of paratacamite-(Mg) on anhydrite.

Physical and optical properties

Crystals of paratacamite-(Mg) (Fig. 1) up to 0.3 mm in size were observed in two different habits. Individual crystals are dominated by the steep rhombohedron $\{201\}$ and the basal pinacoid $\{001\}$ (Fig. 2), providing a pseudo-octahedral habit; other minor forms are observed in SEM images, but are too small and indistinct to measure on the reflecting goniometer. Crystals twinned by reflection on $\{10\bar{1}\}$ form thick to thin prisms elongated on $[212]$ (Fig. 3). The twin operation was confirmed using the *TwinSolve* program in the Rigaku *CrystalClear* software package. A twinning analysis using the program *Geminography* (Nespolo and Ferraris, 2006) indicates that the observed twinning is an example of complex hybrid twinning based on five pseudo-orthorhombic sublattices, each leading to a high twin index, ranging from 13 to 19, and ultimately resulting in an Effective Twin Index of 3.8 (Giovanni Ferraris, personal communication).

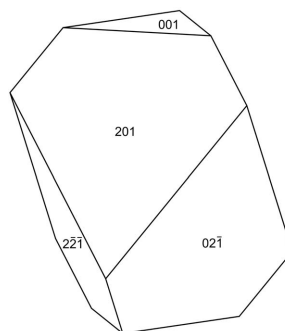


FIG. 2. Crystal drawing of a paratacamite-(Mg), clinographic projection

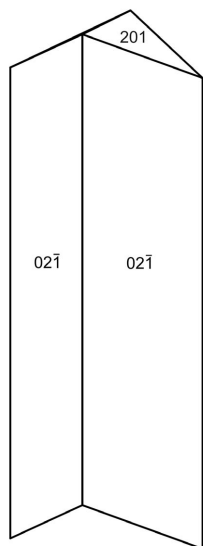


FIG. 3. Crystal drawing of a paratacamite-(Mg) prism, twinned by reflection on $\{101\}$ and elongated on $[212]$, clinographic projection.

Paratacamite-(Mg) is medium to dark green in colour and it has a light green streak. It is transparent and has vitreous lustre. It does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is between 3 and $3\frac{1}{2}$, based upon scratch tests. The tenacity is brittle and the fracture is conchoidal. The mineral exhibits one perfect cleavage on $\{201\}$. The measured density $3.50(2) \text{ g cm}^{-3}$, determined by flotation in Clerici solution, compares well with the calculated density of 3.551 g cm^{-3} based on the empirical

formula. The mineral is readily soluble in cold, dilute HCl.

Optically, the crystals are uniaxial (–) with $\varepsilon = 1.785(5)$ and $\omega > 1.8$. Because crystals decompose rapidly in liquids with refractive index > 1.8 , ω could not be measured. The average index of refraction predicted by the Gladstone-Dale relationship (Mandarino 2007) is 1.764, based upon the empirical formula and single-crystal cell. Slight pleochroism was observed: O (bluish green) $> E$ (green).

Chemical composition

Electron microprobe analyses (22) were carried out on a single crystal of steep rhombohedral habit obtained in proximity to the crystal used for structure determination, using a JEOL 8600 electron microprobe operated in WDS mode. The analytical conditions were 15 kV accelerating voltage, 20 nA beam current. The majority of crystals are small ($< 100 \mu\text{m}$). The crystal analysed presented a polished surface $\sim 100 \mu\text{m} \times 90 \mu\text{m}$ in size; therefore, a beam diameter of $3 \mu\text{m}$ was used. No other elements were detected by EDS. Other likely elements were sought by EMPA, but none was found to be above the limit of detection. Insufficient material was available for direct H_2O determination, so the H_2O content was calculated by stoichiometry based upon the structure determination. The sample was rather unstable in the electron beam, even with reduced beam current, resulting in analytical totals $> 100\%$ and Cl values significantly lower than ideal. The analytical data are presented in Table 1.

TABLE 1. Electron microprobe analyses of paratacamite-(Mg).

	Average* (Wt.%)	Range (Wt.%)	Atoms per formula unit	Standard
CuO	69.34(4.74)	59.98–77.87	3.49	Cu
NiO	0.10(0.09)	0–0.37	0.01	Ni
MnO	0.17(0.08)	0.03–0.37	0.01	Mn
MgO	6.29(2.25)	3.58–10.54	0.62	Olivine
CoO	0.08(0.05)	0–0.15	–	Co
Cl	15.47(0.51)	14.59–16.32	1.75	TlCl
H ₂ O	13.52		6.00	
O $\equiv$ Cl	–3.50			
Total	101.47			

* Standard deviations of the average values are in parentheses.

With respect to individual analyses there was significant variation in MgO and CuO wt.% values across the area of the crystal. Cation normalized compositions ranged between $\text{Cu}_{3.60}\text{Mg}_{0.36}\text{Mn}_{0.01}\text{Ni}_{0.02}\text{Co}_{0.01}\text{Cl}_2(\text{OH})_6$ and $\text{Cu}_{2.95}\text{Mg}_{1.03}\text{Mn}_{0.01}\text{Co}_{0.01}\text{Cl}_2(\text{OH})_6$, with respect to Mg–Cu substitution. The average data gave the empirical formula, based on 8 anions (O + Cl) p.f.u. (per formula unit), as $\text{Cu}_{3.49}\text{Mg}_{0.62}\text{Mn}_{0.01}\text{Ni}_{0.01}\text{Cl}_{1.75}\text{O}_{6.25}\text{H}_6$. The simplified formula, taking into account the results of the single-crystal structure analysis, is $\text{Cu}_3(\text{Mg,Cu})\text{Cl}_2(\text{OH})_6$. Finally, the cation normalized composition, determined from the average empirical formula [$\Sigma(\text{cations}) = 4$], of $\text{Cu}_{3.38}\text{Mg}_{0.60}\text{Mn}_{0.01}\text{Ni}_{0.01}\text{Cl}_2(\text{OH})_6$, was used in the single-crystal X-ray structure analysis for charge balance.

X-ray crystallography

Single-crystal and powder XRD data for paratacamite-(Mg) were collected at 293(2) K on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatic $\text{MoK}\alpha$ radiation. From powder diffraction data, the unit-cell parameters were determined by whole-pattern fitting using the *JADE 2010* software package (Materials Data, Inc., 2011): $a = 13.667(2)$, $c = 14.011(2)$ Å, $V = 2266.5(4)$ Å³. Note that the

super-lattice reflections of paratacamite-(Mg), and holotype paratacamite (Fleet, 1975) are typically too weak to be observed in a conventional powder XRD experiment, but both a super-cell and a sub-cell corresponding to $a' = \frac{1}{2}a$, $c' = c$ can be refined from the powder XRD data. Discrimination between a true $R\bar{3}$ super-cell and $R\bar{3}m$ sub-cell can be made only by using single-crystal diffraction methods. The powder diffraction data are presented in Table 2.

The Rigaku *CrystalClear* software package was used for processing the structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005). *SHELXL-97* (Sheldrick, 2008) was used for the refinement of the structure.

Single-crystal XRD data from a small tabular crystal revealed a strong substructure with cell dimensions $a = 6.8441(8)$ and $c = 14.025(1)$ Å. A series of weak reflections at positions corresponding to half integer values of h and k are present, indicating that the true unit cell is $a = 13.689(1)$ and $c = 14.025(1)$ Å, in the hexagonal setting. Systematic absences are consistent with space groups $R\bar{3}m$, $R3m$, $R\bar{3}$, $R3$ and $R32$. Refinement of the sub-cell in $R\bar{3}m$ converged smoothly to the structure of herbertsmithite, giving $R_1 = 0.0240$ and $wR_2 = 0.0592$ for 239

TABLE 2. Powder X-ray data for paratacamite-(Mg).

I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h\ k\ l$	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h\ k\ l$
87	5.469	5.4597	100	0 2 1	10	1.660	1.6598	10	4 0 7
26	4.686	4.6749	37	0 0 3	4	1.631	1.6328	7	6 2 1
10	4.535	4.5268	15	2 0 2	8	1.604	1.6068	8	4 4 3
3	3.425	3.4222	2	2 2 0			1.6006	5	2 6 2
5	3.018	3.0177	8	0 2 4			1.5583	1	0 0 9
34	2.904	2.8996	53	4 0 1	10	1.508	1.5089	12	0 4 8
100	2.762	2.7614	95	2 2 $\bar{3}$	13	1.493	1.4934	15	2 4 7
		2.7299	19	0 4 2	7	1.472	1.4736	8	0 8 1
8	2.342	2.3375	14	0 0 6	5	1.448	1.4498	7	8 0 2
81	2.265	2.2634	91	4 0 4	3	1.417	1.4183	1	2 6 5
		2.2123	3	4 2 $\bar{1}$			1.4182	4	2 2 9
1	2.134	2.1341	3	4 2 2	19	1.380	1.3807	26	4 4 6
15	2.037	2.0372	22	0 4 5	11	1.364	1.3649	12	0 8 4
10	1.898	1.8980	13	0 2 7			1.3648	1	0 2 10
26	1.819	1.8199	32	6 0 3	3	1.352	1.3535	5	6 4 $\bar{1}$
2	1.751	1.7505	3	2 4 $\bar{5}$			1.3350	1	6 4 2
34	1.710	1.7111	42	4 4 0	4	1.310	1.3102	5	8 0 5
		1.6811	2	2 0 8					

reflections with $F_o > 4\sigma F$. Initial refinement of the super-cell was also made in space group $R\bar{3}m$. The structure was solved by direct methods and resulted in atom coordinates and topology analogous to those of $R\bar{3}$ paratacamite (Fleet, 1975).

The $R\bar{3}$ structure of paratacamite has four crystallographically independent O atoms each in an $18f$ position. The $R\bar{3}m$ refinement merges O1 and O3 of the $R\bar{3}$ structure into a single position located on a mirror plane. This results in three crystallographically independent O atoms, two of which are in $18f$ positions and the third in the lower symmetry $36i$ position. The rhombic distortion exhibited by the $M2O_6$ octahedron of $R\bar{3}$ paratacamite is effectively removed by the incorporation of a lower symmetry equatorial O position. However, the $R\bar{3}m$ refinement did not account for the full set of observable reflections and the residuals were greater than the corresponding $R\bar{3}$ refinement, which was made based upon the atom coordinates of paratacamite established by Fleet

(1975) (Table 3). On this basis, the correct space group was taken as being $R\bar{3}$.

The $M1$ ($3b$) and $M2$ ($9d$) sites were refined initially with joint occupancy by Mg and Cu, while the $M3$ and $M4$ sites were assigned full occupancy by Cu. The refinement converged giving occupancy factors associated with the $M1$ site for Cu of 0.062(2) and Mg of 0.105(2), and the $M2$ site for Cu of 0.187(4) and Mg of 0.313(4). This resulted in an equivalent distribution of Mg (63% occupancy) at both $M1$ ($3b$) and $M2$ ($9d$). The Cu:Mg ratio was slightly higher than that determined from the EMPA. The occupancies were then set to correspond with the results of the EMPA, while maintaining the statistical distribution of Mg; the trace amounts of Ni and Mn present were arbitrarily placed at the $M1$ site. Refinement converged with equivalent isotropic displacement parameters for the $M1$ and $M2$ sites remaining the same within error. The final distribution of Mg between $M1$ and $M2$ was 60% occupancy at each site. It is noteworthy that

TABLE 3. Crystal data and structure-refinement details of paratacamite-(Mg).

Formula weight	403.44	
Temperature (K)	293(2)	
Wavelength (Å)	0.71073	
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}m$
Unit cell		
	a (Å)	
	c (Å)	
Volume (Å ³)	13.689(1)	
Z	14.025(1)	
ρ_{calc} (g cm ⁻³)	2275.8(3)	
μ (mm ⁻¹)	3	
$F(000)$	3.532	
Crystal size (mm)	10.144	
θ range	2325	
Limiting indices	$0.11 \times 0.06 \times 0.01$	
	3.38 to 30.46°	
	$-19 \leq h \leq 19$	
	$-19 \leq k \leq 19$	
	$-19 \leq l \leq 19$	
Reflections /unique	9733/1547	9719/863
R_{int}	0.0296	0.0302
Completeness to $\theta = 30.46^\circ$	99.9%	
Refinement on	F^2	
Data/restraints/parameters	1547/4/89	863/3/55
Goodness-of-fit on F^2	0.990	1.133
Final R [$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$]	R_1	0.0425
	wR_2	0.0928
R indices (all data)	R_1	0.0810
	wR_2	0.1064
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e.Å ⁻³)	0.1134	1.000 and -0.606
	0.816 and -0.682	

the very different scattering factors for Mg ($Z = 12$) and Cu ($Z = 29$) allow high confidence in the refined site occupancies. By contrast, in other members of the atacamite group, the principal cations substituting for Cu, Co ($Z = 27$), Ni ($Z = 28$) and Zn ($Z = 30$), have scattering factor close to that of Cu.

The coordinates of all four H atoms were determined from a difference map and each was given a soft distance constraint of 0.95 ± 0.03 Å with its respective O atom. The final refinement converged to $R_1 = 0.0390$ and $wR_2 = 0.0997$, for 480 unique reflections with $F_o > 4\sigma F$. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0439P)^2 + 16.02P]$ where $P = [\max(0, F_o)^2 + (2F_c)^2]/3$ as defined by *SHELX-97* (Sheldrick, 2008).

The relevant details of the data collection and structure refinement are given in Table 3. The atom coordinates and equivalent-isotropic and anisotropic displacement parameters are in Table 4. Selected bond lengths and angles are provided in Table 5.

Description of the structure and discussion

Paratacamite-(Mg) is isomorphous with paratacamite (Fleet, 1975; Welch *et al.*, 2013). A representation of its structure is shown in Fig. 4. The structure contains sheets of edge-sharing

$\text{CuCl}_2(\text{OH})_4$ octahedra (*M3* and *M4*), which exhibit typical elongate tetragonal Jahn-Teller distortion. Located between the sheets are two crystallographically independent metal sites (*M1* and *M2*), both coordinated by six OH^- ligands. Each of these octahedra shares opposite sets of three edges (corresponding to opposite octahedron faces) with successive layers of $\text{CuCl}_2(\text{OH})_4$ octahedra (*M3* and *M4*). The *M1* site is surrounded by six symmetry-equivalent O atoms (O1). The *M2* octahedron exhibits a rhombic distortion, with elongation in the direction of the aforementioned opposite octahedral faces. The *M2* octahedron has a (2+2+2) configuration, where *trans* ligands are equivalent. Substitution for Cu has been well established to occur only in the interlayer sites of paratacamite and the related minerals anatacamite, clinoatacamite, herbertsmithite, gillardite and leverettite (Malcherek and Schlüter, 2009; Grice *et al.*, 1996; Braithwaite *et al.*, 2004; Clissold *et al.*, 2007; Welch *et al.*, 2013; Kampf *et al.*, 2013b).

The paratacamite-(Mg) examined in this study has a statistical distribution of Mg, giving 60% occupancy for both *M1* and *M2*. To represent the relative occupancies (with Ni and Mn at *M1*), the formula can be recast as $\text{Cu}_3[(\text{Mg}_{0.15}\text{Cu}_{0.08}\text{Ni}_{0.01}\text{Mn}_{0.01})(\text{Mg}_{0.45}\text{Cu}_{0.30})](\text{OH})_6\text{Cl}_2$. This distribution of interlayer Mg does not necessarily represent the behaviour of other cations in the paratacamite structure type.

TABLE 4. Final atom coordinates ($\times 10^4$) and anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) of paratacamite-(Mg).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<i>M1</i>	0	0	5000	11.7(7)	12.1(8)	U^{11}	11(2)	0	0	$0.5U^{11}$
<i>M2</i>	5000	5000	5000	12.0(3)	12.9(8)	12.6(8)	9.6(7)	0.4(7)	0.2(8)	5.7(7)
<i>M3</i>	4162(1)	3322(1)	3329(1)	11.4(2)	10.8(3)	9.8(3)	13.4(4)	-2.2(3)	$0.5U^{23}$	5.0(3)
<i>M4</i>	4151(1)	5818(1)	3333(1)	11.7(2)	10.7(3)	10.5(3)	13.9(4)	1.2(2)	-1.1(3)	5.4(2)
Cl1	0	0	1941(2)	16.0(6)	16.6(7)	U^{11}	15(2)	0	0	$0.5U^{11}$
Cl2	5006(1)	5004(1)	1943(1)	14.7(3)	15.9(7)	16.1(7)	12.2(6)	0.4(6)	0.1(6)	8.0(6)
O1	5613(3)	6246(3)	3962(4)	14(1)	9(2)	10(2)	19(3)	-4(2)	-1(2)	3(2)
O2	5625(3)	4353(3)	3958(4)	14(1)	12(2)	12(2)	17(3)	2(2)	-2(2)	6(2)
O3	3699(3)	4341(3)	3940(3)	16(1)	12(2)	11(2)	21(3)	1(2)	4(2)	5(2)
O4	646(3)	1270(3)	3953(4)	14(1)	11(2)	13(2)	17(3)	-6(2)	-1(2)	6(2)
H1	5988(51)	6911(39)	4306(48)	20						
H2	5942(53)	4000(52)	4296(47)	20						
H3	2927(25)	3970(52)	3964(54)	23						
H4	939(53)	1897(43)	4340(47)	21						

* The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$.
 $U_{\text{eq}} = 1/3(U^{11} + U^{22} + U^{33})$.

TABLE 5. Selected bond lengths (Å) and angles (°) of paratacamite-(Mg).

Interlayer			
<i>M1</i> –O4 (x6)	2.103(5)	<i>M2</i> –O1 (x2)	2.074(4)
O4– <i>M1</i> –O4	180	<i>M2</i> –O2 (x2)	2.100(5)
O4– <i>M1</i> –O4	103.4(2)	<i>M2</i> –O3 (x2)	2.143(5)
		O1– <i>M2</i> –O1	180
		O2– <i>M2</i> –O2	180
		O3– <i>M2</i> –O3	180
		O1– <i>M2</i> –O2	103.0(2)
		O1– <i>M2</i> –O3	103.4(2)
		O2– <i>M2</i> –O3	103.5(2)
Intralayer*			
<i>M3</i> –O1	1.988(4)	<i>M4</i> –O1	1.989(4)
<i>M3</i> –O2	1.988(4)	<i>M4</i> –O3	1.987(4)
<i>M3</i> –O2	1.993(4)	<i>M4</i> –O4	1.986(4)
<i>M3</i> –O3	1.991(5)	<i>M4</i> –O4	1.989(4)
<i>M3</i> –Cl2	2.766(2)	<i>M4</i> –Cl1	2.778(2)
<i>M3</i> –Cl2	2.785(2)	<i>M4</i> –Cl2	2.777(2)
O1– <i>M3</i> –O2	179.5(2)	O1– <i>M4</i> –O4	179.6(2)
O1– <i>M3</i> –O2	81.6(2)	O3– <i>M4</i> –O4	179.5(2)
O2– <i>M3</i> –O2	98.1(3)	O3– <i>M4</i> –O4	97.8(2)
O2– <i>M3</i> –O3	179.2(2)	O4– <i>M4</i> –O4	82.0(2)
O2– <i>M3</i> –O3	82.7(2)	O4– <i>M4</i> –O1	97.9(2)
Cl2– <i>M3</i> –Cl	179.27(5)	Cl1– <i>M4</i> –Cl2	178.99(4)
Cl2– <i>M3</i> –O	97.7(1)	Cl1– <i>M4</i> –O3	98.0(1)
Cl2– <i>M3</i> –O	82.9(1)	Cl2– <i>M4</i> –O4	98.2(1)
Other			
O1–Cl2	3.081(3)		
O2–Cl1	3.063(4)		
O3–Cl2	3.057(5)		
O4–Cl2	3.072(4)		

* The *M3* and *M4* sites are Cu.

Welch *et al.* (2013) examined a single crystal of paratacamite of composition $\text{Cu}_{3.71}\text{Zn}_{0.29}\text{Cl}_2(\text{OH})_6$ from the BM86958 type specimen. The authors suggested that the unusual rhombic distortion observed with the $M2\text{O}_6$ octahedron could result from a superimposition of differently oriented (4+2) Jahn-Teller distorted $\text{Cu}(\text{OH})_6$ octahedra with a non-tetragonally distorted $M(\text{OH})_6$ octahedron, which assumes a statistical distribution of Zn between both interlayer sites. In heating experiments, they found that the geometry of the $M1\text{O}_6$ octahedron does not change, while that of the $M2\text{O}_6$ octahedron changes systematically from its initial rhombic distortion to a geometry equivalent to that of the $M1\text{O}_6$ octahedron. When the two sites merge at the transition temperature, between 353 and 393 K, the super-lattice reflections of

paratacamite disappear and the resultant structure is equivalent to that of the $R\bar{3}m$ substructure. Welch *et al.* (2013) showed that this $R\bar{3}$ to $R\bar{3}m$ phase change is reversible upon returning to ambient temperature.

The $M2$ –O bond lengths for type paratacamite of Welch *et al.* (2013) exhibit a significant (2+2+2) distortion and the corresponding octahedron reported by Fleet (1975) appears with four longer and two shorter bonds ($\text{Cu}2$ –O1 = 1.933, $\text{Cu}2$ –O2 = 2.186 and $\text{Cu}2$ –O3 = 2.204 Å), in a tetragonally compressed and slightly rhombically distorted environment. In comparison, the $M2$ –O bond lengths of paratacamite-(Mg) (Table 5) indicate only a minor (2+2+2) distortion. Quantification of the distortion of the interlayer octahedra was determined by calculation of their quadratic elongation (Robinson *et al.*, 1971) and

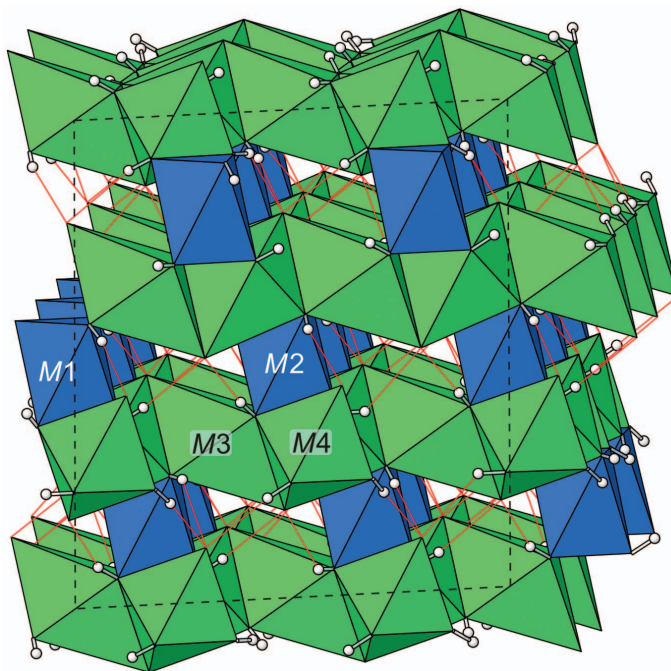


FIG. 4. The crystal structure of paratacamite-(Mg) slightly canted down the a axis with the c axis vertical. H atoms are shown as white spheres. Hydrogen bonds are shown as red lines. The unit cell is indicated by a dashed line.

bond-angle variance using the program *VESTA* (Momma and Izumi, 2008). The $M1O_6$ and $M2O_6$ octahedra in paratacamite-(Mg) exhibit similar quadratic elongations (1.0498 and 1.0495) and bond-angle variances (194.98 and 192.25°²). By contrast, the quadratic elongations reported by Welch *et al.* (2013) for the $M1O_6$ and $M2O_6$ octahedra in unheated paratacamite (at 300 K) are 1.054 and 1.060. The near convergence of the geometry of the $M2O_6$ octahedron with that of the $M1O_6$ octahedron for paratacamite-(Mg) is probably due to the relatively large Mg occupancy of the sites. Therefore, it is likely that the crystal of paratacamite-(Mg) used in our structure study is near the upper limit of compositional stability of the $R\bar{3}$ super-structure at ambient temperatures.

Relation to other species

Structurally paratacamite-(Mg) is closely related structurally to the series of substituted basic copper chloride minerals, the details of which are provided in Table 6. The structures of these minerals are closely related to that of atacamite, $Cu_2Cl(OH)_3$ (Wells, 1949); therefore, they are

generally considered to be members of the atacamite group. Other chemically related minerals with different structures are botallackite, $Cu_2Cl(OH)_3$, (Hawthorne, 1985), kapellasite, $Cu_3ZnCl_2(OH)_6$, (Krause *et al.*, 2006) and haydeite, $Cu_3MgCl_2(OH)_6$, (Malcherek and Schlüter, 2007); kapellasite and haydeite are isostructural. As noted above, the crystal of paratacamite-(Mg) used in our structure study, which has the approximate structural composition $Cu_3(Mg_{0.60}Cu_{0.40})Cl_2(OH)_6$, appears to be near the upper limit of compositional stability of the $R\bar{3}$ superstructure. Atacamite-group phases with greater amounts of Mg, approaching the $Cu_3Mg(OH)_6Cl_2$ endmember, can be expected to have the trigonal $R\bar{3}m$ substructure. The trigonal $R\bar{3}m$ endmember $Cu_3Mg(OH)_6Cl_2$ phase is known synthetically (Colman *et al.*, 2011), but has not yet been found in nature.

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TABLE 6. Minerals structurally related to paratacamite-(Mg).

	Anatacamite ¹	Clinoatacamite ²	Paratacamite ³	Paratacamite-(Mg) ⁴	Paratacamite-(Ni) ⁵	Herbertsmithite ⁶	Gillardite ⁷	Leverettite ⁸
Formula	Cu ₂ Cl(OH) ₃	Cu ₂ Cl(OH) ₃	Cu ₃ (Cu,Zn)- Cl ₂ (OH) ₆ trigonal R $\bar{3}$	Cu ₃ (Mg,Cu)- Cl ₂ (OH) ₆ trigonal R $\bar{3}$	Cu ₃ (Ni,Cu)- Cl ₂ (OH) ₆ trigonal R $\bar{3}$	Cu ₃ ZnCl ₂ (OH) ₆ trigonal R $\bar{3}m$	Cu ₃ NiCl ₂ (OH) ₆ trigonal R $\bar{3}m$	Cu ₃ CoCl ₂ (OH) ₆ trigonal R $\bar{3}m$
Crystal system	triclinic	monoclinic						
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>						
<i>a</i> (Å)	9.1646(9)	6.157(2)	13.654(5)	13.689(1)	13.682(2)	6.834(1)	6.8364(1)	6.8436(6)
<i>b</i> (Å)	9.2029(8)	6.814(3)						
<i>c</i> (Å)	9.2102(8)	9.105(5)	14.041(6)	14.025(1)	13.916(2)	14.075(2)	13.8459(4)	14.0637(10)
α (°)	95.858(6)	99.65(4)						
β (°)	96.290(7)							
γ (°)	96.507(2)							
<i>V</i> (Å ³)	761.97(12)	375.7(2)	2267	2275.8(3)	2256.0(7)	569.3	560.41(2)	570.43(8)
<i>Z</i>	8	4	12	12	12	3	3	3
<i>D</i> (calc) (g/cm ³)	3.725	3.77	3.75	3.532	3.735	3.75	3.76	3.695
Optical character	biaxial	biaxial (–)	uniaxial (–)	uniaxial (–)	uniaxial (–)	uniaxial (–)	uniaxial (+)	uniaxial (–)

¹Malcherek and Schlüter (2009); ²Grice *et al.* (1996); ³Fleet *et al.* (1975); ⁴This study; ⁵Sciberras *et al.* (2013); ⁶Braithwaite *et al.* (2006); ⁷Colchester *et al.* (2007); ⁸Kampf *et al.* (2013b).

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