Anatacamite from La Vendida mine, Sierra Gorda, Atacama desert, Chile: a triclinic polymorph of Cu₂(OH)₃Cl

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With 3 figures and 3 tables

Abstract. The new mineral anatacamite (IMA-CNMNC No. 2008-042) has the ideal chemical formula $Cu_2(OH)_3Cl$. It is triclinic with space group PI. Unit-cell data from single-crystal X-ray studies gave a = 9.1646(9), b = 9.2029(8), c = 9.2102(8) Å, $\alpha = 95.858(6)^\circ$, $\beta = 96.290(7)^\circ$, $\gamma = 96.507(2)^\circ$, V = 761.97(12) Å³, Z = 8. Anatacamite is the triclinic polymorph of atacamite, botallackite and clinoatacamite. The strongest reflections in the X-ray powder diffraction data, calculated from single crystal data, are as follows $d_{obs.}$ (Å) (I): 5.432 (100), 2.747 (94), 2.257 (56), and 2.889 (31). Anatacamite was found in La Vendida mine, Sierra Gorda mining district, northeast of Antofagasta, Chile. It occurs as triangular, tabular crystals up to 2 mm in size grown on prismatic atacamite crystals. Anatacamite shows emerald green colour with a vitreous luster. The crystals show a good cleavage parallel to {111}. The calculated density is 3.725 g/cm³, the calculated mean refractive index is 1.80, pleochroism is not apparent. In La Vendida mine anatacamite is closely associated with atacamite, further minerals of this mineralization are alunite, clinoatacamite, chalcanthite, coquimbite, eriochalcite, jarosite, kröhnkite, magnesioaubertite, tamarugite and voltaite. Chemical analyses gave (wt.%) CuO 74.24, ZnO 0.02, NiO 0.99, Cl 16.98, H₂O_{cale} 12.74, O = Cl -3.84, sum 101.13. The resulting empirical formula based on 4 anions *pfu* is Cu_{1.97}Ni_{0.03}(OH)_{2.99}Cl_{1.01}. Anatacamite is named for its triclinic symmetry and its polymorphism with atacamite. Type material is deposited in the collection of the Mineralogical Museum Hamburg, Germany.

Key words: anatacamite, botallackite, clinoatacamite, atacamite, $Cu_2(OH)_3Cl$, Chile, Atacama, Sierra Gorda, La Vendida mine, Rio Tinto mine, copper chloride hydroxide.

Introduction

Initially considered as clinoatacamite, the new mineral anatacamite (Cu₂(OH)₃Cl), was collected by Mr. Arturo Molina, Iquique, in spring 2003. It was found in Mina La Vendida (22° 53' 30" S 69° 20' 50" W), an abandoned open pit copper mine, which is situated about 5 km WNW off the little village Sierra Gorda, Atacama desert, NW of Antofagasta, northern Chile. The name La Vendida was introduced by the property owner, the 'Santa Catalina Managemente Corp.', in 1990. It was formerly known as the Rio Tinto mine. The mine started as small scale workings for only 10 month in 1920 (KUNTZ 1928) and has later been worked from time to time. The mining activities focused on the exploitation of atacamite and subordinate chrysocolla from the oxidation zone of primary copper and iron sulfides. The mineralization is bound to daciticandesitic volcanic breccias. Today still exists a shallow open pit of 180 x 60 m. A reevaluation of the mine site in 2004 (Maya 2004) specifies a copper content of 0.56 to 1.2 % and 5 to 12 ppm silver.

La Vendida mine is also the type locality for belloite (Cu(OH)Cl) (SCHLÜTER et al. 2000). The new mineral and its name were approved by the IMA Commission on New Minerals, Nomenclature and Classification in September 2009 (No. 2008-042); anatacamite is named for its triclinic symmetry and its polymorphism with atacamite.

The holotype (MD 199) is preserved in the collection of the Mineralogical Museum of the University of Hamburg, Germany. Further information on the type material can be taken from the 'Type Specimen Catalogue Germany' (www1.uni-hamburg.de/mpi/typkatalog/).

The polymorphs of $Cu_2(OH)_3Cl$ have attracted attention in recent years for their magnetic properties, as the Cu-atoms form Kagome-type layers in these minerals. This causes geometric frustration for the ordering of magnetic moments, potentially giving rise to the formation of exotic electronic ground state structures (ZHENG et al. 2005, WILLS & HENRY 2008).

Appearance and physical data

Anatacamite occurs as triangular, tabular, emerald-green crystals, up to about 2 mm in length, grown on $\{011\}$ of prismatic atacamite crystals (Fig. 1 and 2). The epitaxial plane of anatacamite is $(8\overline{3}3)$.

The mineral has a pale green streak and shows no fluorescence. The crystals are transparent with a vitreous luster. They are brittle, show conchoidal fracture and have a good cleavage parallel to $(11\overline{1})$, Anatacamite crystals show $\{11\overline{1}\}, \{1\overline{1}1\}, \{100\}$ and $\{\overline{1}11\}$ forms. Microscopical examinations reveal distinctive pseudo-merohedral twinning. Vickers microhardness is VHN₅₀ = 350 kg/mm², corresponding to a Mohs hardness of about 4–4_{1/2}.

The density calculated from empirical formula and single-crystal unit cell data is 3.725 g/cm³. Anatacamite is biaxial, its mean refractive index calculated from Gladstone-Dale constants using the empirical formula and single-crystal unit cell data is 1.80, pleochroism is not apparent. Anatacamite is not soluble in water, but easily soluble in mineral acids.

Our examinations of the La Vendida mineralization show that besides anatacamite, atacamite and belloite, the oxidation zone furthermore comprises the minerals alunite, clinoatacamite, chalcanthite, coquimbite, eriochalcite, jarosite, kröhnkite, magnesioaubertite, tamarugite and voltaite.



Fig. 2. Drawing of a typical epitaxial atacamite-anatacamite intergrowth.

Chemical composition

Quantitative chemical analyses (50) were carried out by means of a Cameca electron microprobe (SX 100), operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of about 1 μ m (Table 1). The stand-



Fig. 1. Triangular anatacamite crystals on atacamite of same colour from La Vendida mine, Sierra Gorda, Chile. Width of picture: 1.5 mm. Photo: K.-C. Lyncker. Colour pictures of the new mineral anatacamite can be found on our homepage <u>http://www.rrz.</u> uni-hamburg.de/mpi/museum/.

Table 1: Chemical composition of anatacamite* (Cu₂(OH)₃Cl).

Constituent	wt%	Range	Ideal wt%	Probe Standard
CuO	74.24(62)	73.15-76.06	74.49	CuO
ZnO	0.02(3)	0-0.15		ZnS
NiO	0.99(23)	0.38-1.29		NiO
Cl	16.98(13)	16.73-17.33	16.60	Vanadinite
H_2O	12.74(13)	12.48-13.03	12.66	
O=C 1	-3.84	-3.91t o- 3.77	-3.75	
Total	101.13(60)		100.00	

*: Chemical analyses (50) were carried out by means of an electron microprobe (WDS mode, 15 kV, 20 nA, 1 μ m beam diameter, focussed). H₂O was calculated by stoichiometry from the results of the crystal-structure analysis on the basis that H = O.

ards used were CuO, ZnS, NiO and vanadinite (Cl). 12.74 wt.% H_2O was calculated by stoichiometry from the results of the crystal-structure analysis based on equimolar O and H.

The analyses gave the following averages (wt.%): CuO 74.24, ZnO 0.02, NiO 0.99, Cl 16.98, H₂O_{calc} 12.74, $O \equiv Cl$ -3.84, sum 101.13. The resulting empirical formula based on 4 anions *pfu* is Cu_{1.97}Ni_{0.03}(OH)_{2.99}Cl_{1.01}, which can be simplified to Cu₂(OH)₃Cl.

Strain considerations (MALCHEREK & SCHLÜTER 2009) indicate, that only very pure $Cu_2(OH)_3Cl$ crystallizes as anatacamite under appropriate conditions. With increasing impurity content (e.g. Zn) clinoatacamite will be the dominant phase, further replacement of Cu by Zn leads to herbertsmithite ($Cu_3Zn(OH)_6Cl_2$), where one quarter of the Cu atoms is replaced by Zn.

X-ray crystallography

Anatacamite, the triclinic polymorph of atacamite, botallackite and clinoatacamite, has the space group $P\overline{1}$. The unit cell parameters from single-crystal X-ray studies gave a = 9.1646(9), b = 9.2029(8), c = 9.2102(8) (Å), $\alpha =$ $95.858(6)^{\circ}$, $\beta = 96.290(7)^{\circ}$, $\gamma = 96.507(2)^{\circ}$, V = 761.97(12)Å³, Z = 8. The a:b:c ratio calculated from the latter data is 0.9958:1:1.0008. The structure refinement converged to R= 0.041 for 6622 reflections with I > 3 σ (I).

Single-crystal diffraction data have been collected using a Nonius KappaCCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Details of these measurements and the crystal structure data have been published elsewhere (MALCHEREK & SCHLÜTER 2009).

The X-ray powder diffraction pattern (Table 2) was calculated from single crystal data with the program JANA2000 (PETRICEK et al. 2000). Only lines with normalized intensity $I_{calc} > 1$ are shown in Table 2. Columns I_{obs} , d_{obs} were obtained using a Gandolfi-type measure-

ment of an anatacamite crystal with the program Nonius POWDERIZE.

The strongest reflections in the X-ray powder diffraction data are as follows $d_{obs.}$ (Å) (I): 5.432 (100), 2.747 (94), 2.257 (56), and 2.889 (31).

Anatacamite forms a network of edge-sharing distorted octahedra. Within layers normal to the trigonal axis Cu atoms are axially coordinated by two Cl and equatorially coordinated by four OH (intra-layer octahedra). The layers are connected by $Cu(OH)_6$ octahedra (inter-layer octahedra) that share edges with the intralayer octahedra.

Pure Cu₂(OH)₃Cl so far is known to occur in the form of two monoclinic polymorphs (botallackite and clinoatacamite) and one orthorhombic polymorph (atacamite). A rhombohedral structure type (paratacamite) was described by Fleet (1975), but it is now believed that the rhombohedral substructure of paratacamite has to be stabilized by partial substitution of Zn or Ni for Cu (JAM-BOR et al. 1996) at ambient temperature. Herbertsmithite, Cu₃Zn(OH)₆Cl₂, (Braithwaite et al. 2004) is the Zn endmember of such a solid solution. Anatacamite is a triclinic polymorph of Cu₂(OH)₃Cl, with a high degree of trigonal and monoclinic pseudo-symmetry. The triclinic symmetry is induced by the Jahn-Teller distortion (BURNS & HAWTHORNE 1996) of the inter-layer octahedron, which is holosymmetric only in the paratacamite substructure. While Cu-O bond distances within this Jahn-Teller distorted octahedron amount to 2.288, 2.05 and 1.991 Å in clinoatacamite (GRICE et al. 1996), the corresponding distances vary in the ranges 2.306-2.397, 2.019-2.069 and 1.978–2.013 Å in anatacamite (Cu1a, Cu2a-b), indicating a larger distortion in the triclinic polymorph. This is even clearer when compared to the relatively Zn-rich clinoatacamite described by MALCHEREK & SCHLÜTER (2009), where the Jahn-Teller distortion is considerably smaller (Cu-O-distances of 2.157, 2.108, and 2.052 Å) and the volume of the inter-layer octahedron is enlarged by the Zn-substitution.

Table 2. Powder X-ray diffraction data (I_{calc}, d_{calc}) of anatacamite.

I _{cily.}	d _{calc.}	hkl	I _{obs}	d_{obs}
95	5.486	111		
96	5.458	$\underline{1\overline{1}}1$	100	5.432
100	5.444	111		
43	4.697	111	10	4.657
3	4.546	002		
3	4.541	020		n.o.
3	4.519	200		
7	3.426	$2\overline{2}0$		
7	3.421	202	4	3.395
6	3.417	022		
22	2.901	<u>13</u> 1		
22	2.900	<u>1</u> 13	31	2.889
25	2.898	311		
1	2.780	<u>0</u> 13		
45	2.778	$\frac{1}{13}$		
44	2.777	131		
1 45	2.7766	113		
45	2.760	$\frac{113}{131}$	94	2 747
42	2.759	$3\overline{1}1$	74	2.141
39	2.754	$\overline{311}$		
16	2.743	<u>2</u> 22		
16	2.729	<u>22</u> 2		
16	2.722	222		
35	2.349	222	2	2.342
63	2.273	004		
64	2.271	040	56	2.257
63	2.259	400		
2	2.218	<u>3</u> 31		
2	2.216	313		
1	2.212	$\frac{331}{122}$		n.o.
1	2.210	$\frac{155}{313}$		
2	2.208	133		
9	2.053	133		
11	2.040	313	6	2.027
10	2.034	331		
11	1.912	133		
11	1.905	313	7	1.895
11	1.902	331		
6	1.829	<u>3</u> 33		
20	1.823	115		
20	1.823	151	21	1.812
6	1.819	$\frac{3}{511}$		1.012
5	1.017	$\frac{311}{333}$		
<u>-</u> 1	1.515	115		
1	1.700	$\frac{113}{151}$		
2	1.755	115		
2	1.752	151	3	1.745
2	1.748	$\underline{51}1$		
2	1.746	511		
31	1.713	$\overline{440}$		
29	1.711	404	29	1.702
30	1.709	044		
4	1.670	115		
4	1.667	151		n.o.
4	1.659	511		
3	1.635	$\frac{351}{521}$		
3	1.633	$\frac{531}{215}$		
3	1.055	<u>5</u> 15 513	2	1.626
3	1.632	153		
2	1.631	$\frac{135}{135}$		

I _{cily.}	d _{calc}	hkl	Iabs	d _{abs}
1	1.613	351		
1	1.013	215		
1	1.012	$\frac{515}{125}$		
1	1.007	$\frac{1}{442}$		
1	1.000	442 531	2	16
1	1.605	<u>3</u> 31 424	Z	1.0
1	1.604	<u>42</u> 4 153		
1	1.603	$\frac{15}{513}$		
1	1.600	442		
6	1.521	044		
2	1.520	$\overline{2}44$		
6	1.513	404		
2	1.510	424		
6	1.509	<u>44</u> 0		
2	1.506	<u>4</u> 42	4	1 404
6	1.505	<u>1</u> 35	4	1.494
6	1.504	1 <u>5</u> 3		
6	1.497	315		
7	1.494	$\frac{513}{1}$		
5	1.493	$\frac{351}{531}$		
7	1.491	531		
4	1.477	5 <u>3</u> 3		
4	1.473	<u>35</u> 3		n.o.
3	1.471	335		
4	1.451	<u>26</u> 2		
4	1.450	$\frac{226}{622}$		n.o.
5	1.449	125		
2	1.429	153		
2	1.420	315		
1	1.423	351		n.o.
2	1.420	513		
$\frac{2}{2}$	1 419	531		
2	1.119			
0	1.309	220		
0	1.300	202		
1	1 38/	260		
8	1 383	200		
16	1 380	602 262 622	5	1 376
1	1.379	620	5	1.570
9	1.377	$\frac{6}{622}$		
8	1.372	444		
8	1.365	444		
7	1.361	444		
2	1.356	551		
2	1.355	515		
2	1.354	551	3	1.354
4	1.352	151. 515	5	1.551
2	1.351	155		
2	1.314	117		
2	1.313	$1\overline{7}1$		n.o.
2	1.308	711		
2	1.278	117		
2	1.277	171		
7	1.276	2 <u>2</u> 6		
2	1.275	117	3	1 268
6	1.274	<u>26</u> 2	5	1.200
2	1.273	1 <u>7</u> 1		
2	1.269	711		
7	1.268	622,711		

n.o.: not observed

Simulated powder diffraction data obtained with the program JANA2000 (PETRICEK et al. 2000). Only lines with $I_{calc} > 1$ are shown in the table, hence all of the characteristic k+l = odd superstructure reflections have been omitted. I_{obs} , d_{obs} result from a Gandolfi-type measurement (Nonius KappaCCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation) of an anata-camite crystal using the program Nonius POWDERIZE.

	Anatacamite ^a $P\overline{1}$	Clinoatacamite ^{b, c} P21/n	Botallackite ^d P21/m	Atacamite ^o <i>Pnma</i>
a (Å)	9.1646(9)	6.144(1)	5.717	6.030
b (Å)	9.2029(8)	6.805(1)	6.126	6.865
c (Å)	9.2102(8)	9.112(1)	5.636	9.120
α (°)	95.858(6)	90	90	90
β (°)	96.290(7)	99.55(3)	93.07	90
γ (°)	96.507(2)	90	90	90
$V(\text{\AA}^3)$	761.97(12)	375.7(2)	197.1	377.53
Ζ	8	4	2	4

Table 3. Unit cell data: a comparison of anatacamite with its polymorphs.

^a Malcherek & Schlüter (2009), ^b Grice et al. (1996), ^c Jambor et al. (1996), ^d Hawthorne (1985), ^c Parise & Hyde (1986)



Fig. 3 a–c. Epitaxial and structural relation of atacamite and anatacamite: (a) a fragment of the atacamite structure viewed down [211]. Anatacamite coordination can be attained by swapping Cl and O-atoms among neighbouring Cu2-coordination polyhedra, as indicated by the double arrow. (b) corresponding fragment of anatacamite viewed down [211]. (c) structural view of the atacamite-anatacamite interface. Displayed atoms in order of decreasing size: Cl, O, Cu, H.

While anatacamite is easily identified by single-crystal X-ray diffraction, it will be very difficult to distinguish it from clinoatacamite in X-ray powder diffraction experiments. Deviation from the monoclinic metric is too small to induce peak splitting or significant peak broadening. Calculation of the powder diffraction pattern shows that the characteristic superstructure reflections with k+l = odd in the triclinic setting are too weak to be observable in conventional experiments. Accordingly, none of these reflections are above the intensity threshold used in Table 2.

Anatacamite occurs epitaxially intergrown with atacamite. Across the $(8\overline{3}3)an/(0\overline{1}1)_{at}$ -interface, the (011) lattice plane of atacamite continues as the (111) plane of anatacamite (Fig. 3c). The lattice spacings of anatacamite and atacamite match almost perfectly across the interface $(d(11\overline{1})_{an}/d(011)_{at} = 0.9926)$. Along the (111) plane normal of anatacamite densely populated layers of Cu atoms, that occur 4-2-coordinated by four OH and two Cl (Cu3b, Cu3c, Cu4a, Cu4c, intra-layer), as well as 6-coordinated by OH (Cu1a, Cu2a-c, inter-layer), alternate with less densely populated layers of 4-2-coordinated Cu3a and Cu4b (intra-layer) atoms. A similar sequence of layers is seen along the corresponding (011) plane normal of atacamite. Here the densely populated layers are formed by 4-2-coordinated Cu1 and 5-1-coordinated Cu2 atoms. The less densely populated layers are occupied by Cu1. The transition of atacamite to anatacamite (Figure 3 b) across the interface requires an exchange of Cl and O atoms between neighbouring Cu2 coordination environments, indicated by the double arrow in Figure 3 a.

Among the pseudo-trigonal polymorphs, "sub-paratacamite", clinoatacamite and anatacamite, the latter should represent the stable form for the pure stoichiometry $Cu_2(OH)_3Cl$ (MALCHEREK & SCHLÜTER 2009). With increasing availability of Zn and ensuing reduction of the Jahn-Teller distortion at the inter-layer octahedron, clinoatacamite or even herbertsmithite may form. However, in terms of natural occurence, atacamite is the most abundant polymorph of pure $Cu_2(OH)_3Cl$. The alternative formation of anatacamite may be attributed to the availability of atacamite as a substrate for the nucleation of anatacamite from solutions containing minor concentrations of Zn or Ni.

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