

Herbertsmithite, $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, a new species, and the definition of paratacamite

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ABSTRACT

One in four of the Cu-filled cation sites in clinoatacamite, the monoclinic polymorph of atacamite and botallackite, is angle- rather than Jahn-Teller-distorted. Experiments show that this site alone is susceptible to substitution by a non-Jahn-Teller distorting cation of suitable radius and charge, such as Zn^{2+} , and also Ni^{2+} , Co^{2+} , Fe^{2+} , Cd^{2+} and Mg^{2+} . The crystal symmetry changes to rhombohedral when $\sim 1/3$ of the Cu in this site is substituted by e.g. Zn, thus giving paratacamite; the Zn is essential for stability and forms, with larger proportions of Zn, a series to the end-member in which the site is fully occupied by Zn. This end-member, rhombohedral stoichiometric $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, has been characterized using natural specimens from Chile and Iran and is named herbertsmithite. The other cations mentioned behave similarly, producing stabilized rhombohedral paratacamites and end-members analogous to herbertsmithite, which if found in nature, as the Ni analogue has been, should be named species. Clinoatacamite, paratacamite and herbertsmithite have rather similar X-ray powder diffraction patterns, but are readily distinguished by infrared spectroscopy.

Zn-stabilized paratacamite forms blue-green crystals of rhombohedral habit, with vitreous lustre, $\epsilon = 1.828\text{--}1.830$, $\omega = 1.835$, uniaxial negative, weakly pleochroic $O > E$, density: 3.75 g cm^{-3} , Mohs hardness: $3\text{--}3\frac{1}{2}$; space group $R\bar{3}$, $a = 13.654(5)$, $c = 14.041(6) \text{ \AA}$, $Z = 24$, with pronounced $R\bar{3}m$ substructure; six strongest XRD lines 5.452 (100), 2.895 (20), 2.760 (74), 2.262 (52), 1.817 (18), 1.708 (21).

Herbertsmithite forms dark green crystals of rhombohedral habit, with vitreous lustre, $\epsilon = 1.817$, $\omega = 1.825$, uniaxial negative, weakly pleochroic $O > E$, density: 3.95 g cm^{-3} , Mohs hardness: $3\text{--}3\frac{1}{2}$; space group $R\bar{3}m$ with no superstructure observed, $a = 6.834(1)$, $c = 14.075(2) \text{ \AA}$, $Z = 3$; six strongest XRD lines 5.466 (55), 4.702 (14), 2.764 (100), 2.266 (36), 1.820 (13), 1.709 (18).

KEYWORDS: herbertsmithite, paratacamite, anarakite, solid solution, site occupancy and selectivity, new mineral, IR spectroscopy, XRD, Cu chlorides, Anarak, Iran, Sierra Gorda, Chile.

Introduction

In 1972, Adib and Ottemann published a paper describing "anarakite" $(\text{Cu,Zn})_2(\text{OH})_3\text{Cl}$, with $\text{Cu/Zn} = 4.7$, as a new mineral species from two localities near Anarak in Iran, distinct from

zincian paratacamite. However, on the basis of the close match of the X-ray, optical and physical data presented with those of paratacamite as then defined, but ignoring the stated marked difference in infrared (IR) spectra between them (but for which no data were given) the IMA Commission on New Minerals and Mineral Names rejected its species validity, and suggested that it should be considered a zincian paratacamite until proof to the contrary be presented. Kracher and Pertlik

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(1983) presented analytical and X-ray data for a "zincan paratacamite" from Herminia mine, Sierra Gorda, Chile, with a composition close to $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, and concluded that the atomic arrangement of paratacamite is stabilized by partial replacement of Cu by Zn.

Smith (1906) first described paratacamite, as $\text{Cu}_4(\text{OH})_6\text{Cl}_2$, a new polymorph of atacamite, with morphologically rhombohedral crystals, but with some showing biaxial optics, from the Herminia and Generosa mines, Sierra Gorda, and the Bolaco mine, San Cristóbal, all in Chile. Chemical analysis at the time (G.T. Prior in Smith, 1906) did not report the presence of any Zn (presumably he did not look for it, the analyses totalling 100.44%). Frondel (1950), using samples from BM 86958, one of the original specimens studied by Smith (and Prior) (1906), confirmed its distinction from atacamite, and showed it to be optically uniaxial, though sometimes biaxial, and determined its structure as rhombohedral $R\bar{3}2/m$. A chemical analysis (by L.C. Peck), in Frondel's paper (1950) again missed out Zn. Fleet (1975) re-determined the structure, using a single crystal (unfortunately not analysed, and now lost) from BM 86958, as rhombohedral, $R\bar{3}$ with $R\bar{3}m$ substructure, and this structure is the currently accepted one, confirmed by Pring *et al.* (1987) using material from Australia.

Jambor *et al.* (1996), having observed differences in the X-ray diffraction (XRD) patterns of different specimens of 'paratacamite', studied both it and 'anarakite', and as a result described the new mineral clinoatacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$, as a monoclinic polymorph of atacamite and botallackite (therefore biaxial). From detailed studies of natural specimens, and particularly of synthetic materials with a wide range of Zn:Cu ratios from zero up to that of 'anarakite', it was concluded that the clinoatacamite structure (Grice *et al.*, 1996) is stable only when little or no Zn is present, and that the presence of appreciable Zn (or Ni) is essential to stabilize the rhombohedral structure assigned to paratacamite, with 'anarakite' being a zincian variety. The Powder Diffraction File standard pattern for 'paratacamite' (25-1427) is that of clinoatacamite, and many or most specimens considered as 'paratacamite' are probably clinoatacamite. The situation is complicated by the fact that the analysed type specimen of 'paratacamite', BM 86958, contains megascopically indistinguishable crystals of both species, and therefore the published analyses of samples from it are likely to be of

mixtures, probably of phases with differing Zn contents. The definition of 'paratacamite' is therefore called into question, and should be decided before 'anarakite' can be defined (Grice *et al.*, 1996).

Peter Thomson visited the Anarak area of Iran in 1971, and presented a number of specimens to one of us (RSWB). Some of these, from Kali Kafi and Chah Khouni mines, carried small crystals of a zincian basic Cu chloride, which provided IR spectra very different from those of synthetic Zn-free 'paratacamite' (i.e. clinoatacamite), atacamite and botallackite. The emergence of Adib and Ottemann's paper (1972) prompted comparison with their 'anarakite', and this identification was confirmed when its IR spectrum was published in Adib's thesis (1972). Unfortunately not enough material was available for further study until J.A. Baldwin presented RSWB with much better material collected from Mina Los Tres Presidentes, Sierra Gorda, Chile, and which he had analysed. The consequent studies, supported by work on synthetic material, have shown that end-member 'anarakite' is a stoichiometric phase of specific structure, and is therefore of species rank. Unfortunately, specimens of the original 'anarakite' are not available, prohibiting comparison with 'type' material, and our material has consequently been given a new name, herbertsmithite, from Dr G.F. Herbert Smith (1872–1953) late of the British Museum (Natural History) who discovered paratacamite. The species and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The type specimen from Mina Los Tres Presidentes, Chile (Specimen 22 of Table 1), analysed and used for X-ray, IR, physical and optical studies, is lodged at the Natural History Museum, London; register number BM 2003.33.

Definition of paratacamite

The first problem in this definition is the lack of a true type specimen. The analysed and X-rayed holotype specimen is BM 86958, but as mentioned above, the specimen contains both rhombohedral paratacamite and clinoatacamite, megascopically indistinguishable, and all analyses of samples before the distinction was realized are likely to be of mixtures. The work of Jambor *et al.* (1996) suggests that the amount of Zn present may be critical, in that Zn to the extent of $\sim 1/3$ or greater site occupancy (~ 5 wt.% Zn) is essential

HERBERTSMITHITE, A NEW SPECIES

for the stability of the paratacamite structure, and we confirm this (see below). The crystal structure and parameters are those of Fleet (1975), but compositional analysis of an X-rayed single crystal from BM 86958 is required for a true 'type specimen' definition. Other analyses are

presented in Table 1. Note that paratacamite is $R\bar{3}$, with pronounced $R\bar{3}m$ substructure.

Individual grains were sampled at random from BM 86958, the original type specimen of 'paratacamite', from Generosa mine, Sierra Gorda, Chile. Electron probe microanalyses of

TABLE 1. Analyses of clinoatacamite, paratacamite and herbertsmithite.

Sample	Cu	Zn	Cl	Cu/Zn	Cation	Sample	Cu	Zn	Cl	Cu/Zn	Cation
			atom % Zn						atom % Zn		
	Clinoatacamites						Paratacamite–herbertsmithite				
1	59.7	0	16.5	∞	0	13				10.1	9.0
2				∞	0	14	52.9	5.8	15.4	9.4	9.9
3				51.6	1.9	15	51.3	6.7	17.0	7.9	11.6
4				31.3	3.1	16				7.3	12.0
5	55.9	2.0	16.6	28.8	3.5	17	49.2	8.2	14.1	6.2	14.3
6	58.2	2.5	15.4	24.4	4.1	18	48.9	8.7		5.7	15.1
7	56.5	2.5	17.1	23.3	4.2	19	48.5	10.6	17.5	4.7	17.9
8				22.8	4.2	20				3.4	22.8
9	55.6	2.7	16.7	21.0	4.6	21	44.0	14.5	16.1	3.1	24.7
10				19.8	4.8	22	44.8	14.6	17.2	3.1	24.6
11				13.9	6.7	23	44.6	15.3		3.0	25.5
12				10.6	8.6	24	42.3	15.8	16.9	2.8	27.1
						25	41.6	16.2	16.3	2.6	28.0
						26	44.4	15.2	16.5	3.0	25.5

Key to Table 1

Clinoatacamite samples:

1. Chuquicamata, Chile. Off M32176. Jambor *et al.* (1996).
2. Synthetic 1-6 of Dutrizac.
3. Synthetic AD-2 of Dutrizac.
4. Synthetic 7 of Dutrizac.
5. Sierra Gorda, Chile. Off WHP III/372. Analyst P.J. Dunn.
6. Generosa mine, Chile. Embrey and Jones (1981).
7. Sierra Gorda, Chile. Off BM 86958. Analyst P.J. Dunn.
8. Synthetic AD-3 of Dutrizac.
9. Sierra Gorda, Chile. Off BM 86818. Analyst P.J. Dunn.
10. Synthetic AD-4 of Dutrizac.
11. Synthetic P19 of Dutrizac.
12. Synthetic P9 of Dutrizac.

Paratacamite–herbertsmithite samples:

13. Synthetic P24 of Dutrizac.
14. Kali Kafi mine, Anarak, Iran. Off WHP 593/374. Analyst P.J. Dunn.
15. Kali Kafi mine, Anarak, Iran. Off RSWB 71-339. Analyst P.J. Dunn.
16. Synthetic P50 of Dutrizac.
17. Anarak, Iran. Off Meixner Collection HMx/III/182. Analyst P.J. Dunn.
18. Kali Kafi mine, Anarak, Iran. Most Zn-rich crystal analysed off Pinch #508. Jambor *et al.* (1996).
19. Kali Kafi mine, Anarak, Iran. Adib and Ottemann (1972).
20. Synthetic P36 of Dutrizac.
21. Mina Los Tres Presidentes, Sierra Gorda, Chile. Analyst J.A. Baldwin.
22. Mina Los Tres Presidentes, Sierra Gorda, Chile. Analyst P.J. Dunn.
23. Synthetic, from malachite with zinc chloride (RSWB). Analyst (microchemical) R. Perry.
24. Sierra Gorda, Chile. Off NHMW J 2425. Analyst P.J. Dunn.
25. Herminia mine, Sierra Gorda, Chile. Kracher and Pertlik (1983).
26. Theoretical for $Cu_3Zn(OH)_6Cl_2$.

138 spots from 37 grains showed a variation in wt.% Zn, from 0.32 to 4.78%. It is clear that the older analyses, including the type analysis, being from multi-grain samples, are of limited value in assessing Zn content and hence the nature of the samples. As the structural symmetry changeover point from clinoatacamite to paratacamite is at ~5 wt.% Zn, it is clear that most of the grains analysed, and therefore probably most of the crystals on the specimen, are of clinoatacamite, as reported by Jambor *et al.* (1996). Fleet's (1975) paratacamite crystal being a fortuitous sample. Note that the lowest Zn content for a rhombohedral synthetic paratacamite reported by Jambor *et al.* (1996) is 6.2 formula %, corresponding to 3.6 wt.% Zn, well within the compositional range of BM 86958.

Paratacamite should be defined as a rhombohedral $R\bar{3}$ phase of composition $\text{Cu}_3(\text{Cu}, M^{2+})(\text{OH})_6\text{Cl}_2$, in which M^{2+} is a non-Jahn-Teller distorting cation of appropriate radius, occupying $\frac{1}{3}$ to $\frac{1}{2}$ of the non-Jahn-Teller distorted site in the structure described by Fleet (1975). When the M^{2+} occupancy of this site falls appreciably below $\frac{1}{3}$ this site takes on a small Jahn-Teller distortion, causing the crystal symmetry to become monoclinic, as clinoatacamite. Materials near the changeover composition can exist in either symmetry form. The nature of M^{2+} can be distinguished by an appropriate qualifier, e.g. Zn, Ni, etc. -stabilized paratacamite, each of these phases at $\frac{1}{3}$ site occupancy being end-members of solid-solution series to site-filled stoichiometric

rhombohedral phases of composition $\text{Cu}_3M(\text{OH})_6\text{Cl}_2$, which, when they occur naturally, are of species rank and require names, such as the herbertsmithite described in this paper, where $M = \text{Zn}$. These names should apply to phases where the M site occupancy exceeds $\frac{1}{2}$. Other natural examples are the rhombohedral material from Carr Boyd nickel mine, Western Australia, of which the most Ni-rich sample analysed corresponds to a composition $\text{Cu}_3(\text{Ni}_{0.76}\text{Cu}_{0.24})(\text{OH})_6\text{Cl}_2$ (Jambor *et al.*, 1996), and the even more nickeliferous material from the Widgiemooltha deposit, Western Australia (E.H. Nickel in Jambor *et al.*, 1996). This material should now be named. Synthetic materials of end-member composition $\text{Cu}_3M(\text{OH})_6\text{Cl}_2$ reported in the chemical literature include those with $M = \text{Zn}$, Ni, Co, Fe, Cd and Mg, all of which include rhombohedral polymorphs.

Our Zn-stabilized paratacamite from Iran (see Tables 1, 2) forms blue-green crystals tending to a near equant habit, with a vitreous lustre, and a good cleavage that is possibly $\{10\bar{1}1\}$. The mineral has density 3.75 g cm^{-3} (measured with a Berman microbalance) and Mohs hardness 3–3½. It is uniaxial negative, or occasionally biaxial negative with a very low $2V$ ($5\text{--}10^\circ$), in agreement with the observations of Jambor *et al.* (1996). Refractive indices are $\epsilon = 1.828\text{--}1.830$, $\omega = 1.835$ (measured by immersion, using phosphorus-diiodomethane-sulphur liquids; see Table 2) and weakly pleochroic, green to blue-green, with $O > E$. Its IR spectrum is presented in

TABLE 2. Physical and optical properties of herbertsmithite, Zn-stabilized paratacamite and clinoatacamite.

Species Specimen, (Cu/Zn)	Herbertsmithite				Paratacamite		Clinoatacamite ³
	25 (2.6) ¹ 24 (2.8)	21 (3.1) 22 (3.1)	19 (4.7) ²	17 (6.2)	15 (7.9)	14 (9.4)	
Colour	Dark green	Dark bluish green	Bright green	Blue green	Blue green	Blue green	Dark green
Lustre	Vitreous	Vitreous	?	Vitreous	Vitreous	Vitreous	Adamantine
Cleavage	$\{10\bar{1}1\}$ g	$\{10\bar{1}1\}$ g	?	$\{10\bar{1}1\}$? g	$\{10\bar{1}1\}$?	$\{10\bar{1}1\}$? g	$\{012\}$ perfect
Mohs hardness	3	3	3–3½	3½	3	3½	3
Density, g cm^{-3}	3.95	3.85	3.9	3.75		3.75	3.77
ϵ	1.815	1.817	1.842	1.830	1.828	1.828	
ω	1.825	1.825	1.849	1.835	1.835	1.835	
$2V_\alpha$							$75(5)^\circ$

All ϵ , ω indices ± 0.002 . Specimen numbers correspond with those of Table 1

1 Kracher and Pertlik (1983)

2 Adib and Ottemann (1972)

3 Jambor *et al.* (1996)

HERBERTSMITHITE, A NEW SPECIES

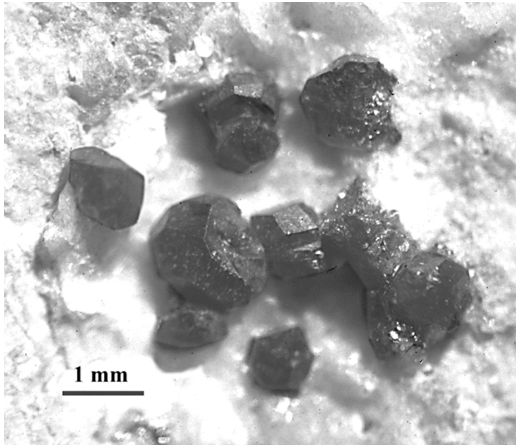


FIG. 1. Herbertsmithite, dark green crystals on pale buff matrix. From RSWB 84-27, Mina Los Tres Presidentes, Sierra Gorda, Chile.

Fig. 1, with absorption maxima given in Table 4. The powder XRD trace of a synthetic sample (Dutrizac's P24 in Jambor *et al.*, 1996) with near minimum Zn content of 9.0 cation % Zn (Cu/Zn atom = 10.1) is very close to those of "zincian paratacamite" presented in Table 1 in Jambor *et al.* (1996) and is given in Table 3, indexed on a rhombohedral cell with $a = 13.659(8)$, $c = 14.048(7)$ Å, $V = 1136.08$ Å³. Fleet (1975) gives $a = 13.654(5)$, $c = 14.041(6)$ Å for his unanalysed crystal from single-crystal measurements.

The new mineral herbertsmithite

Description, mode of occurrence

The herbertsmithite studied from Kali Kafi mine, Anarak, Iran, which is the 'type' locality of Adib and Otteman's (1972) 'anarakite', forms bright green grains, mostly <0.1 mm across, in confused aggregates in 'limonite' gossan. It is directly associated with, and occasionally grown on spectacular, often rich coatings of 1–2 mm bipyramidal wulfenite crystals of pale yellowish to deep reddish-orange colour, these colours varying even within individual crystals, and with hemimorphite, chrysocolla and sometimes rosasite.

The material from Chah Khouni mine, Anarak, Iran (the other locality for 'anarakite' reported by Adib and Ottemann, 1972) consists of dark green crystals with indistinct faces, mostly ~0.1 mm across, and aggregates of such crystals. Some

TABLE 3. Indexed X-ray powder diffraction data for herbertsmithite and Zn-stabilized paratacamite; d_{obs} in Å, I = relative intensity.

1		2		Indices		
d	I	d	I	h	k	l
5.466	55	5.452	100	1	0	1
4.702	14	4.683	14	0	0	3
4.537	3	4.525	3	1	0	2
3.423	5	3.416	6	1	1	0
3.028	1	3.019	2	1	0	4
2.899	11	2.895	20	2	0	1
2.764	100	2.760	74	1	1	3
2.730	13	2.727	13	2	0	2
2.346	4	2.341	8	0	0	6
2.266	36	2.262	52	2	0	4
2.210	2	2.208	3	2	1	1
2.040	4	2.037	7	2	0	5
1.934	1	1.931	1	1	1	6
1.905	5	1.900	8	1	0	7
1.820	13	1.817	18	3	0	3
1.752	1	1.749	2	2	1	5
1.709	18	1.708	21	2	2	0
1.664	1	1.661	2	2	0	7
1.631	3	1.630	4	3	1	1
1.606	1	1.604	2	2	2	3
1.599	1	1.598	2	3	1	2
1.513	4			2	0	8
		1.510	5	1	0	9
1.496	3	1.494	7	2	1	7
1.472	1	1.471	2	4	0	1
1.448	1	1.447	3	4	0	2
		1.419	2	1	1	9
1.381	6	1.380	9	2	2	6
1.363	4	1.363	5	4	0	4
1.351	2	1.351	2	3	2	1
		1.309	1	4	0	5
				3	1	7
1.272	5			20	1	0
		1.270	5	4	1	3
1.245	3	1.245	4	4	1	5
1.174	1			20	1	1
		1.172	1	4	1	6
1.132	1			3	2	7
1.125	1	1.124	1	3	3	3
1.107	1			4	2	2
		1.105	2	4	2	4
1.066	1	1.066	2	5	1	1
1.060	1			4	2	5
		1.039	1	40	1	0
1.020	2	1.019	2			

1. Herbertsmithite, Mina Los Tres Presidentes, Chile. Off specimen 22 of Table 1.

2. Paratacamite; synthetic P24 of Dutrizac, specimen 13 of Table 1, with near-minimum Zn content for rhombohedral structure (Cu/Zn = 10.1). Data collected using a Scintag XDS 2000 powder diffractometer utilizing Cu-K α radiation.

TABLE 4. Wavenumbers of IR absorption maxima for natural herbertsmithite, Zn-stabilized paratacamite, clinoatacamite, atacamite and botallackite (cm^{-1}).

1	2	3	4	5
				3520 s, sp
3410 sh	3450 s, sp	3450 s, sp	3450 s, sp	3440 sh
3380 vs, sp	3380 vs, sp	3360 s	3360 w, sh	3420 s
3320 sh	3310 s, fsp	3310 s	3340 vs	
			3190 w, br	
970 sh	972 m	984 s, sp	982 s, sp	
945 s, fsp	943 s, fsp		946 s, sp	
		920 s, sp	922 s, sp	
		902 vw		
		888 vw	890 s, sp	
		860 s, sp	862 w	853 s
	812 m, br	822 ms	845 s, sp	815 s, sp
753 s, br	750 s			778 s, fbr
				703 s, fbr
597 w, br	590 w, br	572 ms	590 s	525 s, sp
	510 sh	512 s	510 s	502 s, sp
460 s	460 vs	448 vs	475 s	450 ms, sp
	400 m	405 s	438 s	418 s
		380 sh	390 vs	385 s

s = strong, m = medium, w = weak, sh = shoulder, sp = sharp, br = broad, v = very, f = fairly.

1. Herbertsmithite, Mina Los Tres Presidentes, Chile. Off specimen 22 of Table 1. Cu/Zn = 3.1.

2. Paratacamite, Kali Kafi mine, Iran. Off WHP 593/374. Cu/Zn = 9.4.

3. Clinoatacamite, Levant mine, Cornwall. Off RSWB 69-304.

4. Atacamite, Mina la Farola, Chile. Off RSWB 77-50.

5. Botallackite, Levant mine, Cornwall. Off RSWB 74-244.

crystals are flattened, thin and curved in form, up to 0.5 mm across, occasionally with hexagonal outlines. These crystals are found on joint surfaces of metamorphosed dolomitic limestone coated with orange-brown 'limonite', and richly carpeted with small colourless hemimorphite blades, some altered to chrysocolla, and associated with iranite crystals and diaboleite. The herbertsmithite crystals grew on the hemimorphite, but some are themselves overgrown by colourless, late-generation calcite rhombohedra.

The material from Mina Los Tres Presidentes, Sierra Gorda, Chile, is near end-member herbertsmithite in composition. It forms scattered to richly clustered coatings of dark green complex rhombohedra, mostly 0.5–1 mm in diameter (Fig. 1), or somewhat larger flattened crystals and aggregates in parallel growth, with distorted hexagonal outlines, on a white quartzite, and

associated with colourless flattened gypsum crystals, white radiating needles of opal pseudomorphs and minor diopside.

Chemical composition

Herbertsmithite from Mina Los Tres Presidentes was analysed by J. Arthur Baldwin by electron microprobe at the Open University, Milton Keynes, UK, and by Dr P.J. Dunn of the Smithsonian Institution, Washington, using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA , measured on brass. The standards used were NaCl (Cl-K α), ZnO (Zn-K α) and Cu₂O (Cu-K α). The data were corrected using a modified version of the MAGIC-4 program. Dr Dunn used similar techniques to analyse a number of other specimens of members of the

clinoatacamite–paratacamite–herbertsmithite series, including material from Kali Kafi mine.

These and other analyses are presented in Table 1 and compared with published analyses. The tendency for herbertsmithite to have a Cu/Zn atomic ratio close to 3, the ratio of sites, is evident, as are the low Zn values in the clinoatacamite studied.

A 5.36 mg sample of herbertsmithite from Mina Los Presidentes, Chile, was submitted to thermogravimetric analysis by Mr A.J. Mackie of the Chemistry Department, UMIST, Manchester, at a heating rate of $10^{\circ}\text{C min}^{-1}$, under nitrogen. A sharp loss of water from 300°C was complete by 340°C , amounting to 12.5 ± 0.2 wt.% (theoretical loss for proposed formula 12.6 wt.%). Further, more gradual weight loss, corresponding to volatilization of chlorides and loss of oxygen was complete by 620°C , leaving a red residue containing cuprous oxide ($50.0\pm 0.2\%$ of original mass; theoretical 50.0%). Despite this mass corresponding to the theoretical value for pure Cu_2O , powder XRD by Mr M.O. Jones of the Chemistry Department, UMIST, showed that the residue is a mixture of Cu_2O with ZnO. A sample of synthetic herbertsmithite with Cu/Zn = 3.0 gave similar results.

Physical and optical properties

Herbertsmithite crystals have a dark green to blue-green colour and a vitreous lustre. Their colour somewhat resembles that of the chemically related botallackite. All herbertsmithite studied (Table 2) has a good cleavage, which is inclined to the [0001] direction of the rhombohedral crystals, and was determined to be parallel to $\{10\bar{1}1\}$. The Mohs hardness varies slightly between 3 and $3\frac{1}{2}$. The densities of several fragments were measured separately with a Berman microbalance, and found to vary between 3.75 ± 0.02 and 3.95 ± 0.02 g cm^{-3} , the lower values resulting from the intimately intermixed porous goethite and hemimorphite in the material from Iran.

The indices of refraction of the herbertsmithite, measured by the immersion method using phosphorus-diiodomethane-sulphur liquids, are presented in Table 2. All specimens of herbertsmithite studied are uniaxial negative. This observation is in contrast to those of Adib (1972) and Adib and Ottemann (1972), who reported their 'anarakite' to be biaxial positive with $2V = 40^{\circ}$, but is in agreement with that of

Jambor *et al.* (1996) on Zn-stabilized paratacamite. The refractive indices of the samples of herbertsmithite studied are dependent on the Zn content, and a gradual increase in ϵ and ω is noted with increasing Cu/Zn ratio. The pleochroism, green to greenish blue, is weak, with absorption $O > E$. The interference colours are pale to dark green, frequently anomalous in greenish blue to dark blue. No twin lamellation was observed in any of the herbertsmithite grains.

X-ray diffraction

Guinier and diffractometer powder and single-crystal X-ray measurements were taken of several samples of herbertsmithite and Zn-stabilized paratacamite. Samples from specimens 14 and 17 [paratacamite] and 22 and 24 [herbertsmithite] of Table 1 gave similar powder patterns, which generally agree with the 'anarakite' pattern of Adib and Ottemann (1972), the zincian paratacamite pattern of Jambor *et al.* (1996), with the $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$ -type patterns given in Oswald and Feitknecht (1964), the pattern of synthetic $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ (' $\text{Cu}_{1.5}\text{Zn}_{0.5}(\text{OH})_3\text{Cl}$ ') of Feitknecht and Maget (1949b), and of our synthetic herbertsmithite of this composition from reaction of malachite with aqueous Zn chloride (see below). Powder diffraction data for herbertsmithite are presented in Table 3; Jambor *et al.* (1996) give a similar table, comparing data for a paratacamite (from Kali Kafi mine), and a clinoatacamite with Adib and Ottemann's (1972) 'anarakite' data.

Single-crystal data for herbertsmithite (specimen 22, from Mina Los Tres Presidentes) were collected using a Phillips PW 1100 four-circle diffractometer, using graphite monochromatized Mo- $K\alpha$ radiation. For one hemisphere with $\leq 70^{\circ}2\theta$, 1678 reflections were measured, corrected for absorption and averaged to 340 unique reflections ($R_{\text{merge}} = 0.019$), 316 of which were used for the least-squares refinements, which converged to $R = 0.011$, $R_w = 0.015$.

The XRD patterns of herbertsmithite-paratacamite and of clinoatacamite are similar, but clearly distinct and consistent with the unit cells given below, monoclinic in the case of clinoatacamite, although triclinic symmetry cannot be completely ruled out. The main difference between the patterns of herbertsmithite and paratacamite is the presence of superlattice reflections in those of all of the paratacamite samples studied, but not in those of the near end-member herbertsmithite and clinoatacamite samples. Thus, superlattice reflec-

tions appear only when the low- or non-Jahn-Teller-distorted site is partly filled with Zn, suggesting ordering of the Zn substitution.

Herbertsmithite is trigonal rhombohedral, space group $R\bar{3}m$, with specimen 22 having $a = 6.834(1)$, $c = 14.075(2)$ Å, $V = 569.3$ Å³, $Z = 3$ based on a $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ 'molecule'. Specimen 24 yielded parameters $a = 6.832$, $c = 14.065$ Å. Our clinoatacamite, from specimen 5 (with 2% Zn) was found to be monoclinic, strongly pseudotrigonal rhombohedral, $P2_1/a$, with $a = 11.830(3)$, $b = 6.819(1)$, $c = 6.156(1)$ Å, $\beta = 130.49(1)^\circ$, with $Z = 4$, in general agreement with the results of Jambor *et al.* (1996) and Oswald and Guenter (1971), and its powder pattern matched that of Oswald and Guenter's material (1971) and PDF 23-948 (erroneously indexed, assuming a hexagonal unit cell). Optical examination shows polysynthetic twinning, further evidence that it is not trigonal rhombohedral. In this context note also Smith's (1906) and Frondel's (1950) observations that 'paratacamites' show 'anomalous' optical behaviour.

Although it is not easy to distinguish Zn from Cu in the structure determination, herbertsmithite does show strong indications that the two different cation sites in the paratacamite-type structure are occupied by different metals. Bond lengths for herbertsmithite, compared with those of paratacamite (in parentheses; Fleet, 1975) are as follows: Zn–O in the ZnO_6 'octahedron' = 2.119 Å (Cu–O = 2.107 Å), with six equivalent bond lengths but distinct angle distortion. In the CuO_4Cl_2 'octahedra' Cu–O = 1.985(1) Å (1.980 Å) and Cu–Cl = 2.779(1) Å (2.765 Å). The O–Cl length in the OH–Cl hydrogen bonded system is 3.071 Å (3.068 Å).

Synthesis and chemistry

The conditions required for the synthesis of the $\text{Cu}_2(\text{OH})_3\text{Cl}$ polymorphs have been studied by a number of authors (Garrels and Stine, 1948; Feitknecht and Maget, 1949a; Oswald and Feitknecht, 1964; Walter-Levy and Goreaud, 1969; Oswald and Guenter, 1971; Sharkey and Lewin, 1971; Tennent and Antonio, 1981; Pollard *et al.*, 1989; Jambor *et al.*, 1996). Sharkey and Lewin (1971) postulated that the preferred phase to crystallize is the one in which the coordination of its Cu sites most closely matched the coordination of the species predominating in the reaction solution, this being critically a function of activity as well as of pH. The careful study by

Pollard *et al.* (1989) shows that botallackite crystallizes initially as an unstable intermediate over a wide range of conditions, and that it recrystallizes to the other phases dependent on temperature, activity and the presence of other species, e.g. the presence of Ca^{2+} promotes recrystallization to atacamite, although clinoatacamite ('paratacamite') is the thermodynamically preferred phase at ambient temperature (see also Jambor *et al.*, 1996).

We have synthesized these polymorphs by precipitation and replacement reactions as recommended by Sharkey and Lewin (1971) and Pollard *et al.* (1989). Clinoatacamite syntheses were then carried out by precipitation as before, but adding different proportions of Zn chloride to the Cu chloride starting solutions, and adding only sufficient alkali to precipitate the Cu present, thus minimizing the danger of precipitation of mixtures containing basic Zn chloride phases. The products were analysed by IR spectroscopy (see below), and tested for Zn by reaction with diammonium tetrathiocyanatomercurate(II) in acid solution. Starting solutions containing Zn/Cu_{atomic} = 0.25, 1 and even 2 gave precipitates containing very little Zn, and giving IR spectra characteristic of clinoatacamite. Only when the atomic proportion of Zn:Cu in the reaction mixture reached as high as 4:1 or more were appreciable amounts of Zn incorporated in the products, which then gave IR spectra indicating the presence of paratacamite - herbertsmithite, and swamping excesses of Zn gave herbertsmithite. These results are in accordance with those of Martinez *et al.* (1966), who reacted 0.2 M solutions of mixtures of Cu and Zn chloride at ambient temperature with 25% of the amount of NaOH required for complete precipitation of the hydroxides, and analysed the precipitated products. The percentage of Zn was shown to be low from starting solutions containing up to Zn/Cu = 2.3, but to rise rapidly at higher proportions. Jambor *et al.* (1996) reported the results of similar detailed experiments, from which products were synthesized with a wide range of Zn/Cu ratios, quantitatively analysed and submitted to XRD. To obtain a product containing ~2.5 wt.% Zn, Zn:Cu ratios of ~10:1 were found to be required, the most Zn-rich materials, with ~10 wt.% Zn, requiring Zn:Cu of ~40:1. X-ray diffraction showed that products containing Cu/Zn_{atomic} from ∞ to ~10 had clinoatacamite structures, and from 10 to their Zn-maximum of 3.4 had rhombohedral paratacamite structures.

Solutions containing Co and Cu gave cobaltoan clinoatacamites to a maximum of 5 wt.% Co, high starting proportions of cobalt giving mixtures of clinoatacamite and rhombohedral $\text{Co}_2(\text{OH})_3\text{Cl}$ under the conditions used. Nickel-copper mixtures gave mixtures containing Ni hydroxide under the conditions used, though Ni analogues of paratacamite and herbertsmithite have been found in Australia (Jambor *et al.*, 1996; Nickel *et al.*, 1994; Nickel, E.H. in Jambor *et al.*, 1996).

Feitknecht and Maget (1949*b*) boiled Cu powder in acidified 0.1 and 0.25 M solutions of Zn chloride, and obtained precipitates of paratacamite-like structure, with Cu/Zn atomic ratios of exactly 3 in both cases, thus consisting of herbertsmithite. Products of paratacamite-like structure, with ratios of Cu/M^{2+} close to 3 were also obtained from similar experiments involving Ni, Co, Cd and Mg chlorides at room temperature. These cations, like Zn and unlike Cu, do not cause Jahn-Teller distortions.

We carried out further experiments to determine the nature of the products obtained by synthesizing clinoatacamite, atacamite and botallackite in the presence of large to swamping excesses of Zn ions. Precipitated Cu carbonate (giving an IR spectrum corresponding to that of malachite) was left in excess of 0.1 and 1 M aqueous Zn chloride. Samples of the precipitate were removed at intervals and analysed by IR spectroscopy. The spectra indicated a slow conversion to herbertsmithite, faster with the stronger solution, taking a few weeks to completion at ambient temperature, incomplete reaction precipitates being mixtures of herbertsmithite with malachite, sharp unshifted malachite absorptions indicating the absence of rosasite. No evidence for the formation of botallackite was observed, suggesting that if it is an intermediate, its conversion to herbertsmithite is faster than its production from malachite. Microchemical analyses of the final herbertsmithites produced showed Cu/Zn atomic ratios of 2.9 and 3.0, respectively.

Atacamite was prepared in the presence of calcium carbonate by the method of Sharkey and Lewin (1971), but using starting solutions with Zn:Cu ratios of 1:1 and 4:1. In both cases the IR spectra of the products were indistinguishable from those of normal atacamite, and tests with diammonium tetrathiocyanatomercurate(II) indicated that only small traces of Zn were present in the products.

Synthetic brochantite was allowed to stand without disturbance at ambient temperature in 1 M

aqueous Zn chloride. After 4 days the precipitate was sampled, and gave an IR spectrum corresponding with that of a well crystallized botallackite from Levant mine, Cornwall, and was again found to contain only traces of Zn.

The results of these experiments indicate that atacamite, clinoatacamite and botallackite display a reluctance to accept Zn into their structures on formation. Under forcing conditions – the presence of a large excess of Zn – the clinoatacamite structure alone will accept appreciable Zn, shifting the symmetry to that of paratacamite, and eventually forming herbertsmithite, to a stoichiometric ratio of Cu/Zn = 3 in accordance with the ratio and geometries of the cation sites. The Zn enters the weakly Jahn-Teller-distorted site and reduces its distortion, even the largest excess of Zn being unwilling to enter the more strongly Jahn-Teller-distorted lattice site. Other suitable non-distorting dipositive cations may act similarly. Atacamite and botallackite are very resistant to Zn substitution as all the cation sites in their structures are of the strongly Jahn-Teller-distorted bipyramidal type.

An attempt to compare the number of different sites occupied by Cu in herbertsmithite and clinoatacamite by electron spin resonance spectroscopy was unsuccessful, the high concentrations of Cu broadening the signals too much by exchange coupling.

Infrared spectroscopy

Infrared spectra were measured in nujol mulls and in pressed KBr discs within the 400–4000 cm^{-1} range, using various instruments, including Perkin-Elmer PE 397 and 783 spectrophotometers, and a Philips Analytical PU 9600 Fourier Transform instrument.

John Dutrizac kindly supplied us with some of the analysed and X-rayed samples, of a wide range of composition, that he had synthesized and which were used for the work described in Jambor *et al.* (1996). These were analysed by Fourier Transform IR (FTIR) spectroscopy, and proved to be of great value in our work (see below).

The IR spectrum of natural herbertsmithite is compared in Fig. 2 with those of natural Zn-stabilized paratacamite, atacamite, clinoatacamite and botallackite. Wavenumbers of absorption maxima are given in Table 4.

The complex of overlapping bands in these spectra between 3100 and 3600 cm^{-1} is due to O–H stretching vibrations. The absorptions in

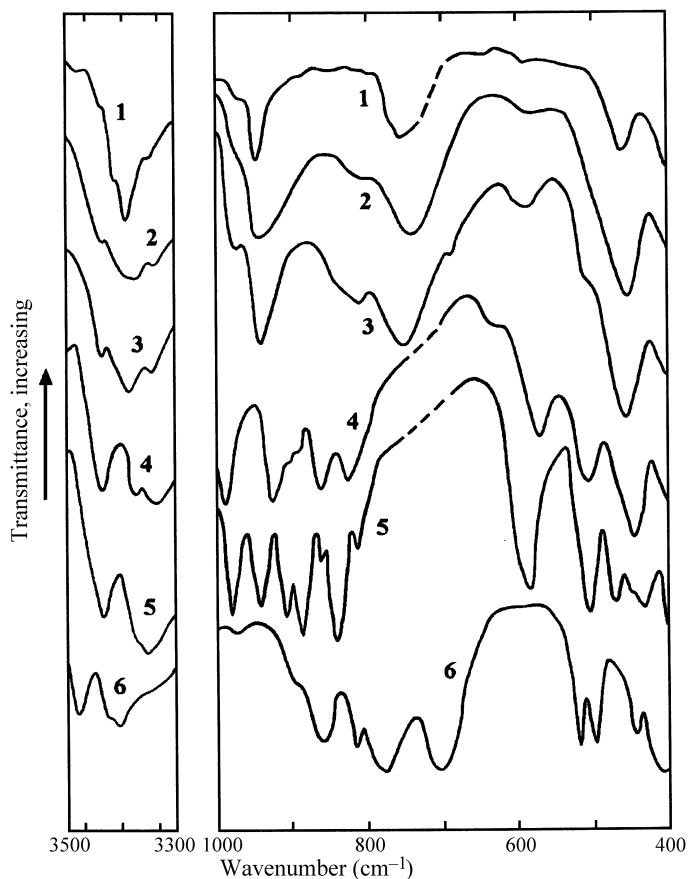


FIG. 2. IR absorption spectra of herbertsmithite, Zn-stabilized paratacamite, clinoatacamite and botallackite, measured in nujol mulls or KBr discs, using a PE 397 spectrophotometer. Concentrations vary among samples. No appreciable absorptions are found between 3100 and 1000 cm^{-1} , apart from those due to nujol. (1) Herbertsmithite, Mina Los Tres Presidentes, Sierra Gorda, Chile. Off specimen 22 of Table 1. Cu/Zn = 3.1. (2) Herbertsmithite, synthetic, from malachite with zinc chloride. KBr disc. Cu/Zn = 3.0. (3) Paratacamite, Kali Kafi mine, Anarak, Iran. Off WHP 593/374. KBr disc. Cu/Zn = 9.4. (4) Clinoatacamite, Levant mine, Cornwall. Off RSWB 69-304. (5) Atacamite, Mina La Farola, Chile. Off RSWB 77-50. (6) Botallackite, Levant mine, Cornwall. Off RSWB 74-244.

the 700–1000 cm^{-1} range are assigned to CuO–H and ZnO–H deformations; in particular the absorption in the 930–945 cm^{-1} region in the spectra of herbertsmithite and paratacamite is probably due to in-plane, and that near 750 cm^{-1} due to out-of-plane CuO–H and ZnO–H deformations, with their usual lower wavenumber. The absorptions in the 400–600 cm^{-1} region are likely to be due to metal–O stretching vibrations.

The IR spectrum of herbertsmithite is seen from Fig. 2 to be similar to that of Adib's "anarakite" spectrum (1972). It is easily distinguishable

from those of clinoatacamite, atacamite and botallackite, and is closely related to that of paratacamite; IR spectroscopy is a clear and rapid method for identifying these minerals. Compared with the spectra of the atacamite polymorphs, that of herbertsmithite-paratacamite is notable for its apparent simplicity, the greatest degree of simplicity occurring near the stoichiometric Cu/Zn = 3 composition.

The IR spectra of the analysed and X-rayed synthetic samples used for the work of Jambor *et al.* (1996) were particularly useful for studying trends, in view of their wide compositional range

and established nature. The positions and intensities of absorption maxima show steady variations with composition, except that sharper changes take place around the monoclinic-rhombohedral structure change boundary. An example, that of the position of the absorption maximum near 930 cm^{-1} (probably an in-plane metal-O-H deformation), is presented in graphical form in Fig. 3, clearly showing the change at the boundary. The spectra of samples within the series paratacamite to herbertsmithite are rather similar, the main trends again being towards simplicity as Zn fills the site; the profile of the side-bands on the main O-H stretching absorption reduces, as do those of the relatively weak bands near 970 and 830 cm^{-1} (see Fig. 2). Infrared spectroscopy is clearly useful for assessing the approximate position of a sample in the series, as well as identifying its species.

The spectra of these phases, mostly due to vibrations of O-H and metal-O bonds, are likely to be dominated by vibrations connected with the less symmetrical sites, because of the selection rules. Thus the relative simplicity of the herbertsmithite-paratacamite spectra may reflect increasing degeneracy and 'forbiddenness' resulting from increased symmetry in the structure, in particular the aforementioned increase in symmetry caused by substitution of the Jahn-Teller-distorting Cu^{2+} by the non-distorting Zn^{2+} in the appropriate site.

In the absence of symmetry-reducing deformations, only one environmental type of O-H is

found in the herbertsmithite-paratacamite structure, bridging pyramidally between two differently sited metal ions, and hydrogen bonded to a chloride ion at an angle of $\sim 166^\circ$ (Fleet, 1975). An O-H deformation vibration in the plane of this angle would be expected to be affected by hydrogen bonding more strongly than a deformation out of this plane.

An attempt was made to synthesize the bromide analogue of herbertsmithite, using an analogous synthetic method, in order to study any changes in its IR spectrum resulting from the reduction in hydrogen bonding consequent on substitution of chloride by the bromide ion. These should enable the in-plane and out-of-plane O-H deformation vibrations to be distinguished by the larger shift in frequency of the former, for the reason given above.

Malachite powder was allowed to stand in 1 M aqueous Zn bromide for 1 month. The product was carbonate-free and gave an analysis Cu, 34.0; Zn, 14.1; Br, 29.7%, corresponding to a formula $\text{Cu}_{2.8}\text{Zn}_{1.1}(\text{OH})_6\text{Br}_{1.9}$, with $\text{Cu}/\text{Zn}_{\text{atomic}} = 2.5$. The Guinier XRD pattern of this product, however, is of the 'C6' ($P\bar{3}m$) structure type (compare the Cu hydroxy-bromide of Aebi, 1948, and some phases synthesized by Feitknecht and Maget, 1949b), unlike that of herbertsmithite. The IR spectrum of this phase is generally similar to that of herbertsmithite, with the predicted changes in O-H deformation frequencies resulting from reduction in hydrogen bonding, but the structure difference reduces the relevance of these changes.

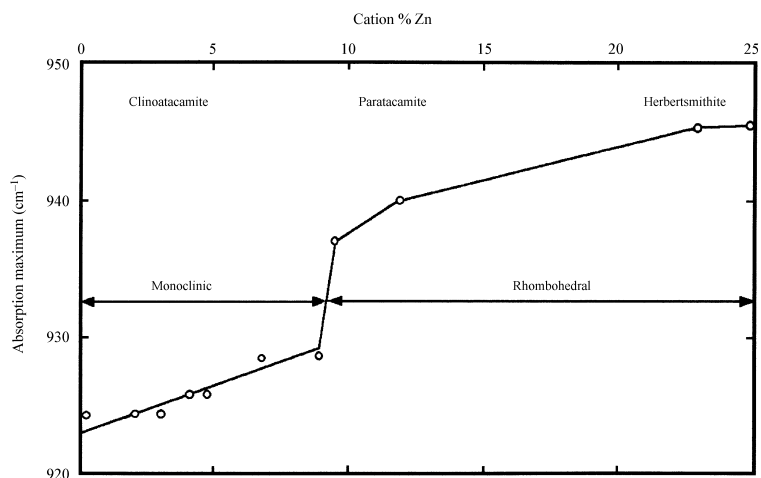


FIG. 3. Position of absorption maximum near 930 cm^{-1} in the IR spectra of members of the clinoatacamite-paratacamite-herbertsmithite series.

Conclusions

Paratacamite is defined as a mineral with the rhombohedral structure determined by Fleet (1975), and composition $\text{Cu}_3(\text{Cu}, M^{2+})(\text{OH})_6\text{Cl}_2$, in which $\text{Cu}/M^{2+}_{\text{atomic}}$ is $\sim 11-7$, corresponding to $\sim 1/3$ to $1/2$ occupancy of the non-Jahn-Teller site by M^{2+} , which is an essential stabilizing non-Jahn-Teller-distorting cation of suitable radius, such as Zn. The nature of this cation should be indicated.

Herbertsmithite is a species, in a solid-solution series with Zn-stabilized paratacamite, of ideal stoichiometric end-member composition $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, with a rhombohedral paratacamite-like structure, the Cu occupying the Jahn-Teller distorted bipyramidal cation sites, and the Zn occupying $>1/2$ of the other cation sites.

Analogous species, with other suitable non-Jahn-Teller-distorting cations replacing the Zn in herbertsmithite, and of similar structure, are known as synthetic products, and may well occur naturally, in series with the relevant paratacamite, and would then require naming. The Ni analogue has already been reported (E.H. Nickel *et al.*, 1994; E.H. Nickel in Jambor *et al.*, 1996).

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