Barstowite, $3PbCl_2.PbCO_3.H_2O$, a new mineral from Bounds Cliff, St Endellion, Cornwall

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Abstract

Barstowite, ideally $3PbCl_2.PbCO_3.H_2O$ is a new mineral from a lead–antimony vein at the south-western end of Bounds Cliff, St Endellion, Cornwall. It occurs as very small (0.2–0.5 mm) subparallel elongate intergrown crystals which form aggregates (up to 3 mm) containing minor inclusions of galena and jamesonite. Other associated minerals are quartz, dolomite, phosgenite, cerussite, sphalerite, pyrite and chalcopyrite. Barstowite is colourless to white and is transparent with an adamantine lustre and white streak. It is brittle, has an imperfect prismatic cleavage, and an uneven fracture. Low reflecting, barstowite has a moderate bireflectance from grey to dark grey in hue and weak to moderate anisotropy. Internal reflections (colourless) are abundant. Measured reflectance values in air and oil are tabulated. Colour values relative to the CIE illuminant C for R_1 and R_2 in air respectively are: $Y\%$ 12.9, 13.3; λ_d 477, 476; $P_e\%$ 3.5, 3.7. VHN_{100} 111 (range 108–117); calculated Mohs hardness is 3. Infrared spectra of barstowite, phosgenite and cerussite are compared.

X-ray studies show that barstowite is monoclinic with space group $P2_1/m$ and a 4.218(2), b 9.180(2), c 16.673(4) Å, β 91.49(3)°. It has a cell volume of 645.38 Å^3 with $Z = 2$. $D_{calc.}$ is 5.76 g/cm^3, $D_{meas.}$ is 5.71 g/cm^3. The strongest six lines of the X-ray powder pattern are [d in Å (I) (hkl)] 4.02 (10) (022); 2.296(8) (040; $12\bar{5}$; 106); 2.377(6) (007; 026); 4.16(5) (004); 2.108(4) (200); 3.79(3) (014). The name is for the late Richard William Barstow, the Cornish mineral dealer.

KEYWORDS: barstowite, new mineral, lead, St Endellion, Cornwall.

Introduction and general geology

BARSTOWITE, ideally $3PbCl_2.PbCO_3.H_2O$, is a new mineral species found in a specimen collected from a NNE–SSW trending lead–antimony vein exposed on the foreshore between low and high water marks at Bounds Cliff, St Endellion, Cornwall [SX 0185 8125—lat. 50°35′48″N, long. 4°47′56″W]. This vein is one of several which outcrop along the North Cornwall coast from Port Isaac to Tintagel. Many of these, and others inland, were worked in the last century (Hamilton Jenkin, 1970; Dines, 1956, pp. 574–8), but there is no evidence of mining activity associated with this vein.

At outcrop, just above low water mark, the vein is 15–30 cm across and consists predominantly of quartz and dolomite with granular galena and minor amounts of cerussite, pyrite, sphalerite, chalcopyrite and jamesonite. Cavities in the vein contain alteration products, predominantly lead minerals such as phosgenite and barstowite, which probably formed as a result of the action of seawater on the assemblage. The host rocks are strongly cleaved pale greenish-grey slates of Upper Devonian age (Warr, 1988), which dip seawards at 20–30°. Consequently, as its outcrop in the cliff is obscured by landslips, the vein can be traced no more than a few metres from the sea. Access to the locality from the cliff

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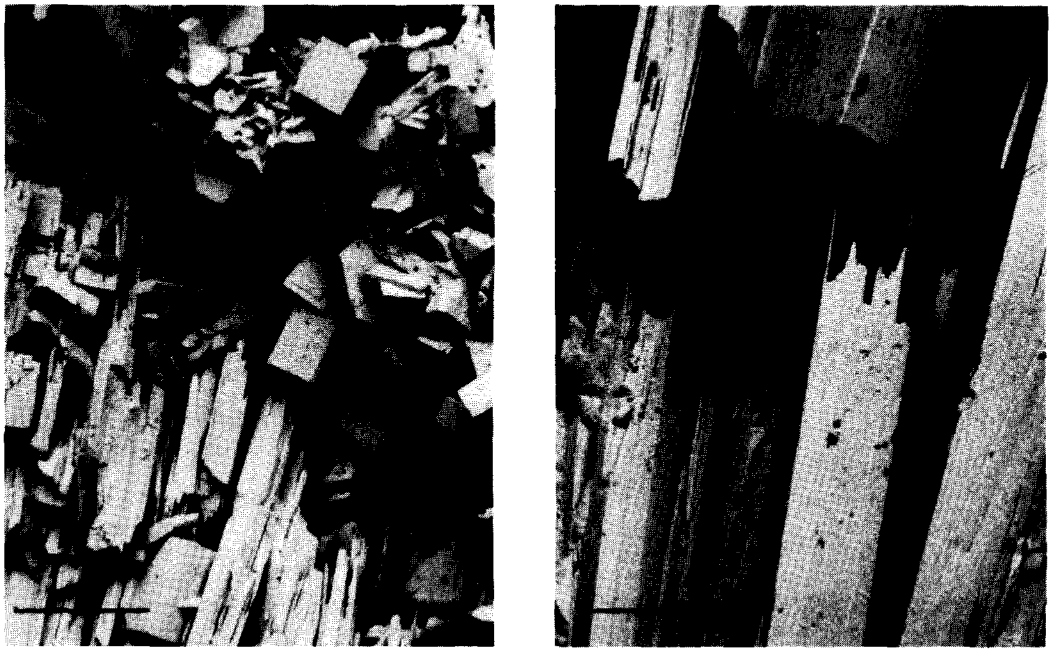

FIG. 1. Scanning electron photomicrographs of irregular prismatic barstowite with phosgenite (Scale bar: left 400 μm; right 100 μm).

path is difficult due to dense undergrowth and the steep and unstable cliffs; the locality is best examined in good dry weather at springtime when the undergrowth is minimal, the tides are at their lowest, and there is no sea swell.

Barstowite is named after Richard William Barstow (1947–1982), the Cornish mineral dealer whose collection is now on display in the City of Plymouth Museum. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The type specimen is preserved at The Natural History Museum, London [statutory name: British Museum (Natural History)] as specimen BM 1990, 25 and polished section E. 1353.

Physical properties

Barstowite is colourless to white, with a white streak and an adamantine lustre. It is brittle with an imperfect prismatic cleavage and an uneven fracture. When cleavages and fractures are absent, the mineral is transparent. Very small (0.2–0.5 mm) subparallel intergrown crystals of barstowite are, superficially, not unlike cerussite (see Fig. 1) and form intergrowths with phosgenite and aggregates (<3 mm) which contain minor inclusions of galena and jamesonite.

The density, which was measured on six grains with a Berman Balance using ethylene dibromide, yielded the following results: 5.69, 6.10, 5.50, 5.59, 5.52, 5.83, average 5.71 g/cm^3. Two grains (2 and 6) were seen to have minute inclusions of galena and jamesonite while all the grains may have had air/water trapped in the interstices of the subparallel intergrown crystals.

A polished section was prepared with some difficulty as the mineral is soft and susceptible to plucking. After grinding on plate glass with 800 mesh silicon carbide, the specimen was taken directly to the 1 μm diamond polishing stage; a well-lubricated Hyprocel pellon lap was used and a good polish achieved rapidly. The mineral is easily scratched and it was decided to cease polishing at this stage. Barstowite has a VHN$_{100}$ of 111 with a range of 108–117 from five indentations, the shapes of which were perfect to slightly concave. The equivalent Moh's hardness is 3.

In reflected light, barstowite is moderately bireflectant from grey to dark grey with weak to moderate anisotropy. Internal reflections are abundant and, as a result, reflectance measurements on the most bireflectant grain could not be made. However, in one grain, an area was found over a cleavage plane where no obvious internal reflections were present and reflectance measure-

TABLE 1. Reflectance data and colour values for barstowite

λnm	R_1	R_2	$^{im}R_1$	$^{im}R_2$
400	14.2	14.8	3.54	3.84
420	14.0	14.65	3.35	3.62
440	13.85	14.4	3.20	3.50
460	13.7	14.1	3.09	3.37
470	13.5	14.0	3.02	3.31
480	13.4	13.9	2.99	3.26
500	13.25	13.7	2.90	3.17
520	13.1	13.5	2.84	3.11
540	12.9	13.4	2.78	3.04
546	12.9	13.35	2.76	3.02
560	12.8	13.2	2.73	2.99
580	12.7	13.1	2.69	2.95
589	12.65	13.1	2.67	2.92
600	12.6	13.0	2.66	2.91
620	12.5	12.9	2.63	2.88
640	12.5	12.9	2.62	2.86
650	12.4	12.8	2.60	2.85
660	12.4	12.8	2.59	2.83
680	12.3	12.75	2.57	2.82
700	12.3	12.7	2.56	2.80

COLOUR VALUES RELATIVE TO CIE ILLUMINANT *C*

	R_1	R_2	$^{im}R_1$	$^{im}R_2$
x	.303	.303	.297	.297
y	.309	.308	.301	.301
Y%	12.9	13.3	2.8	3.0
λ_d	477	476	475	475
P_e%	3.5	3.7	6.8	6.7

Table 2. Infrared absorption frequencies (cm^{-1}) of barstowite, phosgenite and cerussite from Fig.2.

BARSTOWITE	PHOSGENITE	CERUSSITE
3400	3437	3439
2924		
2855		2404
1768	1817	
1716	1710	1727
1619		
1438	1512	1430
1385		1395
1339	1344	
	1130	
1096		1101
1051	1062	1051
845	836	839
719	758	824
671	648	678
598		
467	469	474
394	311	302
268		242

ments in air and in oil were made using the procedures summarised in Criddle *et al.*, 1983, with an SiC standard (Zeiss no 472). The data are given in Table 1. Calculated refractive indices at 589.nm are (for R_1 and R_2 respectively) 2.10 and 2.12.

Infrared spectra

The infrared transmission spectrum of barstowite (Fig. 2) was recorded over the wavenumber range 4400 to 225 cm^{-1} using the KBr disk method, in a Philips PU9800 FTIR spectrophotometer. The spectra of phosgenite and cerussite are included in Fig. 2 for comparison and absorption frequencies are tabulated in Table 2. No absorptions were observed in the region 4400–4000 cm^{-1}. All spectra were baseline corrected to remove the effects of scatter at high wavenumbers characteristic of lead minerals in KBr disks.

The barstowite spectrum has twin peaks at 1438 and 1339 cm^{-1} typical of carbonates containing another anion, Cl in this case. Peaks at 3400 and 1619 cm^{-1} indicate the presence of water of crystallisation and are the basis for the assignment of hydrogen to H_2O rather than OH^- in the formula. A sharp peak at 1051 cm^{-1} in the barstowite spectrum is a feature of carbonates with the aragonite structure, as can be seen in the cerussite spectrum. It would appear at first sight that the barstowite spectrum shows all the cerussite absorptions and hence is contaminated, but when superimposed in an expanded plot, non-coincidence of the peaks is apparent.

The similarity of the barstowite and phosgenite spectra is striking and must reflect a corresponding similarity in molecular grouping within the two minerals.

Chemical composition

A combination of electron probe microanalysis (for Pb and Cl) and elemental analyser (for C and H) was used to determine the chemistry of barstowite. The data are summarised in Table 3. Oxygen was calculated by stoichiometry and, as

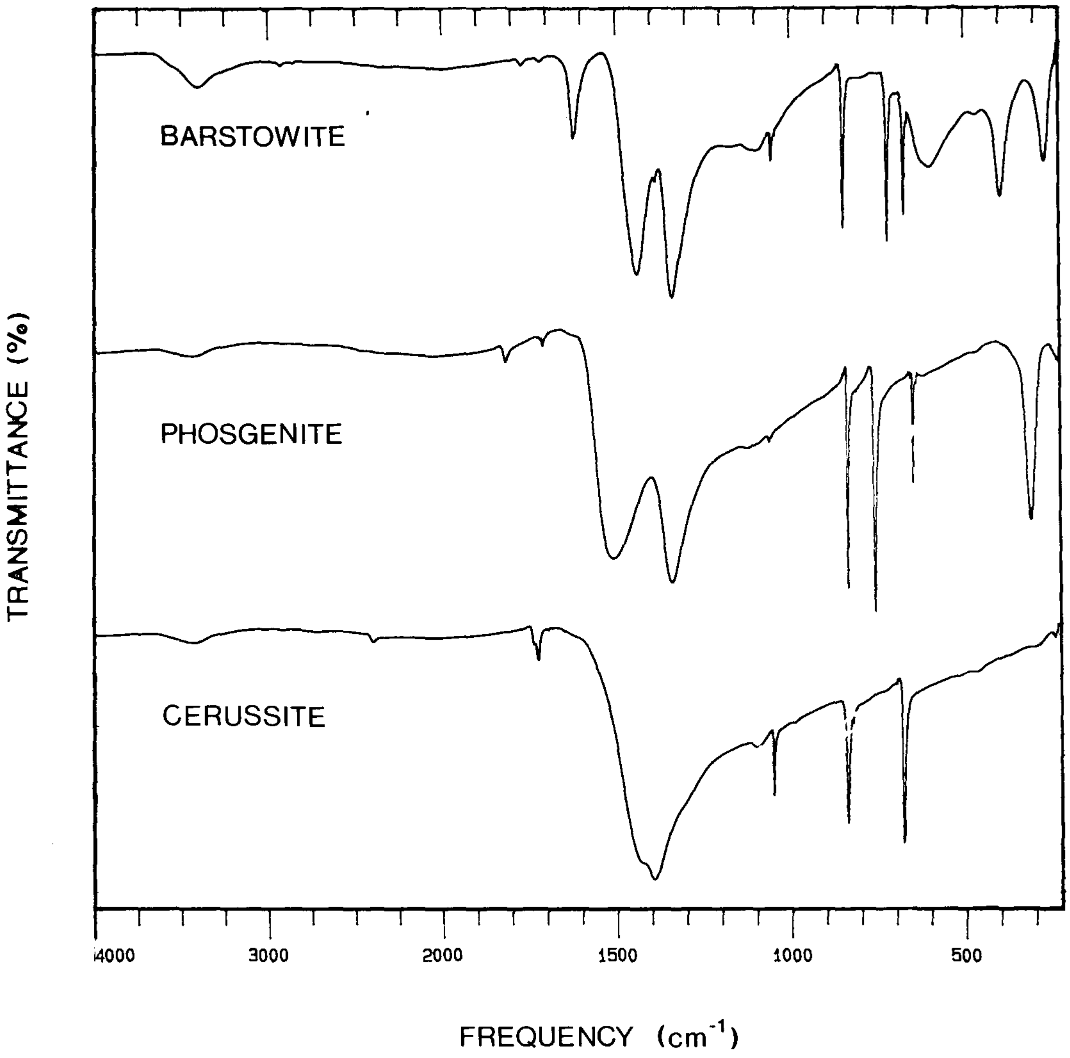

FIG. 2. Infrared absorption spectra of barstowite, phosgenite (BM 85166) and cerussite (BM 1926, 127).

noted, the infrared spectrum suggests that H_2O rather than OH is present. The loss of this H_2O and possibly other volatiles in the electron microprobe beam is believed to be the reason for the slightly high total of the combined analysis.

The empirical formula (based on 17 atoms) is $Pb_{4.02}Cl_{5.82}C_{1.03}H_{1.97}O_{4.16}$ or $Pb_{1.03}(CO_3)_{1.03}$ $.Pb_{2.99}[Cl_{5.82}(OH)_{0.16}]_{5.98}.0.90H_2O$ which gives the simplified formula $3PbCl_2.PbCO_3.H_2O$.

X-ray crystallography

All fragments investigated consisted of sub-parallel intergrown crystals, and it was possible to obtain meaningful results from Weissenberg photographs of two levels only. The unit cell parameters refined from the powder data (Table 4) show that barstowite is monoclinic with space group $P2_1$ or $P2_1/m$; *a* 4.218(2), *b* 9.180(2), *c* 16.673(4) Å, β 91.49(3)° and the cell volume is 645.38 Å^3. For Z = 2, the calculated density is 5.77 g/cm^3.

There is a powder pattern of an unnamed mineral in the JCPDS (25.1396) which is similar to that of barstowite as, also, is its chemistry (Melnikova, 1972). it is an unwritten convention in such circumstances to name the mineral after the earlier author but melnikovite has already

TABLE 3. Chemical composition of barstowite (in wt%)

	Pb	Cl	C	H	O	Total
1	-	-	1.12	0.18	-	-
2	75.82	18.45	-	-	-	-
3	75.33	18.60	-	-	-	-
4	75.26	18.96	-	-	-	-
5	75.47	18.67	1.12	0.18	6.03	101.46
6	74.03	19.00	1.07	0.18	5.72	100.00

1. C and H analysis by combustion using Perkin Elmer Mod.240 elemental analyzer.

2-4. Electron microprobe analyses with Cambridge Instruments Microscan IX, operated at 20kV with mendipite standard (BM 1923,709). Radiations measured, Pb Mα Cl Kα.

5. Average analysis with oxygen by stoichiometry.

6. Ideal formula $3PbCl_2.PbCO_3.H_2O$.

TABLE 4. Indexed X-ray powder diffraction pattern of barstowite FeKα radiation, Mn filter, camera diameter 114.6 mm.
Intensity *I/Io* is estimated.

$d_{meas.}$	I/I_0	$d_{calc.}$	hkl
8.33	1	8.334	002
8.03	1	8.041	011
6.17	2	6.170	012
5.55	1	5.556	003
4.76	2	4.753	013
4.59	1	4.590	020
4.42	1	4.425	021
4.16	5	4.167	004
4.02	10	4.021	022
3.79	3	3.794	014
3.72	1	3.724; 3.715	102; 111
3.54	2	3.539	$02\underline{3}$
3.52	2	3.515	$11\bar{2}$
3.45	1	3.451	$11\underline{2}$
3.40	1	3.402	$10\bar{3}$
3.313	2	3.317	103
3.085	1	3.085	024
3.045	3	3.042	121
2.923	2	2.926	$10\bar{4}$
2.853	1	2.854	$11\bar{4}$
2.779	2	2.778	$00\underline{6}$
2.734	1	2.733	$12\bar{3}$
2.679	2	2.689; 2.680	$12\underline{3}$; 033
2.652	2	2.649	$10\bar{5}$
2.513	1	2.513	$12\bar{4}$
2.477	3	2.477	130
2.464	3	2.467; 2.466	124; 034
2.377	6	2.381; 2.377	$00\underline{7}$; 026
2.345	1	2.348	$10\bar{6}$
2.296	8	2.295; 2.294; 2.293	040; $12\bar{5}$; 106
2.254	1	2.254; 2.250	035; 125
2.212	1	2.213	$04\underline{2}$
2.145	1	2.143	$13\bar{4}$
2.108	4	2.108	$20\underline{0}$
2.098	3	2.098; 2.097	$20\bar{1}$; $10\bar{7}$
2.084	1	2.085; 2.083	$20\underline{1}$; 008
2.057	2	2.057; 2.057; 2.055	$20\bar{2}$; 036; 210
2.030	3	2.032; 2.031	018; 202
2.011	2	2.010	044
1.952	1	1.954; 1.954	$20\underline{3}$; $14\underline{2}$
1.903	2	1.902; 1.901	$14\bar{3}$; $20\bar{4}$
1.890	1	1.890; 1.887; 1.887	045; $10\bar{8}$; 143
1.873	1	1.872	$12\underline{7}$
1.850	2	1.850; 1.849	$11\bar{8}$; 108
1.798	1	1.798	$22\underline{3}$
1.769	1	1.769; 1.769	$21\bar{5}$; 046
1.726	1	1.725	224
1.685	2	1.683; 1.683	150; $11\bar{9}$
1.623	2	1.622	146

entered the literature as a textural variety of pyrite.

Acknowledgements

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The synthesis and composition of georgeite and its reactions to form other secondary copper(II) carbonates

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Abstract

Comparison of the infrared spectra of georgeite and a phase which can be reproducibily synthesised in the laboratory shows that the mineral is an amorphous analogue of malachite, $Cu_2CO_3(OH)_2$. Synthetic studies also explain the chemical conditions under which georgeite may form, as well as those which can cause it to react to either malachite or chalconatronite. Parallels may be drawn between the laboratory observations and known mineral associations of georgeite.

KEYWORDS: georgeite, synthesis, copper, carbonates, infrared spectra.

Introduction

FEW secondary copper(II) carbonate minerals are known from the oxidised zones of cupriferous orebodies. The most frequently encountered are azurite, $Cu_3(CO_3)_2(OH)_2$, and malachite, $Cu_2CO_3(OH)_2$, and these species have been the subject of a considerable body of research by previous workers. Other carbonate minerals which are double or multiple salts are also known, but these are much rarer species (Palache *et al.*, 1951; Fleischer, 1987). Recently, another basic copper(II) carbonate, georgeite, with the stoichiometry $Cu_5(CO_3)_3(OH)_4.6H_2O$, was reported as occurring at the Carr Boyd Mine, Western Australia (Bridge *et al.*, 1979). This species could be thought to be the naturally occurring analogue of the synthetic compound $5CuO.3CO_2$ described by Pickering (1909). A second occurrence of georgeite from the Britannia Mine, North Wales, has been recently reported (Pollard *et al.*, 1989).

During the course of a study of certain secondary copper minerals, we have synthesised an X-ray-amorphous basic copper carbonate, whose infrared spectrum is the same as that of georgeite. We have consequently been able to establish that the stoichiometry of the mineral corresponds to that of malachite, $Cu_2CO_3(OH)_2$. Reaction of georgeite to give either malachite or the double salt chalconatronite, $Na_2Cu(CO_3)_2.3H_2O$, can be effected depending on the experimental conditions employed. These two minerals are associated with georgeite from the Carr Boyd Mine. Georgeite is probably analogous to a compound reported some time ago in the literature. Gröger (1900), in similar experiments to those reported by Pickering (1909), found a $CuO:CO_2$ ratio in an initially precipitated compound from aqueous solution to be equal to 2:1.

Revision of the formula of georgeite has been approved by the I.M.A.

Experimental

In a series of experiments, 0.8 g (47 mmol) of $CuCl_2.2H_2O$ was added to 100 cm^3 of a stirred solution containing Na_2CO_3 (5.3 g, 50 mmol) at 25 °C. A rapid reaction ensued, accompanied by the liberation of carbon dioxide gas, ultimately

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resulting in the formation of a blue precipitate. This solid was isolated at the pump on a glass sinter, washed with water, then with acetone, and dried *in vacuo* over silica gel at room temperature.

Continued stirring of the reaction mixture before isolation of the solid resulted in the transformation of the initial precipitate within a few hours. In another series of experiments, stirring of the solution was stopped immediately after the addition of copper(II) chloride was complete and the effervescence had subsided. The mixture was allowed to evaporate slowly at room temperature. Reactions occurring in the mixtures as they underwent evaporation were monitored by taking small samples of the reaction mixture at regular intervals. Isolation of any insoluble solid phases present was carried out using the same method as was employed for the initial blue precipitate (*vide supra*). In experiments when evaporation was allowed to continue to completion, the resulting mixture of sodium salts and chalconatronite was placed in a sinter and washed with water. The chalconatronite residue thus isolated was then rinsed with acetone and dried *in vacuo* over silica gel.

In order to ascertain whether chalconatronite dissolved congruently in solutions less concentrated than those from which it was isolated, small amounts of the pure mineral were stirred at 25 °C in water and in 0.1M aqueous sodium carbonate solution. In both cases breakdown of chalconatronite to CuO was seen to occur within 24 hours.

The dried synthetic copper(II) carbonates were identified and checked for purity by X-ray powder diffraction techniques, using a 114.6 mm diameter Debye-Scherrer camera and Cu-$K\alpha$ radiation. Measured *d*-spacings were then checked against the data in the JCPD powder file. Infrared spectra of the minerals studied were measured in KBr discs using a Perkin Elmer 783 spectrophotometer.

Results and discussion

The infrared spectra of the synthetic compounds along with those of georgeite from the Carr Boyd Mine and from the Britannia Mine, North Wales (Pollard *et al.*, 1989), are shown in Fig. 1. Comparison of the spectra of the natural georgeite with that of the blue synthetic compound obtained in this study shows that they are virtually identical. No trace of chalconatronite could be detected in the infrared spectra of any of the natural or synthetic georgeite samples examined. Bridge *et al.* (1979) noted, however, that it was difficult to obtain samples of georgeite from the Carr Boyd Mine free from contamination by admixed chalconatronite, $Na_2CuCO_3.3H_2O$, and allowance for the presence of the latter mineral was made in the original analysis of georgeite (subtraction of some 12 wt.% chalconatronite and normalization of the residuals). The results of analyses of synthetic georgeite prepared as outlined above are given in Table 1, and compared with the malachite formula. Georgeite is sky blue in colour. The apparent specific gravity varies from 2.4 to 2.8, but any accurate determination is prohibited by buoyancy effects associated with the very small particle size of the synthetic material. In the original description of the mineral (Bridge *et al.*, 1979), the density was given as 2.55.

There is no doubt that the synthetic material and georgeite correspond to the stoichiometry of malachite, $Cu_2CO_3(OH)_2$. It is not possible, using the new data for georgeite reported here, to prove conclusively whether georgeite is cryptocrystalline malachite or a separate amorphous phase of the same composition. However, it would seem that the mineral does meet the criteria for consideration as a separate mineral species in that it is not malachite, as judged by X-ray diffraction methods. On this basis, the following conclusions can be drawn.

When solutions of Cu^{2+} (aq) and $CO_3{}^{2-}$ (aq) are mixed under the conditions described, the initial precipitate is not malachite, but georgeite. If the mixture is stirred at 25 °C and the volume is kept constant, georgeite recrystallizes to malachite within 3 hours. If however the mixture is not stirred, the georgeite precipitate settles to the bottom of the flask and effectively isolates the solution in contact with it from the bulk of the solution. Under these circumstances, kinetic rather than thermodynamic factors lead to the formation of crystals of chalconatronite in the precipitate of fine-grained georgeite. Nevertheless, with time, if the solution volume remains constant, both the georgeite and the chalconatronite react to yield malachite as the only solid phase. This kinetic control of the reaction is echoed in the observations of Pickering (1907) who noted during the course of similar experiments that whether chalconatronite or malachite formed was 'determined to some extent by arbitrary conditions'.

A somewhat different sequence of reaction is observed if the reaction mixture is allowed to evaporate slowly at room temperature. Irrespective of whether or not the reaction mixtures are stirred, malachite forming as an intermediate in the former case, the solid phases react to give chalconatronite. Under these con-

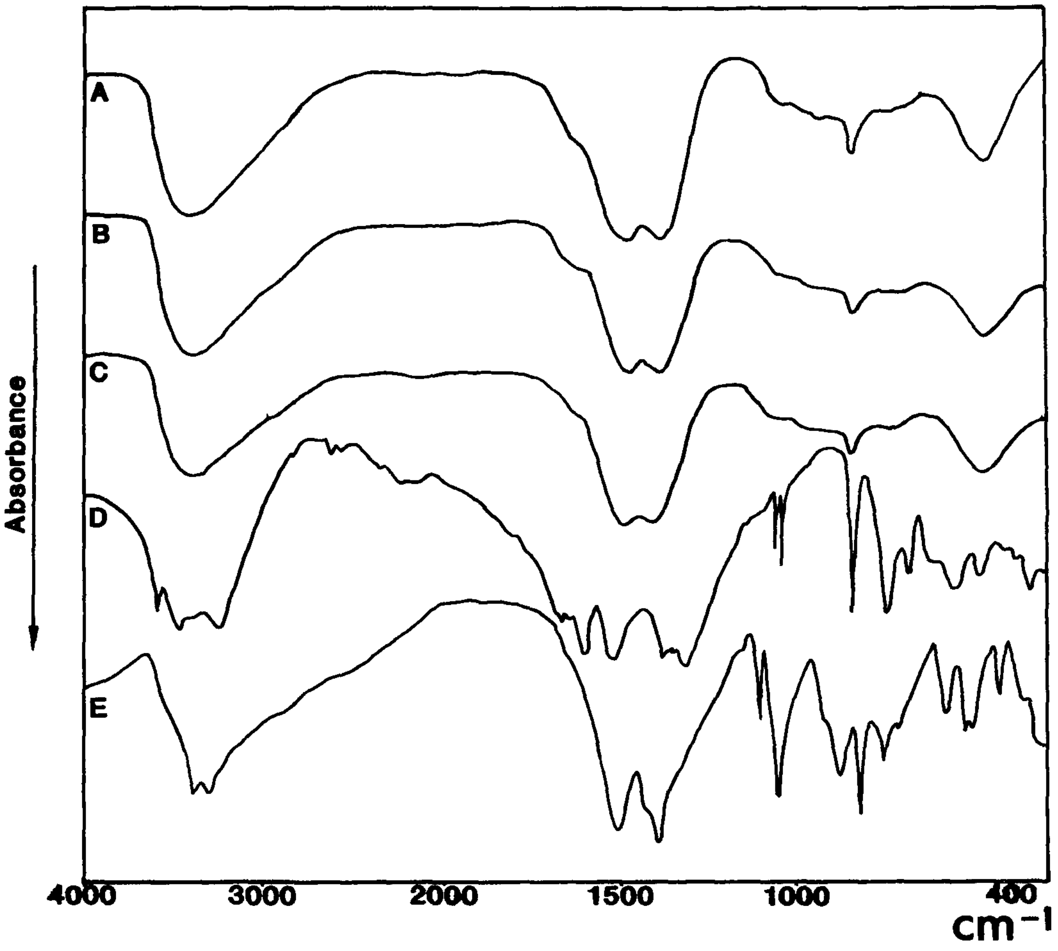

FIG. 1. Infrared spectra of: A, georgeite, Carr Boyd Mine (original sample in KBr disc used for infrared study by Bridge *et al.*, 1979); B, georgeite, Britannia Mine; C, synthetic georgeite, $Cu_2CO_3(OH)_2$; D, chalconatronite; E, malachite. The latter two samples are synthetic materials confirmed by X-ray powder diffraction methods.

ditions, chalconatronite is the thermodynamically stable phase (when carbonate concentrations reach an appropriately high level). Thus as the solution volumes decrease, the reaction of either georgeite to chalconatronite or georgeite to malachite, then to chalconatronite, is observed.

TABLE 1
Analytical results for synthetic georgeite.[a]

	1	2	3^b	4
CuO	72.3	71.0	71.0	71.9
CO_2	20.0	19.7	20.1	19.9
H_2O	7.7	9.3	9.5	8.2

[a] 1,2: synthetic georgeite; 3: georgeite, Carr Boyd Mine, sample supplied by J. Just; 4: calc. for $Cu_2CO_3(OH)_2$. [b] Sum = 100.6.

Earlier workers have addressed the question as to which aqueous complex copper(II) species was responsible for the precipitation of the double salt chalconatronite and for the deep blue colouration of solutions from which it crystallizes (Appleby and Lane, 1918; Pickering, 1907). Unfortunately, the high ionic strength of the solutions required to make chalconatronite thermodynamically stable introduces difficulties for any calculation of a stability constant for chalconatronite. We would simply wish to note that the results presented here are consistent with the view that chalconatronite is produced from solutions that contain significant concentrations of the deep blue bis(carbonato)-cuprate(II) ion, $[Cu(CO_3)_2]^{2-}$.

Depending on which of the above courses of reaction happens to reflect any particular natural conditions, various assemblages of the three carbonates georgeite, malachite and chalconatronite may be developed. Any assemblage would be preserved by desiccation of the reacting system following removal of solution by, say, capillary action (namely removal of excess carbonate ion in contact with solid phases). Georgeite from both known localities corresponds with different stages in the reaction sequences outlined above. In the Britannia Mine (Pollard *et al.*, 1989), georgeite is associated principally with malachite, which is present as small spherules of radiating crystals. Small amounts of iron(III) oxyhydroxides are also present in the specimens collected, and connellite crystals coat the masses of georgeite. In the Carr Boyd Mine all three copper(II) carbonate minerals are present (Bridge *et al.*, 1979), together with, amongst other species, trona.

Finally, we wish to point out that the best known examples of chalconatronite are as an alteration product of archaeological copper alloy objects (Frondel and Gettens, 1955), when the mineral occurs as a result of the recrystallization of malachite caused either by the extreme arid environment of the archaeological context or the post-excavation use of carbonate solutions to prevent subsequent formation of basic copper chlorides on the objects' surfaces (Horie and Vint, 1982). Both of these modes of formation of chalconatronite are also consistent with the phenomena outlined above.

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