

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 reproducibly synthesised in the laboratory shows that the mineral is an amorphous analogue of malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. 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, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, and malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$, 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 $\text{Cu}_5(\text{CO}_3)_3(\text{OH})_4 \cdot 6\text{H}_2\text{O}$, 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 $5\text{CuO} \cdot 3\text{CO}_2$ 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, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Reaction of georgeite to give either malachite or the double salt chalconatronite, $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$, 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 $\text{CuO}:\text{CO}_2$ 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 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 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 α 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, Na₂CuCO₃·3H₂O, 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, Cu₂CO₃(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 Cu²⁺ (aq) and CO₃²⁻ (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-

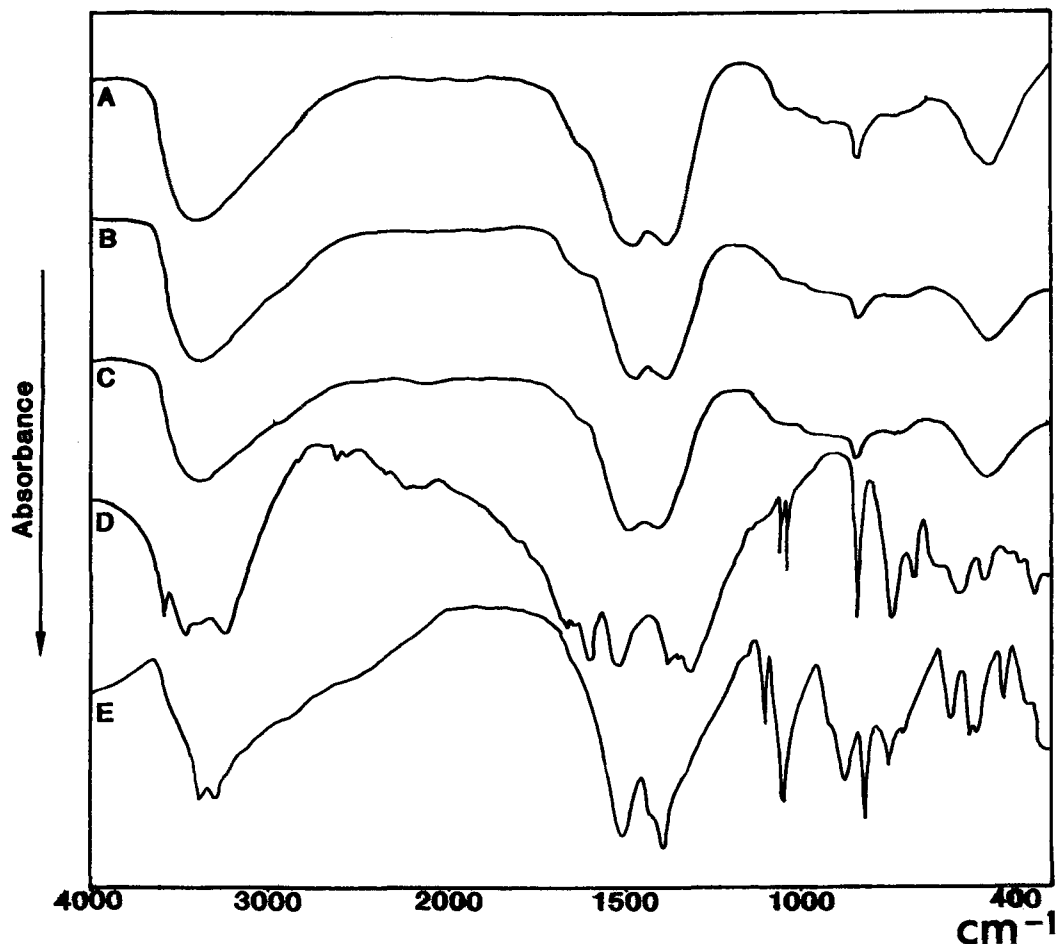


FIG. 1. Infrared spectra of: A, georgeite, Carr Boyd Mine (original sample in KBr disc used for infrared study by Bridge *et al.*, 1979); B, georgeite, Britannia Mine; C, synthetic georgeite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$; D, chalconatronite; E, malachite. The latter two samples are synthetic 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 I
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 ₂ O	7.7	9.3	9.5	8.2

^a1,2: synthetic georgeite; 3: georgeite, Carr Boyd Mine, sample supplied by J. Just; 4: calc. for $\text{Cu}_2\text{CO}_3(\text{OH})_2$. ^bSum = 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, $[\text{Cu}(\text{CO}_3)_2]^{2-}$.

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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References

- Appleby, M. P. and Lane K. W. (1918) *J. Chem. Soc.*, **113**, 609–22.
 Bridge, P. J., Just, J., and Hey, M. H. (1979) *Mineral. Mag.*, **43**, 97–8.
 Fleischer, M. (1987) *Glossary of Mineral Species*, 5th ed. Mineralogical Record Inc., Tucson.
 Frondel, C. and Gettens, R. J. (1955) *Science*, **122**, 75–6.
 Gröger, M. (1900) *Z. Anorg. Chem.*, **24**, 127–38.
 Horie, C. V. and Vint, J. A. (1982) *Studies in Conservation*, **27**, 185–6.
 Palache, C., Berman, H., and Frondel, C. (1951) *The System of Mineralogy*, 7th Edition. Wiley and Sons, New York, Vol. 2.
 Pickering, S. U. (1909) *J. Chem. Soc.*, **95**, 1409–29.
 Pollard, A. M., Thomas, R. G., Williams P. A., Bevins, R. A., and Turgoose, S. (1989) *J. Russell Soc.*, **2**, 23.

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