

THERMAL DECOMPOSITION OF THE BASIC COPPER CARBONATES MALACHITE AND AZURITE

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ABSTRACT

Thermogravimetry (TG) and evolved gas analysis (EGA) studies of malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and azurite, $2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, heated in helium carrier gas at $10^\circ \text{ min}^{-1}$ show that malachite decomposes in a single step at 380°C , in which water and CO_2 are lost simultaneously. By contrast, the two azurites investigated both decompose under these conditions in two approximately equal steps, losing one-half of their CO_2 and water content in each step. The product formed in the first stage of the decomposition is a mixture of tenorite (CuO) and material with X-ray characteristics similar to azurite, ruling out reaction sequences involving malachite or CuCO_3 . From structural considerations, a decomposition mechanism is proposed which is consistent with the observed intensity changes in the X-ray pattern of the azurite-like intermediate phase.

INTRODUCTION

The two most commonly occurring basic copper carbonate minerals are malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and azurite, $2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. When heated, both minerals lose water and CO_2 , forming cupric oxide, CuO . A previous study by Morgan [1] of the decomposition of malachite by combined DTA–EGA methods using evolved-gas detectors specific to water and CO_2 has suggested that both gaseous species are evolved simultaneously in an endothermic reaction which peaks at 403°C [1]. Morgan did not include azurite in his study.

In the only other reported thermal decomposition study, Seguin [2] reported that both malachite and azurite decompose in two steps; the first, at about 95°C , was attributed to water loss, and the second, at 375°C in malachite and 350°C in azurite, was attributed to CO_2 loss [2]. These conclusions were not tested by EGA experiments, and neither was the X-ray powder diffraction analysis of the intermediates and products deemed conclusive by Seguin because of disorder in the structures of these materials [2]. The decomposition reaction proposed by Seguin for malachite involves the initial formation of Cu_2CO_3 which eventually decomposes to form CuO ,

whereas azurite was thought to form a mixture of Cu_2CO_3 and CuCO_3 , which again decompose in air to CuO [2]. In inert atmospheres, the final product was said to be a mixture of CuO and Cu_2O [2].

The present study was undertaken to resolve the differences in the decomposition sequences of malachite as proposed by Morgan [1] and Seguin [2], and to apply EGA techniques to the decomposition of azurite. Complementary information about the reactions in both minerals was sought by X-ray powder diffraction and infrared spectroscopy.

EXPERIMENTAL

Materials

The malachite used in this study was a sample from S. Australia, being part of an unnumbered specimen from the New Zealand Geological Survey Mineral Collection. The green crystals were separated from the ground mass by hand picking, and were shown by X-ray powder diffraction to be well-crystallized single-phase malachite.

Two azurite samples were studied; the first, from Broken Hill, N.S.W., Australia, was from specimen 11039 of the New Zealand Geological Survey mineral collection. The second azurite sample was from Kawau Island, New Zealand. X-Ray powder diffraction of the bright-blue crystals handpicked from these samples showed both azurites to be well-crystallized phases, the Broken Hill sample also containing a small amount of quartz impurity (< 10%).

Methods

Thermogravimetry was carried out in a Stanton TG-770 thermobalance connected to an Extranuclear quadrupole mass spectrometer. The samples were heated at $10^\circ\text{C min}^{-1}$ in He carrier gas (0.04 l min^{-1}). After various stages of reaction, the products were examined by X-ray powder diffractometry and infrared spectroscopy, the latter in pressed KBr discs using a Perkin-Elmer 580 spectrophotometer.

RESULTS AND DISCUSSION

Malachite

The thermal analysis traces for malachite are shown in Fig. 1, which indicates that the decomposition occurs in a single step, in which water and CO_2 are lost simultaneously at 380°C , as estimated from the DTG and EGA

peak temperatures. This result confirms the previous finding of Morgan [1] rather than that of Seguin, and, further, casts doubt on the validity of the latter's kinetic study and the mechanistic conclusions drawn from it [2]. The total weight loss measured here (28.6%) is in good agreement with the theoretical figure of 28.0%, composed of 19.9% CO_2 and 8.1% water. Although the response characteristics of the mass spectrometer for CO_2 and water are not quantitatively identical, the areas of the water and CO_2 peaks are in approximate agreement with the theoretical weight ratio. The complete mass spectrum of the evolved-gas atmosphere at 380°C does not indicate the presence of any species other than the cracking fractions of water and CO_2 . X-Ray powder diffraction of the product of decomposition shows it to be exclusively tenorite, CuO .

Azurite

The thermal analysis traces for the New Zealand and Australian azurites are shown in Figs. 2 and 3, respectively, which indicate that both azurites

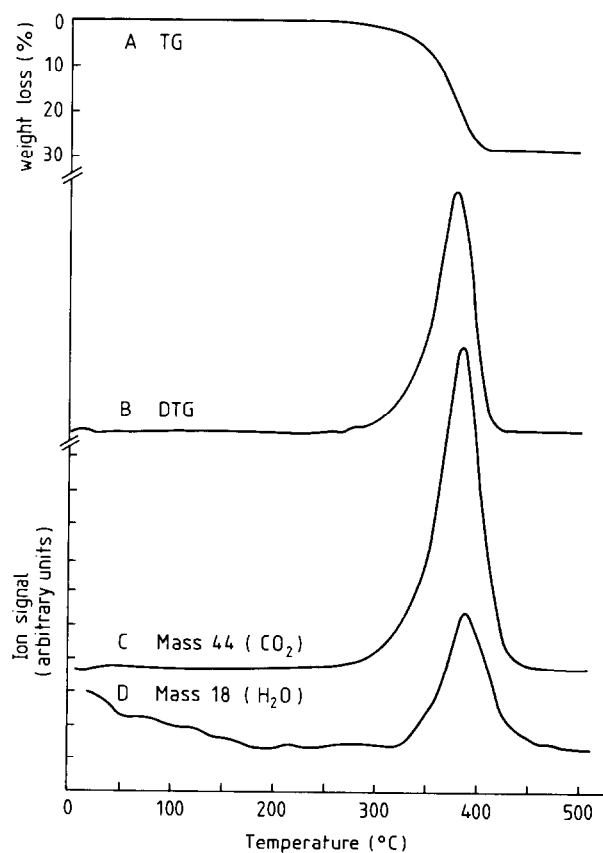


Fig. 1. Thermal analysis curves for malachite, Australia. Heating rate, 10°min^{-1} ; carrier gas, He (0.04 l min^{-1}). A, TG curve; B, DTG curve; C, EGA curve [mass 44 (CO_2)]; D, EGA curve [mass 18 (water)].

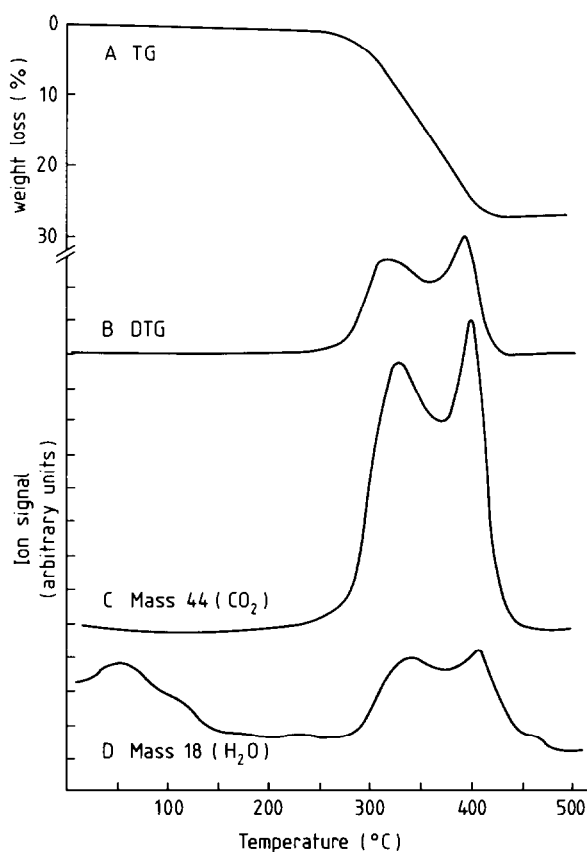


Fig. 2. Thermal analysis curves for azurite, Kawau Island, NZ. Heating rate, $10^{\circ} \text{ min}^{-1}$; carrier gas, He (0.04 l min^{-1}). A, TG curve; B, DTG curve; C, EGA curve [mass 44(CO_2)]; D, EGA curve [mass 18 (water)].

lose weight in two steps, with peaks at $320\text{--}335^{\circ}\text{C}$ and $390\text{--}395^{\circ}\text{C}$. The weight losses in each step are approximately equal (15.6% and 12.1% for the New Zealand azurite and 16.6% and 13.0% for the Australian sample); these weights could only be roughly determined because of the overlapping nature of the two reactions. The total weight-losses observed for the New Zealand and Australian azurites (27.7% and 29.6%, respectively) are in reasonable agreement with the theoretical value of 30.7%, of which 25.5% results from CO_2 loss and 5.2% from water loss.

However, the most interesting result is the observation that both decomposition steps involve the loss of both water and CO_2 (Figs. 2 and 3); furthermore, an estimate of the relative areas under the overlapping water and CO_2 peaks, made on the assumption that the peaks are symmetrical, indicates that very nearly equal amounts of water and CO_2 are evolved in the two decomposition steps. The assumption of symmetric peaks is not strictly valid, since in all these EGA peaks, the rise is more gradual than the decay,

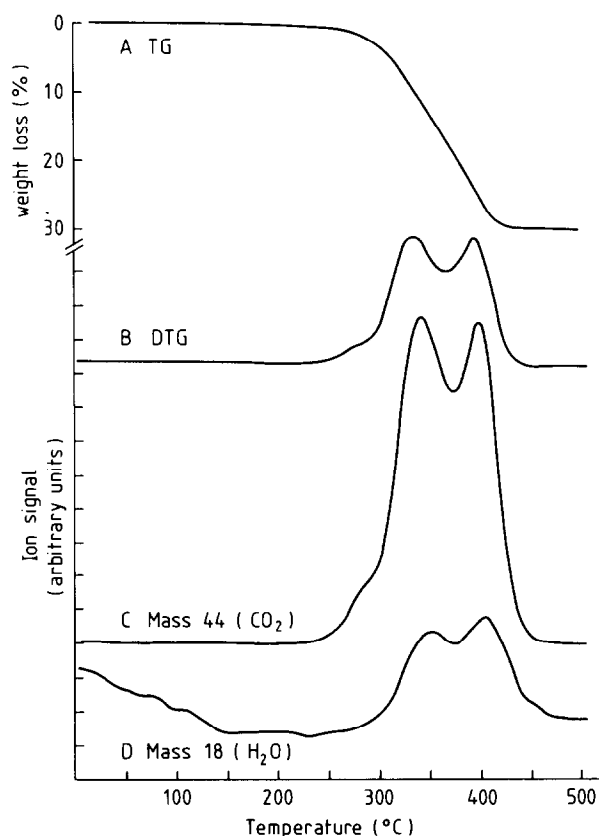
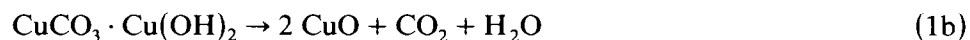
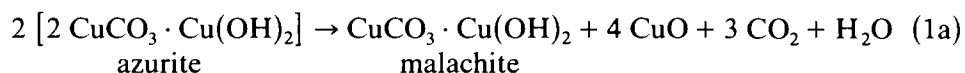


Fig. 3. Thermal analysis curves for azurite, Broken Hill, Australia. A, TG curve; B, DTG curve; C, EGA curve [mass 44 (CO_2)]; D, EGA curve [mass 18 (H_2O)].

leading to the lower-temperature peak area being overestimated and the higher-temperature peak being underestimated. Such an effect was in fact found in the present peak area estimates. The energy difference between the first and second stages of the decomposition is not great, the two stages being much more poorly resolved in other flowing atmospheres such as air or oxygen-free nitrogen, and almost unresolved in static air, except at very slow heating rates.

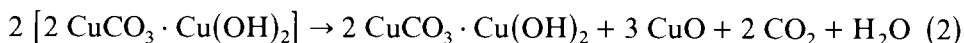
Two possible reaction schemes can be written for a two-step decomposition sequence in azurite. The first involves the formation of malachite as an intermediate



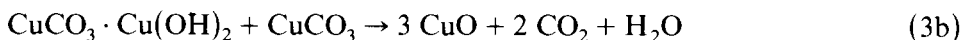
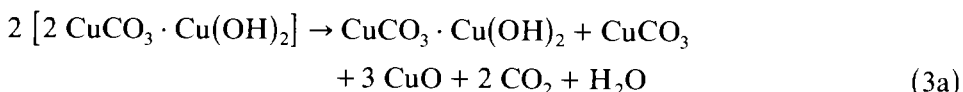
The theoretical weight losses for reaction (1a) are 19.1% CO_2 and 2.6% water, while reaction (1b) corresponds to a loss of 6.4% CO_2 and 2.6% water. Thus,

the observed results are not consistent with a reaction involving a malachite intermediate.

The second possible reaction scheme involves the initial decomposition of one-half of the azurite molecule



In the second stage, the other half of the azurite molecule would decompose by the same equation. Both reaction stages would result in the loss of 12.8% CO_2 and 2.6% H_2O , thus satisfying the requirements of the experimental EGA results. A similar weight-loss result would, however, also be achieved if the formation of malachite was accompanied by the appearance of undecomposed CuCO_3 , which then decomposed in the second stage, simultaneously with the malachite decomposition



In order to differentiate between reactions (2) and (3), the decomposition was carried out in a thermobalance and stopped immediately after the first stage, but before the second stage, by switching off the furnace, which, being water-cooled, responds extremely rapidly. The partly decomposed material was examined by X-ray powder diffraction and infrared spectroscopy. No indication of either malachite or CuCO_3 was found in the partly-decomposed samples, which contained only CuO and a material similar to azurite, thus ruling out reaction (3) as a possibility. Although similar to azurite, the X-ray trace of the intermediate indicated a number of intensity changes in the major reflections. Its infrared spectrum was substantially similar to that of the unreacted material, plus additional CuO bands (Fig. 4). The minor changes in the spectrum of the intermediate material include broadening in the hydroxyl stretching region ($3000\text{--}4000 \text{ cm}^{-1}$), and the appearance of a broad new band at 1625 cm^{-1} (Fig. 4B) indicating the presence of molecular water in considerably greater concentration than in the unreacted mineral. The appearance of a new band at 1030 cm^{-1} corresponds to a hydroxyl out-of-plane bending mode which occurs only weakly in unheated azurite [3], and is not seen at all in the present unreacted azurites. The only other spectral difference noted in the partly-reacted material is the loss of one of the carbonate vibrations at 745 cm^{-1} (Fig. 4B). Thus, the phase resulting from the first decomposition step is very similar to the unreacted mineral, with some minor differences attributable to the loss of some hydroxyl water and CO_2 .

A detailed examination of the X-ray trace of the partially-decomposed material was undertaken, making use of the minor amount of quartz impurity present in the Australian azurite as an angular calibration standard. The

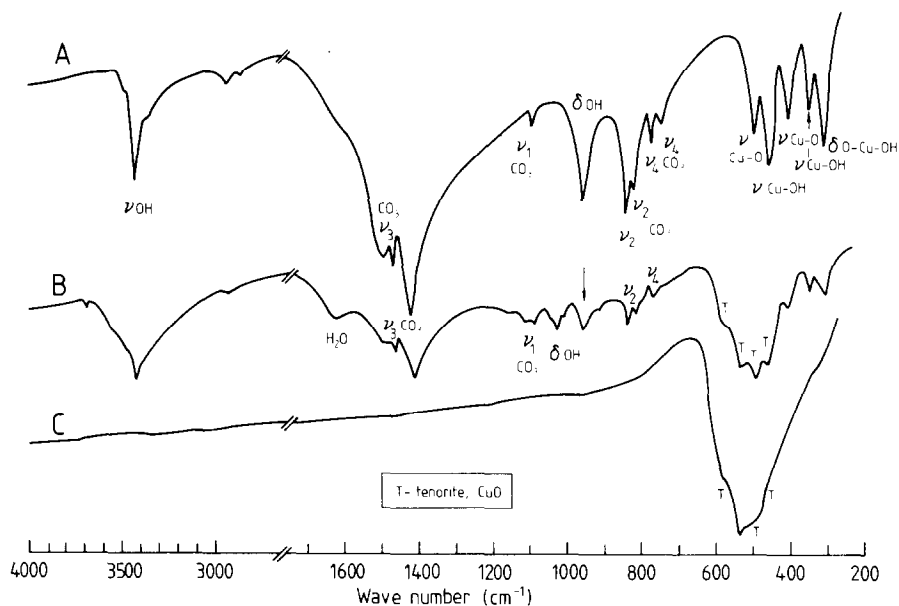


Fig. 4. Infrared spectra of unheated and heated azurite, Broken Hill, Australia. A, Unheated; B, partially decomposed in He at 330°C; C, fully decomposed in He at 550°C.

measured positions of a number of the major reflections were processed by the computer program of Evans et al. [4], which computes the d -spacings for all allowed reflections based on the known cell parameters of the material, and progressively changes the cell parameters until the measured d -spacings agree with the calculated spacings to within a specified tolerance. Substituting the known cell parameters of monoclinic azurite [5], the parameters of the Australian azurite, both unheated and partly decomposed were thus calculated (Table 1).

Table 1 indicates that despite the loss of 50% of the carbonate and hydroxyl groups, the cell dimensions are not very much affected by this

TABLE 1

Monoclinic cell parameters of azurite, Broken Hill, N.S.W., both unheated and partially decomposed at 330°C (cell parameters from ref. 5 included for comparison)

Parameter	Azurite (ref. 5)	Azurite, Broken Hill	Azurite, heated to 330°C in He
a (Å)	5.008	5.012	5.037
b (Å)	5.844	5.839	5.799
c (Å)	10.336	10.339	10.221
β (°)	92.45	92.24	92.20
cell volume (Å ³)	302.2	302.3	298.3

decomposition, the largest change being in the *c*-axis which contracts by about 1%. However, the changes observed in the intensities of the various reflections of the partly-decomposed material provide useful information about the possible structure of the intermediate material. In both azurites, the 002 and 011 reflections are weakened by 30–40% by heating. Most of the other reflections are intensified, relative to the unheated material, some by up to 100%. To provide a valid comparison, the peak intensities were scaled to a common factor. Both the Australian and New Zealand azurites showed similar intensity changes on heating, with some minor differences. However, these small differences were not unexpected, since the X-ray intensities in the unheated materials were not identical with each other, or with the most recent tabulated powder pattern [5]. According to the most recent crystal structure determination [6], the copper atoms in azurite are in square-planar configuration, each coordinated to two carbonate oxygens and two hydroxyls (Fig. 5).

One-third of the copper atoms (marked Cu1) are in special lattice posi-

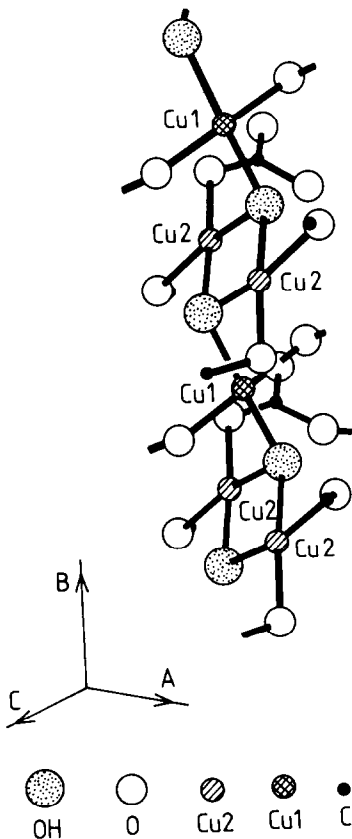


Fig. 5. Computer-generated perspective drawing of part of the azurite structure, viewed along the *c*-axis, showing details of the square-planar coordination of Cu1 and Cu2 atoms.

tions and are surrounded by carbonates and hydroxyls in the *trans* configuration, whereas the remaining copper atoms (marked Cu2) are in general positions with site symmetry C_1 , the ligands being in the *cis* configuration. The copper atoms are linked by the ligands in such a way that each hydroxyl group is shared by three copper atoms, whereas each carbonate oxygen is bonded to one copper atom. The bond lengths around each copper are not of equal length; one hydroxyl and one carbonate bond associated with each copper is significantly longer (and therefore weaker) than the others.

A close inspection of the atom linkages in the azurite structure reveals the existence of two identical "sets" of copper atoms, each set containing two Cu2 atoms in general positions and one Cu1 atom in a special position. The carbonate and hydroxyl groups associated with each "set" of copper atoms are specific to that set, with the exception of one carbonate group, which links that set to the other set. If the decomposition is assumed to initiate with the rupture of one of the weaker bonds in one particular set (say a Cu-OH bond), this will trigger the rupture of the next weakest bond in the same set (a Cu-OCO₂ bond). Thus the decomposition would progress alternately through hydroxyls and carbonates of the same set, until the last carbonate, which links that set to the next. Such a mechanism would lead to changes in the positions only of atoms related by centre of symmetry and not of atoms related by glide-plane, and is thus consistent with the observed fact that intensity changes accompany the reaction, but no new X-ray reflections appear.

Upon the rupture of the final carbonate bond of the first "set" of atoms, exactly one-half of the water and carbonate will have been evolved, with the formation of a coherent copper oxide (tenorite) network within that set. The retention of tenorite in the partly-decomposed lattice is reasonable, since the copper atoms in this phase are also square-planar, with Cu-O bond lengths of about 1.88 and 1.96 Å [7], very similar to the distances in azurite. Thus, the accommodation of CuO in the lattice should be possible with the minimum disruption, again consistent with experimental observation.

The rupture of the final carbonate bond of the first "set" will initiate the decomposition of the second "set" of atoms, but it is not immediately obvious why the process should pause briefly at this point, as shown by the inflexions in the thermal analysis curves; depending on the precise sequence in which the atoms of the first "set" decompose, the first bond to be ruptured in the second "set" could be one of the stronger bonds, or alternatively some steric factor may be operating. To further investigate the possible sequence of events within the first "set", the structural data for azurite [6] were substituted into a computer program which calculates the intensities of all possible reflections, and the effect of removing specific ligands was thus calculated. The intensity changes computed on the basis of the alternate removal of carbonate and hydroxyl from one "set" of copper atoms are consistent with most of the observed intensity changes, but the

calculation was unable to distinguish details of the sequence in which the ligands decompose. Thus, although unambiguous proof of the proposed mechanism is not available by this means, this mechanism satisfactorily accounts for the experimental observations.

CONCLUSIONS

Malachite thermally decomposes to CuO in a single step, with simultaneous loss both of CO₂ and water. By contrast, azurite decomposes in two stages which can be resolved under appropriate reaction conditions. Approximately one-half of the CO₂ and water is evolved in each step.

X-Ray diffraction and infrared spectroscopy shows that the material formed in the first stage of the decomposition has similar characteristics to a mixture of CuO and an azurite with altered X-ray reflection intensities. From structural considerations, this result could be explained by the alternate loss of hydroxyl and carbonate groups from one "set" of copper atoms which represent one-half of the total copper in the structure. The reaction is initiated by the rupture of one of the weakest bonds in the set, and the final stage of decomposition of the first set initiates the decomposition of the second set, via a common carbonate group. The resulting CuO remains in situ in the azurite lattice. No evidence was found for the suggestion of Seguin [2] that under inert atmospheres, Cu₂CO₃ is formed, which eventually decomposes to a mixture of CuO and Cu₂O.

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