STUDIES OF BASIC COPPER AND ZINC CARBONATES: I—SYNTHETIC ZINC CARBONATES AND THEIR RELATIONSHIP TO HYDROZINCITE

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ABSTRACT

Hydrozincite, a second naturally occurring basic zinc carbonate, and five synthetic zinc carbonates were studied by chemical, thermogravimetric, differential thermal, *x*-ray powder, and infrared techniques. Hydrozincite has the formula $Zn_5(CO_3)_2(OH)_6$; the second natural and four of the synthetic zinc carbonates correspond to $Zn_5(CO_3)_2(OH)_6.nH_2O$ and form a group having their main endothermic peak at 267 ± 12°C. and termination, forming ZnO, at 300 ± 10°. Hydrozincite has its endothermic peak at 334° and termination at 380°. From heating and *x*-ray powder studies, it is concluded that the nH_2O consists of absorbed water.

Infrared curves of hydrozincite show three absorption maxima in the region of bound OH whereas a single absorption band is present in the remaining zinc carbonates. The latter carbonates, both natural and synthetic, are non-stoichiometric and, with one exception, possible dimorphous with hydrozincite.

INTRODUCTION

In the field of inorganic chemistry much has been written concerning the precipitation and composition of synthetic basic zinc carbonates. Comprehensive compilations such as those of Mellor (1923) and Gmelin (1956) list large numbers of such compounds which have been prepared, though in most cases systematic examination using modern techniques to establish the homogeneity of the synthetic preparations is lacking. Chemical analyses of such compounds in many cases do not disclose the presence of mixtures, and optical verification of homogeneity is made difficult by a generally minute grain size. Moreover, the proportions of adsorbed and structurally bound water or hydroxyl in these carbonates are not known, and because of this, it is likely that in many cases erroneous formulae have been derived. Thus Mikusch (1908) attempted to alleviate the variety and seeming complexity of the compounds by proposing that $5ZnO.2CO_2.4H_2O$ is the only basic carbonate existing as a stable chemical individual. Mellor (1923) aptly concludes that "Our knowledge of the basic zinc carbonates is imperfect and fragmentary".

The naturally occurring hydroxyl-bearing zinc and copper carbonates are represented by the following five minerals accorded species status:

hydrozincite	$Zn_5(CO_3)_2(OH)_6$
aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$
malachite	$Cu_2(CO_3)(OH)_2$
rosasite	$(Cu,Zn)_2(CO_3)(OH)_2$
azurite	$Cu_3(CO_3)_2(OH)_2$

Subsequent papers of this series will deal with aurichalcite, rosasite, and further mineralogical studies of hydrozincite. Topics will include an x-ray study of aurichalcite, a method of determining the mineral's Cu/Zn ratio, and an investigation of the validity of rosasite retaining species rank. The present paper is concerned chiefly with the composition of hydrozincite and associated compounds as determined on natural and synthetic materials.

HYDROZINCITE

Hydrozincite is a carbonate-hydroxide of zinc which is reported in Palache *et al.* (1951) to have the composition $Zn_5(OH)_6(CO_3)_2$. Many analyses diverge considerably from this composition and, as pointed out by the above authors, the correct structural formulation is uncertain. The present writer's interest in this particular subject began when a zinc carbonate mineral submitted to this laboratory by A. Y. Smith of the Geological Survey of Canada was identified as $5ZnO.2CO_2.4H_2O$. The formula, which could also be written as $Zn_5(OH)_6(CO_3)_2.H_2O$, thus agrees with that of hydrozincite except for one molecule of water. The x-ray powder patterns of hydrozincite and the hydrated mineral are also somewhat similar. Subsequent preliminary work on both natural and synthetic basic zinc carbonates showed that although composition may vary considerably, a particular group of compounds retain the aforementioned similarity to the hydrozincite x-ray powder pattern and the group could be crystallographically related to this mineral. It was also found, however, that none of the synthetic materials give x-ray powder patterns which precisely duplicate those obtained from natural hydrozincites. Secondly, the widely divergent analyses and the variation in optical properties reported for natural material described as being hydrozincite suggests that more than one basic zinc carbonate has been grouped under this name. A detailed study was therefore undertaken in the hope of clarifying the following:

(1) the composition of hydrozincite and its correct formula form.
(2) the relationship of naturally-occurring $5ZnO.2CO_2.4H_2O$ to hydrozincite with the view of establishing whether the former is a new mineral.

(3) the relationship of the synthetic zinc carbonates to hydrozincite and the nature of excess (beyond the formula requirements of hydrozincite) CO_2 and H_2O present in the synthetic material.

With these points in mind, attention has been focussed on the following compounds.

1. Hydrozincite $5ZnO.2CO_2.3H_2O$

The material studied is from Constantine, Algeria. The 1 × 2 × 2½ specimen consists of megascopically massive to minutely fibrous bands about ¼ inch thick. Some bands strongly fluoresce pale blue in ultraviolet light, others do not; the material is, however, otherwise identical. *X*-ray powder patterns were also taken of material from Dundas, Tasmania (powdery material); Aurora, Missouri (powdery); Kamagai, Etchu Province, Japan (massive); Union County, Tenn. (powdery); Mifflin, Wisc. (powdery); Goodsprings, Nevada (crystals from the Geological Survey collection and crystals received from Clifford Frondel); Durango, Mexico (crystals); Dunham Tp., Quebec (powdery). Except for a variation in the intensity of a line at 1.55Å, all the above specimens give identical *x*-ray patterns.

2. $5ZnO.2CO_2.4H_2O$ (natural)

As mentioned previously, this mineral corresponds to hydrozincite with an additional molecule of water and the formula could therefore be written as $Zn_5(CO_3)_2(OH)_6.H_2O$. The above titular formula is, however, commonly cited in published works and is the stable basic carbonate proposed by Mikusch.

The natural mineral was first found as small, megascopically massive encrustations on the walls and roof of the abandoned Dorchester Copper Mine, Westmorland County, New Brunswick. Subsequent identifications were made on material from the Hector-Calumet mine, Galena Hill, Yukon, and on several specimens collected near the adits of the Lucky Jim mine at Zincton in the Slocan area of British Columbia.

3. $5ZnO.2CO_2.4H_2O$ (synthetic)

(a) Fluffy white powder corresponding to the above composition was precipitated by gassing CO_2 into a water slurry of zinc oxide. Chemical analyses of the powder are in good agreement with the formula requirements.

(b) Baker's C.P. zinc carbonate (sample No. 5 below) was added to a beaker of tap water and the contents heated in an oven at 40° C. for one week. The resulting product gives *x*-ray patterns identical to those of natural $5ZnO.2CO_2.4H_2O$.

4. Corrosion product of metallic zinc

Numerous basic zinc carbonates formed by the corrosion of metallic zinc in water have been reported. For example, Taboury & Gray (1937) determined the presence of $3ZnO.CO_2.2H_2O$, and $4ZnO.CO_2.3H_2O$. Anderson & Fuller (1939) reported $4ZnO.CO_2.4H_2O$ and Morral (1940) reports $2ZnCO_3.3Zn(OH)_2$ = hydrozincite. Zinc carbonate corresponding to the composition of hydrozincite is also described by Cloutier *et al.* (1936) as a precipitate from alkaline carbonate solutions.

Experimental studies carried out in this laboratory showed that basic zinc carbonates corresponding to many different formulas can indeed be formed by corrosion of metallic zinc in water. Analyses of several precipitates gave CO_2 and H_2O contents ranging from 6 to 14 per cent and 12 to 18 per cent respectively. The corrosion products formed depend in large measure on temperature, the variables related to amount and rate of water flow, the presence of additional compounds even though relatively insoluble, immersion time, and length of exposure to air. The particular compound selected for the present study was formed by corroding metallic zinc in a beaker of water for several months and allowing the resulting precipitate to dry at room temperature for an equal length of time. The homogeneity of the sample was verified by *x*-ray powder patterns. These proved to be identical to natural $5ZnO.2CO_2.4H_2O$ and synthetic material 3(b).

5. $10ZnO.5CO_2.8H_2O$ (C.P.-old)

Material corresponding to this formula was obtained from a cork-stoppered bottle of Baker's "Zinc Carbonate, C.P.". The material is known to have been in storage for at least thirty years. This same compound was also formed by bubbling CO_2 for several hours into a water and ice slurry of $5ZnO.2CO_2.4H_2O$.

6. "Baker Analysed" Zinc Carbonate

The analytical ZnO content of commercial basic zinc carbonates is somewhat variable. The above newly stocked material is reported to contain 74.5 per cent ZnO. Merck brand basic zinc carbonate examined by Huttig *et al.* (1939) is reported to be $5ZnO.2CO_2.4H_2O$ (theoretical ZnO = 71.8 per cent). The *x*-ray powder pattern obtained from our Baker material is very similar to the natural and synthetic compounds in No. 2, 3(b), and 4 above.

CHEMICAL ANALYSES

Chemical analyses of the basic zinc carbonates are given in Table 1. The CO_2 and H_2O for each recorded analysis were determined on a 100–200 mg. sample. The ZnO contents are by difference from 100 per cent. The values reported for sample 3(a) are averages obtained from six H_2O and three CO_2 determinations.

TABLE 1. CHEMICAL ANALYSES OF BASIC ZINC CARBONATES
Sample numbers correspond to those previously given in the text.

	No. 1			No. 2			
	Analytical	Theoretical		Analytical			Theoretical
ZnO	73.57	74.12	ZnO	72.70	71.97	72.27	71.77
CO_2	16.05	16.03	CO_2	14.50	14.73	14.49	15.52
H_2O	10.38	9.85	H_2O	12.80	13.30	13.24	12.70

	No. 3(a)	3(b)		No. 4	No. 5		No. 6	
ZnO	72.07	72.48	72.47	73.44	69.76	70.46	76.13	75.79
CO_2	15.01	16.62	16.57	12.87	18.14	17.84	13.22	13.61
H_2O	12.92	10.90	10.96	13.69	12.10	11.70	10.65	10.60

Analyst: S. Courville.

The analyses of hydrozincite (No. 1) and the Dorchester type of mineral (No. 2) are in good agreement with the theoretical formulae. As will be demonstrated below, synthetic compounds 3(a), 3(b), 4, and 6 also belong to the Dorchester type of compound even though the analytically determined values diverge from the theoretical requirements. Examples of such divergence are the low H_2O values for 3(b) and 6, and the low CO_2 values obtained from 4 and 6. Sample 5, it will be shown, is not related to the Dorchester group of compounds.

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSES

Differential thermal and thermogravimetric analyses of the zinc carbonates were kindly carried out by R. H. Lake of the Mines Branch. All the samples were undiluted and run in air at a heating rate of 12° C. per minute. For the thermogravimetric analyses the heating rate was 385 ± 5° C. per hour.

1. Hydrozincite, $5ZnO.2CO_2.3H_2O$

The specimen examined is analyzed material (Table 1, No. 1) from Constantine, Algeria. The D.T.A. (differential thermal analysis) curve is shown at the top of figure 2. Hydroxyl and CO_2 are given off in one endothermal break beginning at approximately 285°, reaching a peak at 334°, and ending at approximately 380°. The decomposition product is ZnO. The T.G. Diagram (Fig. 1, top) also shows a corresponding single step and a weight loss of 25.5 per cent. The theoretical weight loss of CO_2 and H_2O is 25.9 per cent and the loss according to the chemical analysis 26.4 per cent.

2. Natural $5ZnO.2CO_2.4H_2O$

The specimen is from the Dorchester Copper Mine, New Brunswick. The loss begins at about 70° with a small endothermal break reaching its peak at 130° (Fig. 2, second from top). From D.T. and T.G. analyses given below, it is known that this small break indicates a weight loss approximating that of one molecule of water. The remainder of the CO_2 and H_2O is lost in a large endothermic break which begins at about 190°, reaches a peak at 279°, and terminates at about 320°. The final decomposition product is ZnO. Insufficient material was available for T.G.A.

3. Synthetic $5ZnO.2CO_2.4H_2O$

For sample 3(a), the D.T. curve (Fig. 2, third from top) is similar to that obtained from the Dorchester mineral. The small endothermic break with its peak at 105° and the first step in the T.G. curve correspond to a weight loss approximating that of one molecule of water. The measured weight loss to 177° is 3.5 per cent and the theoretical loss of $1H_2O$ is 3.02 per cent. Nearly all the remaining CO_2 and H_2O is given off in a large endothermal break with its peak at 267° and termination at

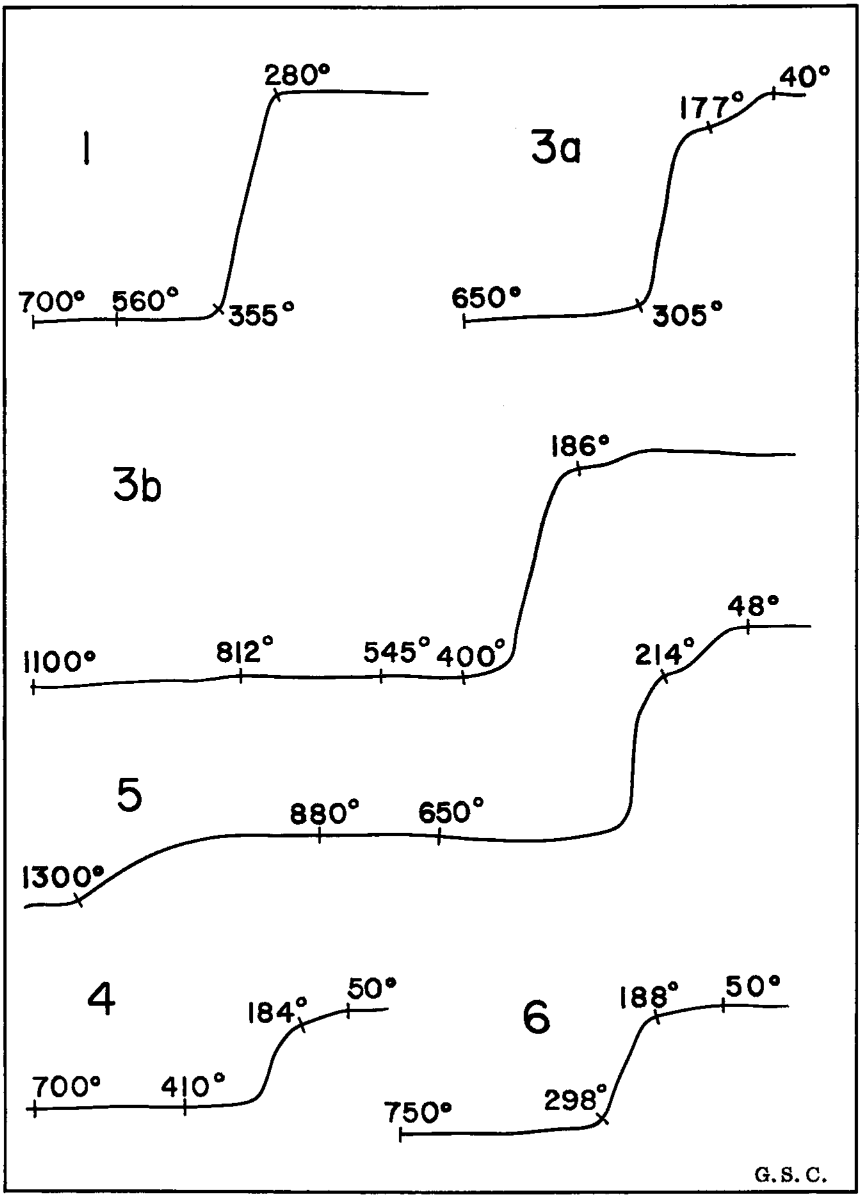

FIG. 1. Thermogravimetric curves for basic zinc carbonates. Sample numbers correspond to those given in the text. Except for samples 1 and 5, decomposition to ZnO is reached at 300 ± 10° C.

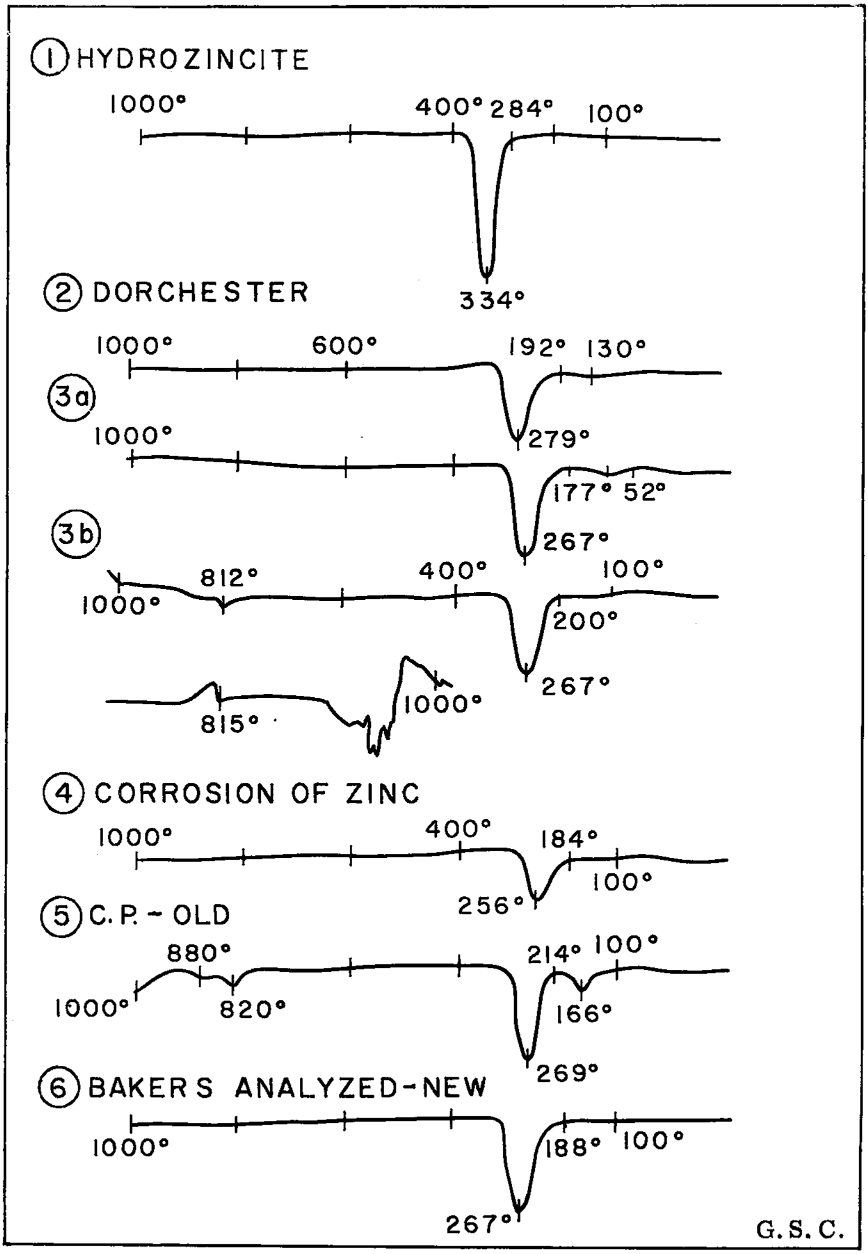

Fig. 2. Differential thermal curves for basic zinc carbonates. Sample numbers correspond to those given in Fig. 1 and in the text. Both heating and cooling curves are shown in 3(b)—erratic portion at about 950° probably results from sample shrinkage.

305°. The weight loss at the latter point is 26.9 per cent. A slight residual loss of an additional 1.8 per cent takes place between 305°–650°. The final decomposition product is ZnO. The total weight losses are: T.G. 28.7 per cent, theoretical 28.22 per cent, analytical 27.93 per cent. The chemical, T.G., and D.T. analyses of samples 2 and 3(a) are thus in good agreement with the formula requirements of $5ZnO.2CO_2.4H_2O$.

For sample 3(b), a complete D.T. as well as two additional partial curves were run in the low temperature region. In all cases the small preliminary endothermal break is consistently shallow and the weight loss only 2 per cent. As is the case in 3(a), the main endothermal break reaches its peak at 267° although decomposition is not complete until much higher temperatures are reached. At 400°, the total weight loss is 24.0 per cent, at 812°, 24.7 per cent, and at 1100°, 26.3 per cent. The small endothermic break at 812° does not appear to be related to decomposition as weight loss does nor accompany it. Moreover, on cooling the break reappears as an exothermic peak beginning at 816°. Presumably, then, this phenomenon is the result of a crystallographic transformation to a high temperature polymorph of ZnO. An analogous effect is apparently also present in sample 5 (Fig. 2).

An *x*-ray powder pattern made on 3(b) material which had been fired to just beyond the main endothermic break gave only ZnO (zincite) lines.

4. Zinc corrosion product

The chemical analysis corresponds to an apparent composition of $6ZnO.2CO_2.5H_2O$. As is the case in the D.T. curve for $5ZnO.2CO_2.4H_2O$, the loss of one molecule of water is indicated by a small endothermic break with its peak at about 135°. The weight loss is 3.3 per cent up to 184°, at which temperature the remainder of the CO_2 and H_2O are lost in the main endothermal break with its peak at 256° and termination at approximately 300°. The total weight loss up to 700° is 25.7 per cent, the theoretical loss based on the above formula is 26.73 per cent, and the final decomposition product ZnO.

5. $10ZnO.5CO_2.8H_2O$ (C.P.-old)

The first endothermal break (Fig. 2, second from bottom) is more pronounced and occurs at a slightly higher temperature than is observed in the previously examined carbonates. Up to 214°, the measured weight loss is 4.94 per cent whereas the theoretical weight loss from the release of three molecules of water is 4.6 per cent. The compound at this point would therefore correspond to $10ZnO.5CO_2.5H_2O$. The release of five molecules of water and of CO_2 is signalled by an additional weight loss of 19.8 per cent and the appearance of the main endothermal break with its peak at 269°. The residue is $4ZnCO_3.6ZnO$, or alternatively, $10ZnO.4CO_2$. The same compound is reported as an intermediate dissociation product of synthetic "basic zinc carbonate" studied by Duval (1953, p. 278). Final decomposition to ZnO begins at 880° and terminates at approximately 1300° (Fig. 1, curve 5). The total weight losses of CO_2 and H_2O are 30.95 per cent, (theoretical), 30.24 per cent (chemical), and 32.2 per cent (T.G.).

6. "Baker Analysed" Zinc Carbonate

T.G. and D.T. curves for this compound are shown at the bottom of Figs. 1 and 2 respectively. Up to 188°, a weight loss of only 1.3 per cent is recorded. If this is attributed to adsorbed water, the apparent formula of the compound becomes $9ZnO.3CO_2.5H_2O$ and the recalculated analytical values compare with the respective theoretical quantities as follows: H_2O—9.32, 9.44; CO_2—13.61, 13.83; ZnO—77.07, 76.73.

Decomposition to ZnO is indicated by the solitary endothermal peak at 276°. The total weight loss is 23.4 per cent (T.G.); 22.93 per cent (chem., less adsorbed water); 23.27 per cent (theoretical).

X-RAY POWDER DIFFRACTION STUDY

With the exception of hydrozincite, which is monoclinic, the zinc carbonates available are too fine-grained for single crystal examination. *X*-ray powder studies have been carried out using filtered copper radiation and both 5.7 and 11.4 cm. diameter cameras. Representative patterns are shown in Fig. 3.

It was previously mentioned that despite the variation in the chemical analyses, synthetic samples 3(a), 3(b), 4 and 6 are considered to belong to the Dorchester type of compound. The *x*-ray patterns of samples 3(b) and 4 (the latter not shown in Fig. 3) are absolutely identical to the patterns of the Dorchester, Slocan, and Keno Hill minerals. Synthetic material 3(a) is unquestionably also equivalent to the naturally occurring minerals, but comparison of the *x*-ray patterns in Fig. 3 will show that some differences are present. Likewise, the *x*-ray pattern of sample 6 is similar to those of 3(a) and 3(b), but it also has the additional two lines shown in Fig. 3.

Although the marked intensity differences between the patterns of hydrozincite and the Dorchester mineral suggest that they differ structurally, the similarity of the first few lines in their patterns could also indicate a possible common crystallographic relationship. On this basis, the *x*-ray powder patterns of hydrozincite and sample 3(a) can be indexed on essentially equivalent cells with the following dimensions:

hydrozincite: $a = 13.53$ Å, $b = 6.30$, $c = 5.41$, $\beta = 95°51'$
compound 3(a): $a = 13.76$ Å, $b = 6.35$, $c = 5.38$, $\beta = 96°00'$

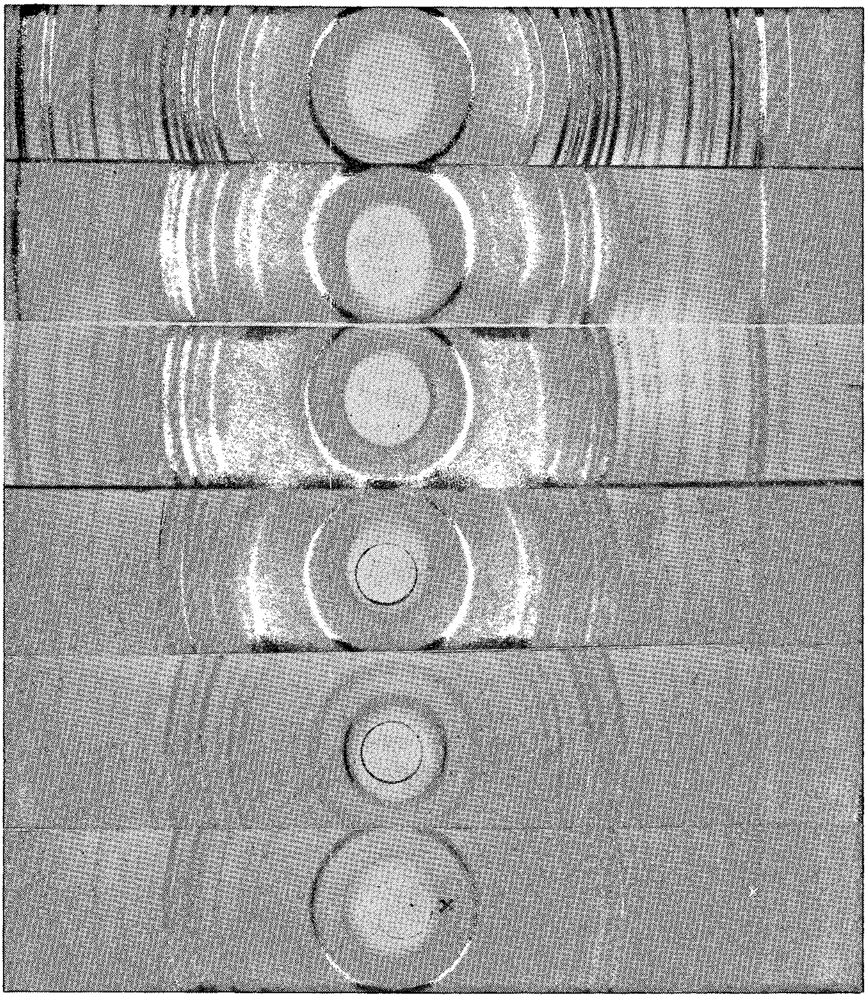

FIG. 3. *X*-ray powder photographs of basic zinc carbonates. Top to bottom: hydrozincite from Constantine, Algeria Sample 1; the Dorchester, New Brunswick mineral Sample 2; synthetic samples 3(a), formed by carbonation of ZnO; 3(b), formed by partial decomposition of sample 5(C.P.-old); 5(C.P.-old); 6, "Baker Analysed" zinc carbonate. All patterns taken with 11.4 cm. camera and filtered copper radiation. The significance of the marked lines in the bottom pattern is discussed in the text.

There are, however, two objections to the derivation of the above cell for compound 3(a). First, the one outstanding feature common to all the *x*-ray patterns shown in Figure 3 is the prominent, strongest line which appears at 6.8 Å. This line also appears in compound 5 (C.P.-old), which is completely different from the remaining zinc carbonates. The potential significance of the 6.8 Å line must therefore be accordingly diminished. Secondly, compound 6 belongs to the Dorchester group, but the *x*-ray pattern cannot possibly be indexed with hydrozincite-type cell dimensions because of the appearance of the first line at 11.1 Å. On this basis, it would appear that the synthetic compounds and the Dorchester mineral do not have a simple crystallographic relationship to hydrozincite.

DISCUSSION OF RESULTS

On the basis of the data assembled to this point, it would appear that the basic zinc carbonates studied have neither a common set of cell dimensions nor a single structural basis. Rather, they appear to conform to a minimum of three structural types. The first of these, hydrozincite, has no parallel among the remaining zinc carbonates, all of which have principal endothermal breaks with peaks in the 260–280° region. Among the latter group, sample No. 5 (C.P.-old) is characterized by the appearance of an intermediate dissociation product and a final decomposition to ZnO which does not begin until 880° is reached. This, too, would therefore appear to be a distinctly different zinc carbonate compound.

The data for sample 3(b) are also unusual, but despite the range in CO_2 and H_2O contents of the remaining compounds, their D.T. curves do not show significant differences. The possibility of adsorbed water is suggested by a comparison of the D.T. and T.G. curves and chemical analyses of samples 2 to 6. Differential thermal curves were therefore re-run on samples 3(a), 3(b), and 5 (C.P.-old) to an appropriate temperature beyond their small initial endothermic breaks and the fired charges examined by *x*-ray powder patterns. Except for a few possible small intensity variations, no change in the *x*-ray patterns was detected. As a further check, samples of specimen 3(a) were also heated in an oven at temperatures ranging from 100 to 200° C. *X*-ray powder patterns of the resulting products proved to be identical to the starting material, and to ZnO. In one case both compounds were present. The above data fairly conclusively suggest that the basic zinc carbonates contain considerable adsorbed water. The analytically-derived formula of samples 2 and 3(a) therefore change toward agreement with the formula contents of hydrozincite, that is, $5ZnO.2CO_2.4H_2O \rightarrow 5ZnO.2CO_2.3H_2O$. Likewise for sample No. 5 (C.P.-old), $10ZnO.5CO_2.8H_2O \rightarrow 10ZnO.5CO_2.5H_2O$, which reduces to $2ZnO.CO_2.H_2O$.

Unfortunately, some problems are not yet solved. Samples 4 (zinc corrosion product) and 6 ("Baker Analyzed" Zinc Carbonate) do not correspond to $5ZnO.2CO_2.3H_2O$ because of a CO_2 deficiency of about 3%. On the other hand, it may be more reasonable to accept the lower CO_2

values as being closer to the true formula requirements, so that, rather than they being CO_2 deficient, it is the other compounds that contain an excess of CO_2. On this basis, the composition of "Baker Analysed" Zinc Carbonate (sample 6) would be the most representative of the stable chemical individual from which the higher CO_2 and H_2O bearing carbonates of this group are derived. The fundamental formula would thus be $9ZnO.3CO_2.5H_2O$, and accordingly, the weight loss on decomposition to ZnO should amount to 23.23 per cent. The four samples considered to be in this group are 3(a), 3(b), 4, and 6. Taking the appearance of the main endothermal break as the point at which adsorbed material has been eliminated and decomposition of the compound itself begins, the CO_2 and H_2O weight losses of the above are, respectively, 25.2 per cent (23.4 per cent plus 1.8 per cent lost over a temperature range of 345°), 24.3 per cent, 22.4 per cent, and 22.1 per cent. Although these data do not rigidly adhere to a postulated "fundamental formula" hypothesis, the general conformity is nevertheless fairly good. The formula selected may not be the correct one, and it is possible that in its derivation weight loss attributed to adsorbed water may have been adsorbed CO_2. To check this possibility, sample 3(b) was fired in argon at a heating rate of 6° per minute and the temperature of the D.T. unit held at 175 ± 10° for 30 minutes. Escaping gas was bubbled through a lime solution. The lack of any indication of a precipitate after two runs suggests that only H_2O is present as adsorbed material. With the subtraction of such water from the analytically derived H_2O values of 3(a), 3(b), 4, and 6, their individual divergence from the mean content of 9.66 per cent H_2O is much less than 1 per cent. However, the recalculated CO_2 values do not appreciably move towards uniformity. The presence of adsorption phenomena thus provide only a partial explanation of the variation in CO_2 and H_2O values obtained from samples which give essentially identical *x*-ray powder patterns. Likewise, the variation in optical properties and refractive indices of various basic zinc carbonates are probably only in part related to the degree of hydration even though analogous effects due to adsorbed water are classically represented in many of the zeolites. To the present writer, the most plausible explanation of all the effects is that these carbonates are non-stoichiometric compounds containing adsorbed water.

INFRARED STUDY

Infrared data were obtained with a Perkin-Elmer Model 221 double beam recording infrared spectrophotometer. Samples were prepared using KBr and the procedure given by French *et al.* (1954). The infrared spectra obtained for five of the zinc carbonate samples are shown in Figure 4.

The infrared study confirms that hydrozincite differs from the remaining zinc carbonates. The fairly sharp and well-resolved band at 3.1 microns in hydrozincite appears in the other carbonates as a broad band at higher frequencies. According to Huang & Kerr (1960), water absorbed in KBr appears at 2.85 and 6.00 microns; water of crystallization also appears in the same region. OH groups (Keller & Pickett, 1949) absorb between 2.7 and 3.1 microns, depending on the degree of hydrogen bonding. As unbound OH appears at the higher frequencies, the presence in hydrozincite of strong absorption peaks at 3.0–3.10 microns indicates the presence of bonded OH groups. The remaining zinc carbonates have maxima in this region at 2.90–3.00 microns. These single broad peaks fall within the range of absorbed water and combined OH, although the O–H stretching frequency of the latter is higher than in hydrozincite. Analogous strong bands at about 3 microns appearing in the basic carbonates examined by Hunt *et al.* (1950) are reported as probably being due to bonded OH. For Merck Reagent basic zinc carbonate, the absorption maximum for OH appears at about 3.02–3.04 microns. This wave length value is higher than those recorded for the synthetic zinc carbonates examined in the present study, though the OH also appears as a single broad absorption band. Likewise, all the infrared curves in Figure 4 have a shoulder at 6.0–6.1 microns which probably originates from absorbed water, but this effect is not evident in the curve given by Hunt *et al.*

As the differences between the hydroxyl absorption bands of hydrozincite and the Dorchester compounds are of considerable significance, additional infrared curves for new samples of all the zinc carbonates, except 5 (C.P.-old), were also run on a Perkin-Elmer Model 21 infrared unit. As further checks, infrared data were also obtained from samples 3(a) and 3(b) which had been appropriately heated to drive off adsorbed water, and an unheated specimen of 3(a) was run in Nujol. The net result is that the original conclusions regarding the hydroxyl bonding are not changed.

Anhydrous carbonates characteristically show a single strong absorption band (due to CO_3 groups) at about 7 microns. In the basic carbonates, twin maxima appear near this wave length. Strong hydroyxl bands are found in the 6.7–7.7 micron position (Setkina, 1959), but the twin maxima in this case are attributed to CO_3 groups (Huang & Kerr, 1960).

It is interesting that the Dorchester mineral (No. 2) and synthetic compound 3(a) give identical infrared curves, and that furthermore, these curves are comparable to Merck Reagent examined by Hunt *et al.* It was thought that the appearance of the additional absorption band of weak intensity at 9.1 microns in sample 3(b) might be a manifestation of its higher CO_2 content. However, this band also appears in the curve of sample 4, which has a relatively low CO_2 value. It might also be added

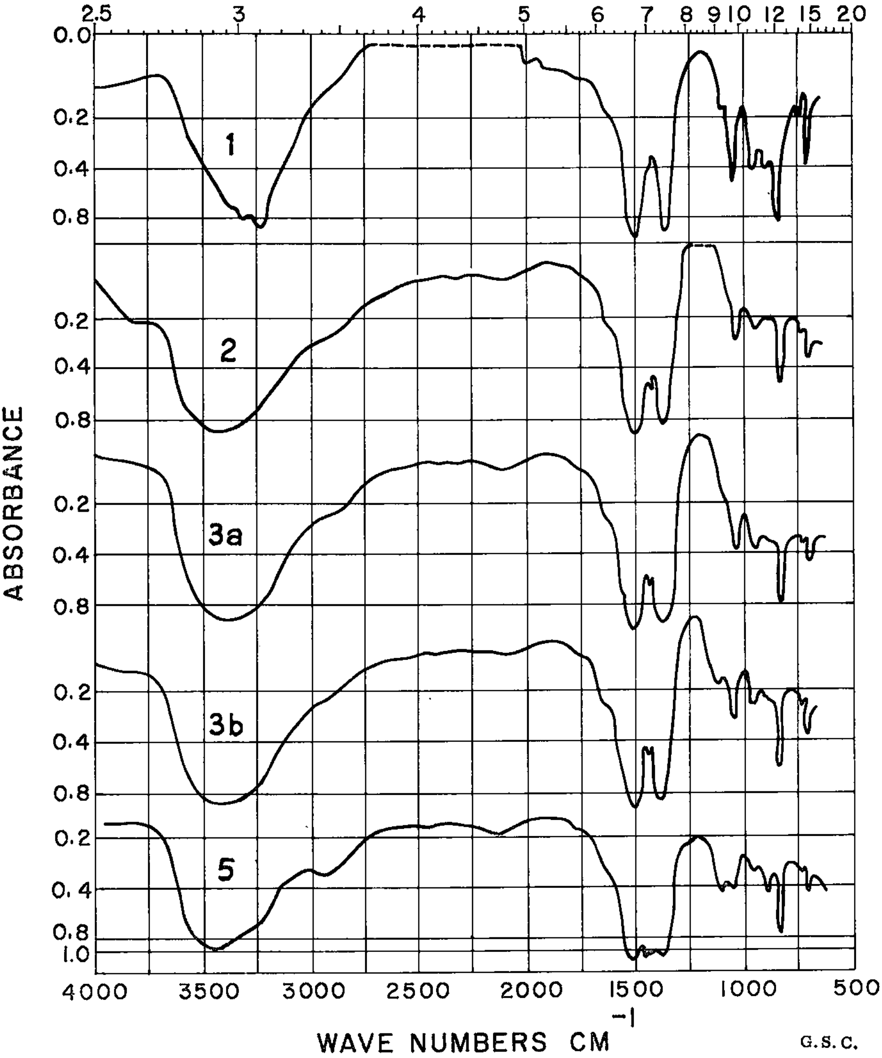

FIG. 4. Infrared curves for basic zinc carbonates. Diagrams are reduced tracings of original data. Numbers designating each curve correspond to samples discussed in the text.

that sample 6, "Baker Analysed" zinc carbonate, has an infrared curve identical to that of the Dorchester mineral.

Sample 2, 3(a), 3(b), 4, and 6 are thus considered to form a group which have, in the 7–15 micron region, spectra quite different from those of samples 1 and 5 (hydrozincite and C.P.-old).

SUMMARY AND CONCLUSIONS

The term "hydrozincite" has in the past been rather loosely used both in mineralogy and inorganic chemistry to denote a basic zinc carbonate corresponding to the general formula requirements of a compound alternately designated as $5ZnO.2CO_2.3H_2O$ and $Zn_5(CO_3)_2(OH)_6$ (or $2ZnCO_3.3Zn(OH)_2$). By means of x-ray powder photographs, Feitknecht (1933) concluded that synthetic basic zinc carbonate is $2ZnCO_3.3Zn(OH)_2$ with two layers of $ZnCO_3$ fitting between three layers of $Zn(OH)_2$. In this arrangement, water could be held between layers in a manner similar to that in zeolites[1] and expelled without altering the distance between layers. Feitknecht also proposed that these zinc carbonates do not contain their constituents in stoichiometrical proportions because additional $Zn(OH)_2$ easily adds onto the structure. Using a somewhat different approach, the present writer has also concluded that several of the synthetic zinc carbonates examined are merely variants of a fundamental compound. Some of the data indicate that the formula $9ZnO.3CO_2.5H_2O$ is a possibility. However, if the analytical values of samples 3(a), 3(b), 4, and 6 are recalculated after eliminating adsorbed water, the mean CO_2 content is 15.1 per cent and the mean H_2O content is 9.7 per cent. These values are fairly close to the formula requirements of $5ZnO.2CO_2.3H_2O$ (theoretical CO_2 16.03 per cent, H_2O 9.85 per cent), and are thus in harmony with Feitknecht's fundamental compound.

The mineralogical implications of these data are evident. From chemical analyses the Dorchester type minerals have the apparent formula $5ZnO.2CO_2.4H_2O$. As it has been shown that part of this water is held by adsorption, the formula more realistically approaches $5ZnO.2CO_2.3H_2O$. The Dorchester type of mineral and hydrozincite may have the same formula requirements, but the minerals nevertheless show significant differences in their x-ray powder patterns, and D.T., T.G., and infrared curves. On this basis, it is concluded that the Dorchester mineral is a new mineral, possibly dimorphous with hydrozincite[2]. Finally, it is probable that many proposed formulae for basic zinc carbonates are erroneous in derivation due to the presence of non-stoichiometric and adsorption effects.

ADDENDUM

Two additional papers having a direct bearing on the zinc carbonate problem have become available to the writer since this manuscript was first submitted. Braithwaite & Ryback (1963) have published an infrared curve for "hydrozincite" from Llanidloes, Montgomeryshire. As they

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[1] Equivalent to the adsorbed water in zeolites discussed by Milligan & Weiser (1937).

[2] A stacking–disordered phase of hydrozincite according to Ghose (*Acta Cryst.*, **16**, A 36, 1963).

point out, their curve corresponds to that of reagent zinc carbonate described by Hunt *et al.* (1950), and hence, assuming equivalence of other properties, to the Dorchester mineral described here.

In the second of the papers, Zabinski (1958) gives a chemical analysis, *x*-ray powder pattern, and D.T. curve for "hydrozincite" which formed on planking in the Orzel Bialy mine, Poland. As the physical properties and *x*-ray data are like those of the Dorchester material, the Polish mineral is also tentatively classified as belonging to this particular group.

In final summation, and at the risk of belabouring the point, it is perhaps worthwhile adding a few comments in anticipation of certain questions which may have arisen. How much significance, for example, can be attached to the infrared data? In the writer's opinion, the appearance of multiple absorption peaks in the hydrozincite hydroxyl region is a valid criterion for distinguishing this mineral from the Dorchester compound. It may be argued that the broad peak in the latter is due to the presence of adsorbed water, but if this is true, and the heating experiments are ignored, then it is equally reasonable to assume that hydrozincite differs in that it apparently does not adsorb water. On the other hand, it is felt that little weight can as yet be attached to adsorption data for the remaining portions of the curves. While it is true that the data for sample 5 (C.P.-old) indicate that changes in the spectra of the zinc carbonates are not likely to be large, it seems more appropriate at this stage to attach minimal importance to these differences for determinative purposes.

One also might be tempted to downgrade the D.T. data as criteria for distinguishing these minerals, particularly in view of the fact that correlation of the results obtained by various workers may in some cases be difficult (as, for example, the uncertain classification of Zabinski's D.T., curve). In this regard, D.T. analyses of hydrozincites from Cumillas, Spain (Beck, 1950), and Lehigh County, Penn. (Kauffmann & Dilling 1950) are considered to be equivalent to results obtained here. One only need compare the curves for azurite and malachite (see Beck, p. 1001) to realize why importance is attached to inequalities of the magnitude found among the hydrozincite and Dorchester type carbonates.

Although the present writer has experienced no difficulty in classifying his fourteen specimens of natural zinc carbonates into hydrozincite or Dorchester types, it is nevertheless clear that examination of additional samples by other workers will provide an immediate practical test as to the feasibility of maintaining the proposed classification.

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