

PROPERTIES OF A SYNTHETIC MAGNESIUM-ALUMINUM
CARBONATE HYDROXIDE AND ITS RELATIONSHIP TO
MAGNESIUM-ALUMINUM DOUBLE HYDROXIDE, MA-
NASSEITE AND HYDROTALCITE¹

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ABSTRACT

A synthetic mineral prepared by titrating a mixed solution of $MgCl_2$ and $AlCl_3$ with $NaOH$ in a CO_2 -free system and then dialyzing the suspension for 30 days at $60^\circ C$ was a hydrated Mg-Al carbonate hydroxide with the formula $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ and properties of manasseite and hydrotalcite. The synthetic mineral is hexagonal with $a=6.14_1$, $c=15.61_2$ Å and $Z=1$. Dehydration and corresponding contraction of basal spacings were reversible up to $300^\circ C$ and irreversible above $450^\circ C$. Above $300^\circ C$ both OH water and CO_2 were evolved, and at $450^\circ C$ the structure was destroyed. A one-dimensional structure analysis indicates a structure consisting of brucitic layers alternating with hydrous aluminum layers.

INTRODUCTION

When a solution containing $MgCl_2$ and $AlCl_3$ is titrated with $NaOH$, a double hydroxide of Mg and Al is formed having a characteristic structure (e.g., Feitknecht, 1942; Feitknecht and Gerber, 1942). These authors showed that other divalent ions such as Ca, Co, Mn, Cd in solution with Al or Fe^{3+} also give double hydroxides upon the addition of a base. Mortland and Gastuche (1962) analyzed precipitates prepared in this way and found that with a molar ratio of $0.7 < Mg/(Mg+Al) < 0.8$ a pure Mg-Al double hydroxide free of gibbsite or brucite was formed. From a comparison of X-ray powder diffraction data, they concluded that the pure double hydroxide precipitated in two forms with slightly different parameters and was different from the Mg-Al double hydroxides described by Feitknecht and Gerber (1942).

The powder diffraction data of Mortland and Gastuche, however, are close to those given for manasseite and hydrotalcite in Smith (1965). This similarity is not surprising since manasseite and hydrotalcite could be considered as Mg-Al double hydroxides, except for the substitution of one CO_3 for two OH ions. Thus it seems likely that the so-called double hydroxides prepared by titrating $AlCl_3$ and $MgCl_2$ are indeed closely related to manasseite and hydrotalcite. This study was undertaken, therefore, to determine the composition and structure of Mg-Al double hydroxide and to assess the relationship to manasseite and hydrotalcite.

¹ Contribution No. 203.

PREPARATION OF THE PRECIPITATE

The precipitate was prepared by titrating with 1N NaOH a solution consisting of AlCl_3 and MgCl_2 having a total concentration of 0.1M and a $\text{Mg}/(\text{Mg}+\text{Al})$ molar ratio of 0.8. The molar ratio of 0.8 was selected because preliminary experiments showed that at this molar ratio a precipitate free of brucite or gibbsite was obtained. The NaOH was added in a stepwise manner and the pH was measured after each addition to give a titration curve. A stream of CO_2 -free nitrogen was passed through the solution during the titration to minimize contamination of the precipitate with CO_2 . For comparison a solution of MgCl_2 was titrated with NaOH in a similar way.

The buffering at pH 9.5, obtained when MgCl_2 alone was titrated with NaOH, was due to the precipitation of $\text{Mg}(\text{OH})_2$ (Fig. 1, curve 1). The buffering between pH 4.0 and 4.5, obtained with the MgCl_2 and AlCl_3 mixture, was due to the precipitation of $\text{Al}(\text{OH})_3$ (curve 2). The second buffering range between pH 7.7 and 8.5 was more than one pH unit below that obtained when $\text{Mg}(\text{OH})_2$ was precipitated. This buffering range corresponds to that obtained under similar conditions by Turner and Brydon (1962) and may be due to

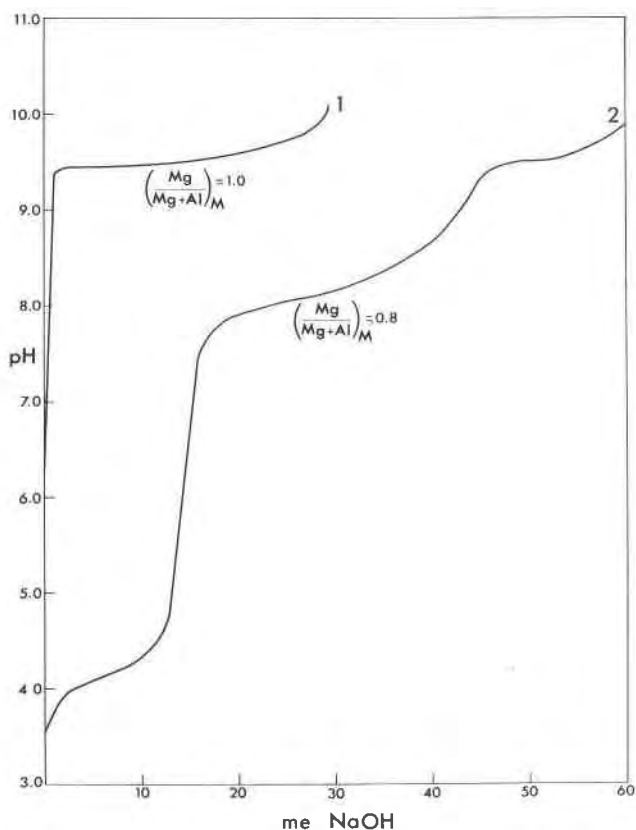


FIG. 1. Titration curves of 0.1M solutions of magnesium chloride and aluminum-magnesium chloride.

adsorption bonding between the hydroxides of Mg and Al with the latter as the negative compound (Treadwell and Bernasconi, 1930).

The suspension, obtained from the titration of the solution containing both AlCl_3 and MgCl_2 , was transferred to a polyethylene bag and dialyzed for one month at 60°C against distilled water which was changed daily. The suspension was then freeze-dried and the resulting powder used for the remainder of the study.

CHEMICAL ANALYSES

Part of the freeze-dried sample was dissolved in dilute nitric acid and Al was determined by the aluminon method (Robertson, 1950) and Mg by the atomic absorption method. The Cl content was determined by X-ray spectrometry and CO_2 and H_2O by dry combustion using WO_3 to ensure complete combustion (Steiermark, 1961).

The composition of the precipitate prepared in this study is close to those of the two polymorphs manasseite and hydrotalcite with the formula, $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ (Table 1). The precipitate had relatively high CO_2 content, which presumably was incorporated from the air during dialysis and after freeze drying, Brandenberger (1933) and Mump-ton, *et al.* (1965), have noted the rapid carbonation of related minerals. The Cl content was negligible, unlike the considerable Cl contents of some double hydroxides reported by Feitknecht (1942).

X-RAY ANALYSIS

X-ray diffraction powder patterns were obtained using Fe-filtered Co radiation with a 114.7 mm camera containing the specimen in a thin-walled glass capillary (Table 2). Some X-ray line broadening was evident which is attributed to small particle size and imperfect crystallinity of the precipitate and to statistical distribution of CO_3 in its structure, discussed in a later section. Except for small differences in $(00l)$ reflections (which are shown below to be dependent on relative humidity) the powder data of the precipitate are very close to those reported by Mortland and Gastuche (1962). As to the values for manasseite and hydrotalcite, the powder data of the precipitate prepared in this study agree more closely with those of manasseite than with those of hydrotalcite indicating that the precipitate belongs to the hexagonal rather than to the rhombohedral group. The X-ray powder diffraction lines of the precipitate, therefore, were preliminarily indexed in the hexagonal system using the unit-cell data for manasseite, $a=6.13 \text{ \AA}$ and $c=15.37 \text{ \AA}$. The unit-cell dimensions of the precipitate, calculated using a pair of well-defined small spacings (1.541 and 1.498 \AA) of the indexed pattern, are $a=6.14_1 \text{ \AA}$ and $c=15.61_2 \text{ \AA}$. The data in Table 2 show good agreement between the observed Q_{hkl} values ($Q_{hkl}=1/d_{hkl}^2$) and the Q_{hkl} values calculated on the basis of the derived cell dimensions.

TABLE 1. CHEMICAL ANALYSES

Wt. %*	Precipitate ¹	Manasseite ²	Manasseite ³	Hydrotalcite ⁴
MgO	38.2	36.76	39.38	39.84
Fe ₂ O ₃		0.20	0.21	0.90
Al ₂ O ₃	16.5	19.65	16.59	15.16
CO ₂	6.4 (±0.3)	6.98	7.48	7.26
Cl	0.1 (±0.01)			
H ₂ O	38.4	36.13	36.34	36.83
Rem.		0.35		0.14
Total	99.6	100.07	100.00	100.13

* Based on air-dry weight.

¹ Precipitate prepared in this laboratory.

² Sample from Snarum, Norway. Pure sample, but contains gibbsite. Rem. is SiO₂. Frondel (1941).

³ Analysis of sample 2 recalculated to 100% after deduction of 0.35% SiO₂ and 6.38% gibbsite (on the basis of 6 Mg atoms per cell). Frondel (1941).

⁴ Sample from Snarum, Norway. Presumed to be a mixture of hydrotalcite and manasseite. Rem. is insoluble. Manasse (1915).

THERMAL ANALYSIS

The thermal stability of the precipitate was investigated by DTA and TGA. The DTA was carried out at a heating rate of 10°C/min (Morita and Rice, 1955). The TGA was obtained at a heating rate of 5°C/min with an analytical balance and a Fisher Balance Assembly mounted over a cylindrical furnace containing a suspended Pt dish. The balance was calibrated with an equal weight of calcined sample.

The DTA curve of the precipitate is similar to that given for hydrotalcite (Mumpton, *et al.*, 1965, p. 1904), although its endotherm peaks are somewhat different in magnitude and occur at slightly different tem-

TABLE 3. CELL CONTENTS

	Precipitate ¹	Manasseite ²	Mg ₆ Al ₂ CO ₃ (OH) ₁₆ ·4H ₂ O
Mg	6.0	6.0	6
Al	2.0	2.0	2
C	0.9	1.1	1
H	24.4	24.9	24
O	23.0	23.6	23

¹ Calculated from analysis 1, Table 1.

² Calculated from analysis 3, Table 1.

peratures (Fig. 2). The significance of these differences is not clear since specific differences in operating conditions are not known. The first two endotherms with peaks at 248°C and 267°C in the DTA curve of the precipitate are assigned to the loss of water of crystallization, although some absorbed water could be included in this loss. This reaction accounts for the weight loss between 25°C and 200°C in the TGA and DTGA curves shown in Figure 3. The third endotherm with its peak at 447°C is attributed to the loss of both OH water and CO₂ from the structure and corresponds to the weight loss between 300°C and 450°C in the TGA and DTGA curves (Fig. 3).

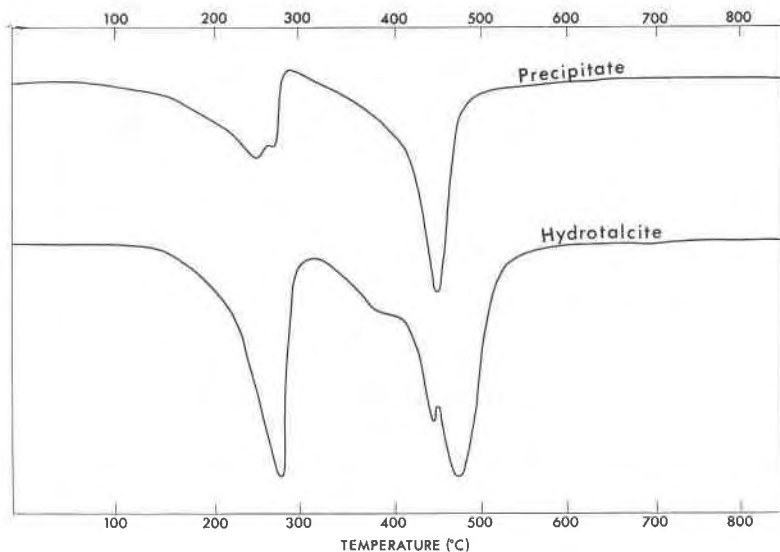


FIG. 2. Differential thermal analysis curves of the precipitate and hydrotalcite.

Additional thermal data were obtained by dry combustion of the sample for CO₂ analysis at increasing temperatures (Steyermark, 1961). These data were plotted in Figure 4 and show that nearly all of the CO₂ was evolved between 400° and 600°C. This agrees with the results for manasseite obtained by Manasse (1915).

EFFECT OF RELATIVE HUMIDITY AND HEAT ON BASAL REFLECTIONS

The effect of relative humidity on basal reflections at room temperature was investigated by X-ray analysis of an unheated oriented specimen at 40 percent and 85 percent relative humidity. The effect of heat on basal reflections was examined by heating oriented specimens on glass

TABLE 2. X-RAY DIFFRACTION DATA FOR Mg-Al HYDROXIDE PRECIPITATES, MANASSEITE AND HYDROTALCITE

Precipitate ^a				Precipitate ^b (Form II)			Manasseite ^c			Hydrotalcite ^d				
<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{rel}	<i>Q</i> _{obs}	<i>Q</i> _{calc}	$\Delta Q \times 10^{10}$ ^{**}	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{rel}	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{rel}	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> _{rel}
002	7.84	100	0.0163	0.0164	-1	001	7.64	vs	002	7.67	100	006	7.69	100
004	3.90	60	0.0655	0.0656	-1	002	3.81	s	103	3.83	20	018, 0.12	3.88	70
006	2.60	40	0.1474	0.1476	-2	003	2.59	ms	201, 113	2.60	50	024	2.58	20
106	2.33	25	0.1837	0.1829	8	004	2.53	w	202	2.49	30	0210	2.30	20
211	1.990	30	0.2525	0.2514	11	004	2.34	m/w	203	2.34	40	125, 0216	1.96	20
116	1.990	30	0.2525	0.2536	-11	004	1.986	w	204, 115	2.17	40			
008	1.950	6	0.2630	0.2624	6	206	1.893	v/vw	210, 205	2.00	40			
212	1.950	6	0.2630	0.2638	-8				206	1.84	60			
305	1.541	35	0.4211	0.4205	6				208	1.56	20			
1.0.10	1.498	25	0.4456	0.4455	1	1.522	ms		221	1.52	30	220, 223	1.53	20
313	1.419	7	0.4966	0.4963	3	1.491	ms		119	1.49	30	226	1.50	20
0.0.12	1.302	6	0.5899	0.5904	-5	1.412	w			1.42	10			
227	1.265	9	0.6249	0.6250	-1	1.307	w (broad)			1.33	10	4010	1.28	10
1.0.12}	1.265	9	0.6249	0.6257	-8	1.265	w (broad)			1.25	10			
3.0.10	1.172	2	0.7280	0.7281	-1					1.24	10			
3.0.13	0.994	4	1.0121	1.0110	11					1.17	10			
0.0.16}	0.976	5	1.0498	1.0496	2	0.9967	v/vw (broad)			1.09	10			
3.1.12}	0.976	5	1.0498	1.0498	0	0.9757	v/vw (broad)							
<i>a</i> = 6.141 Å			\bar{V} = 509.88 Å ³		<i>D</i> (calc) = 1.966									
<i>c</i> = 15.612 Å					<i>D</i> (obs) = 1.96									

^a Data obtained in this laboratory.^b Mortland and Gastuche (1962).^c Smith (1965) card No. 14-525. Sample from Dypingdal, Snarum, Norway.^d Smith (1965) card No. 14-191. Sample from Sölvverkets Kisgrube, Snarum, Norway.^{**} $\Delta Q = Q_{obs} - Q_{calc}$.

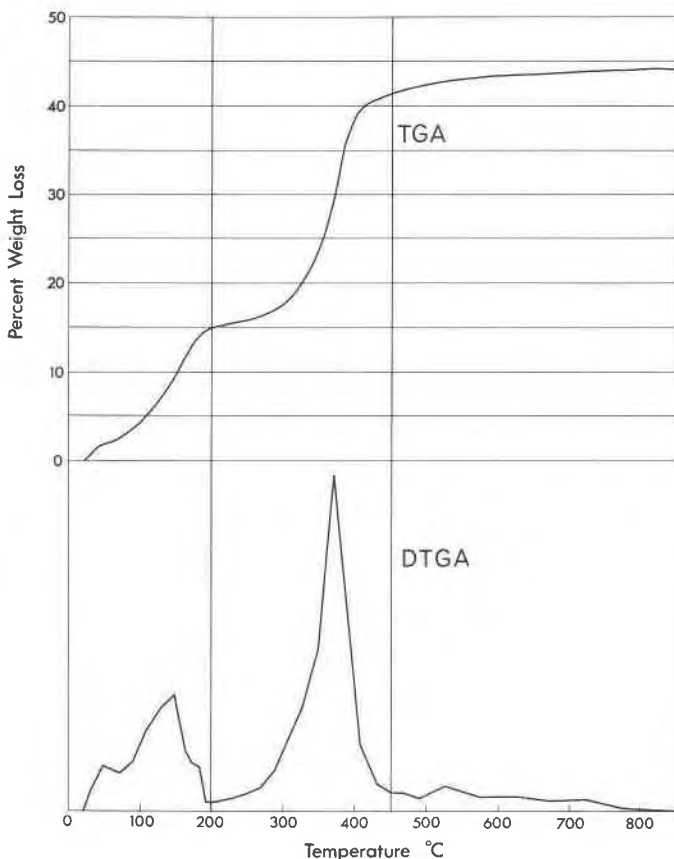


FIG. 3. Thermogravimetric and differential thermogravimetric analysis curves of the precipitate.

slides to different temperatures in the furnace of a TGA apparatus at a rate of $5^{\circ}\text{C}/\text{min}$. After cooling over P_2O_5 , the oriented specimens were X-rayed at close to 0 percent relative humidity with a Philips Diffractometer.

As shown in Figure 5, an increase in relative humidity from 40 percent to 85 percent at 25°C significantly increased basal spacings. Heating to 180°C caused a slight decrease in basal spacing, but at 150°C and 180°C an additional first-order reflection appeared at a lower basal spacing. From 220°C to 300°C only one first-order basal reflection at about 6.6 \AA was present. After heating at 450°C , no peaks were evident in the diffractograms indicating destruction of the crystal structure.

After heating, the oriented specimens were rewetted, dried overnight at room temperature, and then X rayed at room temperature and 40 per-

cent relative humidity. All the specimens, except the one heated to 450°C, gave first-order basal reflections at the original spacing with no loss in intensity (Fig. 5).

These results indicate that the amount of water of crystallization determines the basal spacing between 7.9 Å and 6.6 Å. The 7.9 Å spacing represents the fully hydrated phase, and the 6.6 Å spacing characterizes the fully dehydrated phase. Dehydration appears to be completed between 180°C and 220°C and is reversible up to 300°C indicating no appreciable destruction of crystal structure at this temperature. Branden-

TABLE 4. ONE-DIMENSIONAL STRUCTURE FACTORS (F_{00l}) AND THE DERIVED AND OBSERVED INTENSITIES FOR AN IDEAL MODEL† OF THE PROPOSED STRUCTURE

$00l$	F_{calc}	$I_{\text{calc}} \sim \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos \theta} (F_{\text{calc}})^2$	I_{obs}
002	-59.2	100	100
004	+88.5	53	60
006	+91.8	23	40
008	+39.9	2	6*
0.0.10	-6.0	0.03	—
0.0.12	+113.4	7	6
0.0.14	-39.9	1	—
0.0.16	+61.8	3	5*

* Includes intensity of a prismatic reflection.

† Based on the chemical formula $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$

berger (1933) also concluded that the X-ray diffraction properties of a similar hydrated Ca-Al double hydroxide varied with its content of water of crystallization.

INFRARED ABSORPTION ANALYSIS

Infrared absorption spectra were obtained with a Perkin-Elmer Model 21 Spectrophotometer on KBr pellets containing 0.20 percent of the sample. The spectrum of the precipitate (Fig. 6) is like the spectrum of hydrotaalcite published by Mumpton, *et al.*, p. 1903 (1965). In both patterns the stretching vibrations of water are represented by a band at 3480 cm^{-1} and a shoulder at about 3000 cm^{-1} ; the stretching vibrations of carbonate are shown by bands at about 1480 cm^{-1} and 1380 cm^{-1} .

CALCULATION OF STRUCTURAL FORMULA

The formula of the precipitate was calculated using the data of chemical and thermal analyses. Based on the break in the TGA and DTGA curves at 200°C (Fig. 3) and on the strong but reversible contraction in

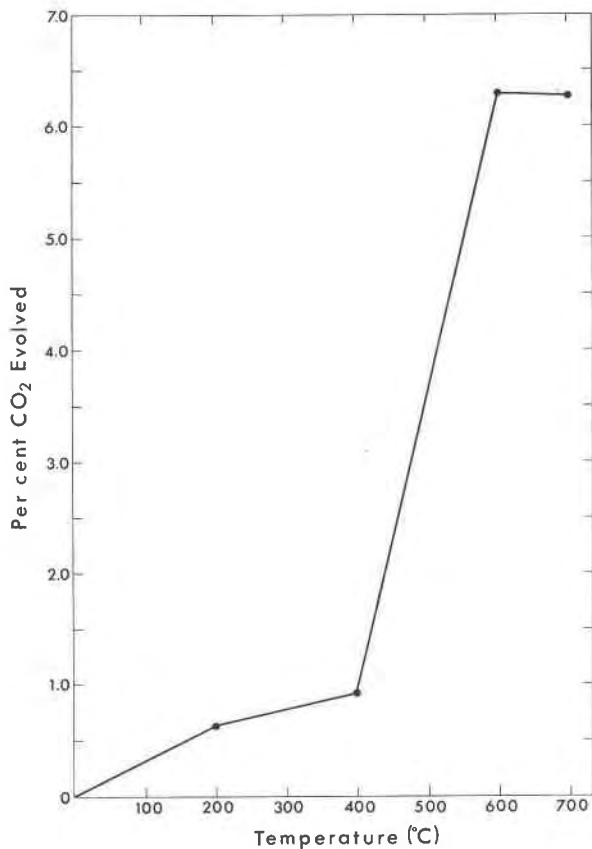


FIG. 4. Evolution of carbon dioxide from the precipitate heated to various temperatures.

basal spacings between 180°C and 220°C (Fig. 5), the weight loss below 200°C was attributed to absorbed water and water of crystallization, and that above 200°C to OH water and CO₂. Because the amounts of adsorbed water and water of crystallization were not accurately known, the formula was first calculated on the basis of the data in Table 1 recalculated as percent of the sample weight at 200°C. The weight loss below 110°C (3.2%) was then assigned to absorbed water and excluded from the calculations. The weight loss between 110°C and 200°C (12.1%) was attributed to water of crystallization and corresponds to four H₂O molecules in the formula. The calculated formula for the precipitate (Table 3) agrees closely with the experimental values for manasseite and they both conform to the general formula, Mg₆Al₂CO₃(OH)₁₆·4H₂O.

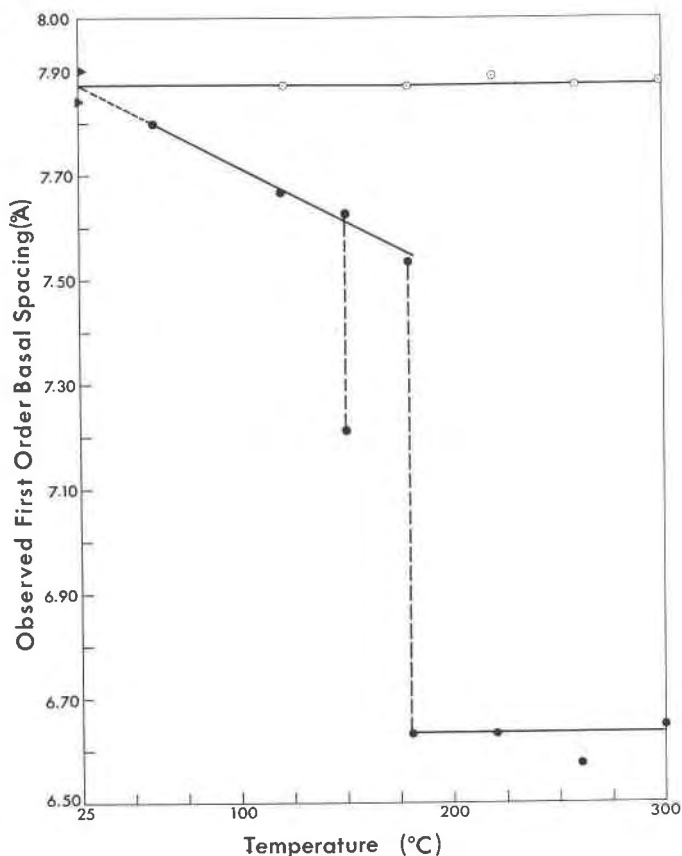


FIG. 5. Effect of relative humidity (solid triangles), heating (solid circles) and rehydration (open circles) on basal spacings of the precipitate. Data from diffractograms of oriented specimens giving a regular sequence of basal reflections.

STRUCTURAL ANALYSIS

As shown in Table 2, the largest basal reflection occurred at the half height of the c -dimension which indicates a hexagonal subcell with dimensions, $a = 6.14 \text{ \AA}$ and $c = 7.79 \text{ \AA}$. This subcell contains the half molecule $\text{Mg}_3\text{Al}(\text{OH})_8(\text{CO}_3)_{\frac{1}{2}} \cdot 2\text{H}_2\text{O}$ which requires the repetition of an equivalent atom array at a distance of 7.79 \AA and implies that the distribution of CO_3 ions must be statistical.

The thermal data and the results of the dehydration experiment (Figs. 2, 3 and 5) indicated that, except for the loss of H_2O below 200°C , the thermal decomposition of the precipitate was similar to that of brucite in

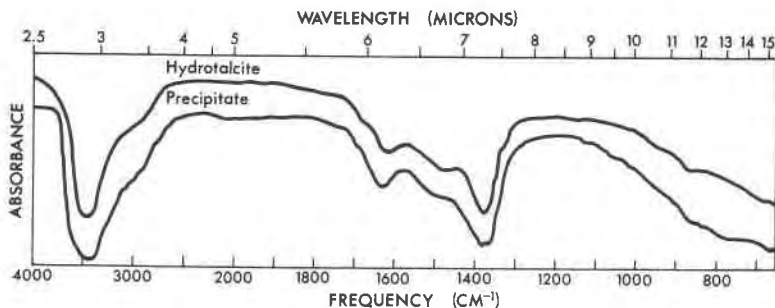


FIG. 6. Infrared spectra of the precipitate and hydrotalcite.

that the OH was evolved between 300°C and 450°C. When oxygen ions are in hexagonal closest packing, as in brucite, the hexagonal base with edge 6.2 Å permits four oxygens in each layer. Three layers of four close-packed oxygens would give a subcell height of 7.20 Å as compared to the observed 7.79 Å value. A structural model was assumed, therefore, consisting of a brucitic layer containing 3 Mg and 8 OH (two layers of close-packed oxygen ions) and a loosely stacked layer containing 1 Al, $\frac{1}{2}$ CO₃ and 2 H₂O per subcell. A diagram of this model is shown in Figure 7.

Based upon the proposed structure, a one-dimensional structure analy-

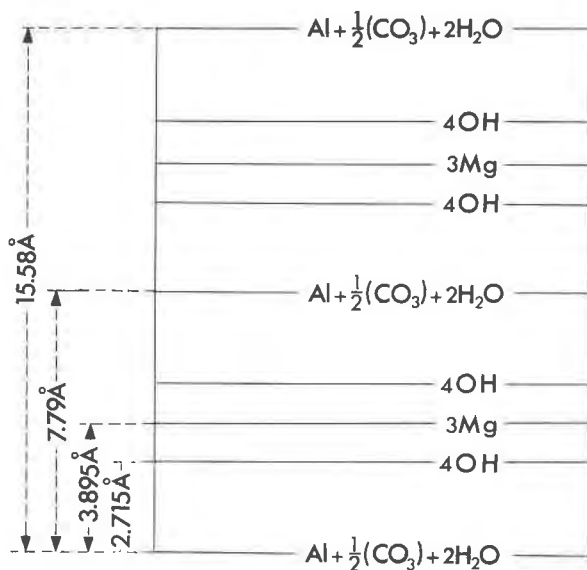


FIG. 7. Diagram of the proposed structure of the precipitate.

sis was used and the structure factors (F_{calc}) and the intensities (I_{calc}) were calculated. The agreement between the I_{calc} and I_{obs} values (Table 4) supports the validity of the proposed structure.

CONCLUSIONS

X-ray diffraction, chemical, thermal and infrared analyses showed that the precipitate prepared by titrating mixed solutions of AlCl_3 and MgCl_2 and dialyzing the suspension (Mortland and Gastuche, 1962) was not a pure hydrated Mg-Al double hydroxide, as has generally been believed, but a hydrated Mg-Al carbonate hydroxide with similar properties and the same formula as manasseite and hydrotalcite, $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$.

A one-dimensional structure analysis indicated a structure consisting of brucitic layers alternating with hydrous aluminum layers.

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