

## MIXED MAGNESIUM-ALUMINIUM HYDROXIDES

### I. PREPARATION AND CHARACTERIZATION OF COMPOUNDS FORMED IN DIALYSED SYSTEMS

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**ABSTRACT:** The materials formed by dialysis of the precipitates formed by the reaction of NaOH with mixed Mg-Al solutions are described. In addition to aluminium and magnesium hydroxides, two hydrocarbonates having Mg/Al ratios of about 5:1 and 2:1 are formed, essentially pure, from solutions with Mg/Mg + Al molar ratios of 0.8 and 0.7, respectively. X-ray powder data shows that they have partially ordered hexagonal layer structures with unit layer dimensions  $a = 3.048 \text{ \AA}$ , layer thickness  $7.60 \text{ \AA}$  for the Al-rich compound and  $a = 3.072 \text{ \AA}$ , layer thickness  $7.92 \text{ \AA}$  for the Al-poor compound. X-ray and chemical data show that the new compounds resemble the minerals hydrotalcite and manasseite and also the compounds described as Mg-Al hydroxides by Feitknecht.

Octahedrally co-ordinated layers occur widely in inorganic and mineral structures. With mainly siliceous tetrahedrally co-ordinated layers they are the principal building units for the alumino-silicate layers of layer silicates. In chlorites, octahedral layers occur not only as part of the alumino-silicate layer but also as interlayer charge balancing units. The cell dimensions of many layer silicates are determined largely by their octahedral layers (Radoslovich, 1963). The octahedral layer is also thought to play an important role in the synthesis of clay minerals from solutions. For example, Hénin & Caillère (1961) suggested that the development of layer structures is promoted by the presence of embryo octahedral hydroxide layers, which

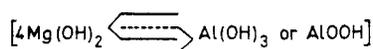
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act as templates for organizing the silica into tetrahedral layers. The work reported here was part of a study of the formation and properties of octahedral layers (see Gastuche, 1964, for a review).

### PREVIOUS WORK

Feitknecht & Gerber (1942) prepared a series of double hydroxides with Mg/Al ratio between 1.5 (6:4) and 4 (8:2), by precipitation with a small excess of caustic soda from mixed solutions of magnesium and aluminium chlorides. The compounds formed gave a characteristic X-ray powder diagram that resembled the pattern given by the green cobalt (II, III) hydroxide and hydroxychloride (Feitknecht & Fischer, 1935) and, by analogy with them, Feitknecht & Gerber indexed the X-ray powder pattern of the mixed magnesium-aluminium hydroxides on the basis of a rhombohedral lattice having  $a_H = 3.10 \text{ \AA}$  and  $c_H = 23.8 \text{ \AA}$ . Feitknecht & Held (1944) showed that the Mg-Al compounds do not have exact stoichiometric formulae. Many preparations contained chloride and the amounts of Mg, Al, Cl and OH ranged widely, but no difference in cell dimensions was detected between preparations having different compositions.

Feitknecht & Gerber concluded that by analogy with green cobalt (II, III) hydroxide, these compounds were layer structures, belonging to the group of compounds that Feitknecht (1954) called 'double-sheet structures'. The structure proposed by Feitknecht & Gerber for the Mg-Al hydroxides was one in which the principle layers were  $\text{Mg}(\text{OH})_2$  layers with the brucite structure; these were interleaved with disordered  $\text{Al}(\text{OH})_3$  or  $\text{Al O}(\text{OH})$  layers. They gave as ideal formulae:



but gave no detailed information. In particular the nature of the disordered interleaved Al-bearing layer was not specified.

Turner & Brydon (1962) observed that compounds similar to those described as double hydroxides by Feitknecht *et al.* are formed when  $\text{Al}(\text{NO})_3$  and  $\text{Fe}(\text{NO})_3$  are titrated to pH 9-10 with MgO. They attributed the buffering of aluminium-saturated clays, when titrated above pH 7 with MgO, to the precipitation of mixed Mg-Al hydroxides. Again, Brydon & Ross (1966) proposed that double hydroxides of Mg-Al, Mg- $\text{Fe}^{3+}$  or possibly Mg-(Al,  $\text{Fe}^{3+}$ ), control the buffering capacity shown by chlorite minerals at pH 8 to pH 9 when treated with  $10^{-4} \text{ M}$  hydrochloric acid.

In the work reported here precipitates formed by adding caustic soda to mixed chloride solutions were aged in a dialysed medium using the procedure described by Gastuche & Herbillon (1962) and Gastuche, Bruggenwert & Mortland (1964) for Al and Al- $\text{Fe}^{3+}$  systems, respectively. Aging under these conditions extracts the ionic impurities strongly held in the gel framework and promotes crystallization of aluminium hydroxides for the Al system, and iron-bearing aluminium

hydroxides or aluminium-bearing hematites for the mixed Al-Fe<sup>3+</sup> system. Aging of the Mg-Al precipitates under similar conditions did not produce magnesian gibbsite or aluminous brucite. As soon as aluminium is introduced into the magnesium system, or vice-versa, compounds that are shown to be magnesium-aluminium hydroxycarbonates are formed. Two compounds were obtained with different Mg/Al ratios; they have similar X-ray patterns but the *d* spacings differ slightly; the most obvious difference is in their basal spacings that are 7.9 and 7.6 Å, approximately.

### SAMPLE PREPARATION

Solutions, 0.25 M in total cation content, prepared from MgCl<sub>2</sub>·6H<sub>2</sub>O and AlCl<sub>3</sub>·6H<sub>2</sub>O were mixed in various proportions and precipitated by NaOH at pH 10 with vigorous stirring. The flocculated precipitates were placed in cellulose dialysis bags and immersed in flasks containing 1 litre of distilled water at 60° C. The water was changed daily for 1 month. The sample was then removed and oven dried at 105° C.

TABLE 1. Al/Mg molar ratios in initial solutions

Sample No.	Al/Mg	Sample No.	Al/Mg
1	0/100	A	15/85
2	10/90	B	17/83
3	20/80	C	20/80
4	30/70	D	23/77
5	40/60	E	25/75
6	60/40	F	27/73
7	70/30	G	30/70
8	80/20	H	33/67
9	90/10	I	35/65
10	100/0		

Two sets of preparations were made (Table 1). The first (samples 1-10) covered the whole range of Mg/Mg+Al ratios in the initial solutions. Preliminary results for this set have already been published (Mortland & Gastuche, 1962). New compounds appeared over the entire range of composition of the mixed initial solutions, mixed with brucite when prepared from solutions containing much magnesium, and mixed with bayerite, from aluminium-rich solutions. Impurities were not detected in samples 3 and 4, which gave similar X-ray powder patterns (Table 2) but with slightly different *d*-spacings. Another set of samples (A-I) was made to investigate more fully the range of the composition of the solutions in which new compounds were formed.

Chemical analyses of the materials after dialysis showed that the solid samples contained proportionately less magnesium than the original solutions from which they were formed.



## SAMPLE CHARACTERIZATION

X-ray diffraction, chemical analysis, thermal analysis, infrared absorption spectra, electron microscopy and X-ray fluorescence spectral analysis were used to characterize the reaction products.

### *X-ray diffraction*

The materials were all micro-crystalline so only powder diffraction methods could be used. All samples were first examined as randomly-oriented specimens using powder camera and diffractometer methods. Oriented films of samples 3 and 4 were also examined (Brown, 1951) to distinguish basal and non-basal reflections. Accurate  $d$ -spacings of selected reflections from some samples were measured by scanning  $1/16^\circ$  ( $2\theta$ ) per minute with a diffractometer using dickite from Bodorgan, Anglesey (Smithson & Brown, 1957; Newnham, 1961) as a spacing standard.

### *Infrared spectra*

Samples were pelleted in KBr in the proportion of 0.25% and examined with a Beckman I.R.4 double beam spectrometer using  $\text{CaF}_2$  optics in the  $3\ \mu$  range and NaCl optics in the  $9\text{--}15\ \mu$  range.

### *X-ray fluorescence spectra*

The wavelength of the Al  $K_\alpha$  radiation from one sample (4) was compared with that from  $\text{AlPO}_4$  and from kaolinite to obtain information about the co-ordination of the aluminium (White, McKinstry & Bates, 1958).

### *Chemical analysis*

Some samples were analysed for  $\text{Al}_2\text{O}_3$ , MgO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , the latter being taken as the difference between the weight lost at  $1000^\circ\text{C}$  and the  $\text{CO}_2$  content. Because only small amounts were available, the results are not considered to be of the highest accuracy.

The cation exchange capacity was determined by the method of Mackenzie (1951). The chloride content was measured by dissolving 100 mg in 0.1 N nitric acid and determining chloride by the retarded chloride electrode method. Exchangeable chloride was determined by extracting with N  $\text{NaNO}_3$  solution and measuring chloride in the extract.

### *Thermal analysis*

Both differential thermal and thermogravimetric curves were obtained for some samples. In addition, the  $\text{CO}_2$  content was determined after heating to a temperature just above that at which the first weight loss was completed.

## RESULTS

*Phases produced*

Fig. 1 shows the phases formed from the entire range of initial solution compositions. Pure magnesium solutions yielded brucite and pure aluminium solutions gave a mixture of aluminium hydroxide species, bayerite with gibbsite and some nordstrandite. With mixed solutions new compounds were formed, together with brucite when the initial solutions contained much magnesium and with bayerite for aluminium-rich compositions. Neither the  $\text{Mg}(\text{OH})_2$  nor the  $\text{Al}(\text{OH})_3$  show changes in cell dimensions that would be caused by isomorphous substitutions. From initial solutions with  $\text{Mg}/\text{Mg} + \text{Al} = 0.83$  to  $\text{Mg}/\text{Mg} + \text{Al} = 0.67$ , the mixed Mg-Al hydroxycarbonates are formed without detectable amounts of other phases.

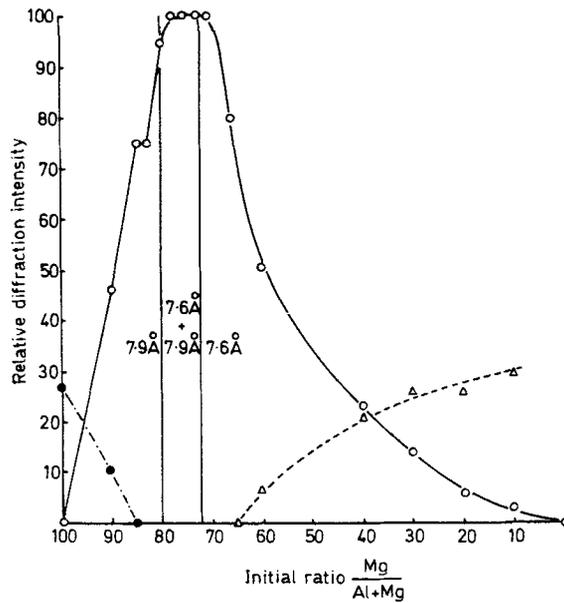


FIG. 1. Phases produced from solutions with different Mg/Mg + Al ratios. Intensities of the 7.6–7.9 Å hydroxycarbonate reflection (O), of the 4.71 Å bayerite reflection ( $\Delta$ ) and of the 4.75 Å of brucite ( $\bullet$ ) are plotted against solution composition.

*X-ray powder data for synthetic hydroxycarbonates*

The X-ray powder patterns of samples 3 and 4 were similar but distinct (Table 2). They resemble most the pattern reported by Feitknecht & Gerber (1942) for magnesium–aluminium double hydroxide and those given by Roy, Roy & Osborn (1953) for natural and synthetic hydrotalcites. Also included for comparison are patterns from the Powder Data File for hydrotalcite and manasseite and a diffractometer pattern of a sample labelled hydrotalcite from Snarum, Norway. This was found to be a mixture of predominant hydrotalcite with manasseite (see Frondel, 1941) and its pattern was indexed on the basis of a rhombohedral lattice

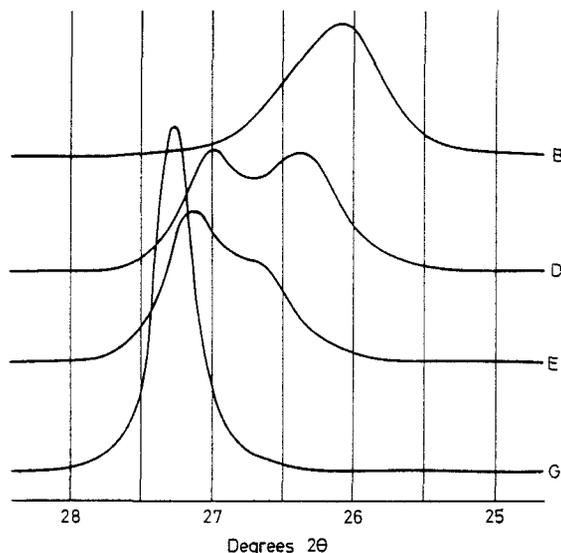


FIG. 2. Diffractometer traces of the 3.6–4.0 Å region for samples, B, D, E and G (Co  $K\alpha$ , 1/16 degree  $2\theta$  per min).

$a_H = 3.068 \text{ \AA}$ ,  $c_H = 23.43 \text{ \AA}$  for the hydrotalcite component and a hexagonal cell with  $a = 3.068 \text{ \AA}$ ,  $c = 15.62 \text{ \AA}$  for the manasseite component.

Although the powder camera patterns of the second set of preparations (A–I) indicated that these materials had a continuous range of basal spacings, slow scanning with a diffractometer showed that samples with compositions lying between those of samples 3 and 4 were mixtures (Fig. 2 and Table 3). The line breadths of the basal reflections are considerably less for the 7.6 Å modification (G and 4) indicating better developed crystals. Asymmetry of the 3.9 Å reflection from samples 2, A, B and C towards higher angles and slight asymmetry of the 3.8 Å reflection towards lower angles from samples F and G possibly indicates that small amounts of components with different spacings exist along with the main component. Sample 6 gave a symmetrical reflection and a distinctly smaller basal spacing, 7.580 Å compared with 7.596 Å for G and may represent the structural end-member but this sample contained some aluminium hydroxide impurity.

#### Thermal analysis

Fig. 3 shows d.t.a. curves for samples 1–10. The mixed hydroxides (pure in 3 and 4) give two peaks at 330° and 500° C for sample 3 and at 350° and 540° C for sample 4. Thermogravimetric curves showed that weight was lost in two distinct steps. In the first step, up to 280° C, about 12% of the initial weight was lost; between 280° and 460° C a further 30% was lost. Analysis of material after the first weight loss showed that no  $\text{CO}_2$  had been lost. Both  $\text{CO}_2$  and water were lost in the second step.

TABLE 3. Data on basal reflections of synthetic hydroxycarbonates

Sample No.	Initial Mg/Mg + Al	Basal spacings (Å)		Width at half height (degrees 2 $\theta$ ) of 3.8–3.9 Å reflection	Nature of 3.8–3.9 Å reflection
2	0.9	7.90	3.94	0.60°	Symmetrical
A	0.85	7.92	3.948	0.69°	Symmetrical
B	0.83	7.93	3.960	0.80°	Slight asymmetry towards lower spacings
C	0.80	7.87	3.937	0.70°	Slight asymmetry towards lower spacings
D	0.77	7.78	3.93 and 3.84		Two peaks of about equal intensity
E	0.75	7.68	3.88 and 3.82		Two peaks, 3.82 Å larger
F	0.73	7.65	3.81	0.44°	Slight asymmetry towards larger spacings
G	0.70	7.60	3.798	0.30°	Very slight asymmetry towards larger spacings
H	0.67	7.60	3.798	0.33°	Very slight asymmetry towards larger spacings
6	0.4	7.59	3.790	0.46°	Symmetrical
Dickite				0.18°	Symmetrical

*Infrared spectra*

Figs 4 and 5 show the infrared absorption spectra of some of the preparations. The spectra of the 7.9 and 7.6 Å materials differ. In both, the OH stretching vibration is remarkably simple and appears for the 7.9 Å material (B in Fig. 4) as a broad band centred at about 2.80  $\mu$  (3571  $\text{cm}^{-1}$ ); the corresponding absorption band for the 7.6 Å material (G in Fig. 4) is sharper and occurs at 2.85  $\mu$  (3508  $\text{cm}^{-1}$ ). For both, this absorption band is intermediate in frequency between that of brucite, sample 1, and the group of peaks that form this band for sample 10 which contains bayerite, gibbsite and nordstrandite. In the 7–14  $\mu$  region, the 7.9 Å material shows only a broad doubled  $\text{CO}_3^{=}$  band at 1400 and 1490  $\text{cm}^{-1}$ . The 7.6 Å material (G in Fig. 5) has a sharp and well-defined  $\text{CO}_3^{=}$  band at 1370  $\text{cm}^{-1}$  and broad absorption bands at 960, 860 and 757  $\text{cm}^{-1}$ . These may be Al–O vibration bands and Al–OH deformation bands. For gibbsite Kolesova & Ryskim (1959) report Al–O vibration bands at 798 and 747  $\text{cm}^{-1}$  and Al–OH deformation bands at 1020 and 969  $\text{cm}^{-1}$ .

*Aluminium co-ordination*

The wavelength of the Al  $K_\alpha$  radiation indicated that the aluminium was in six-fold co-ordination.

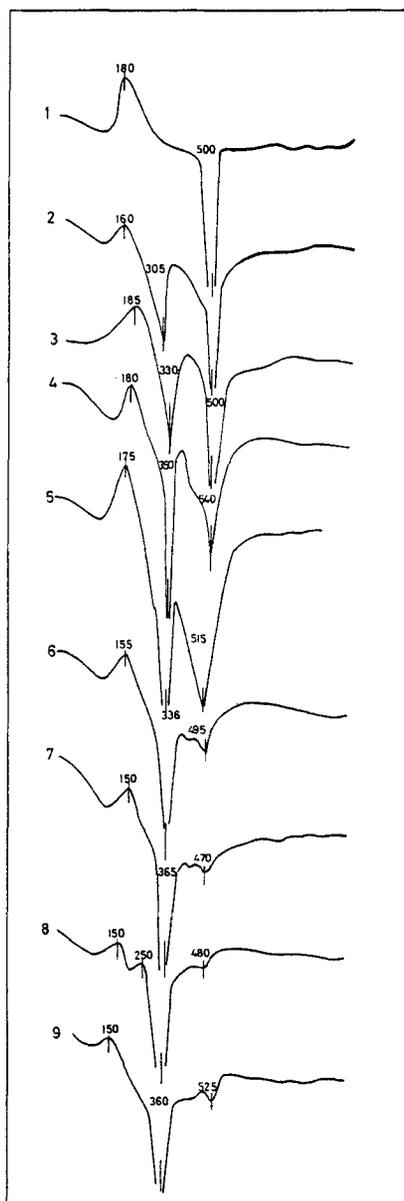


FIG. 3. D.t.a. curves for samples 1-9.

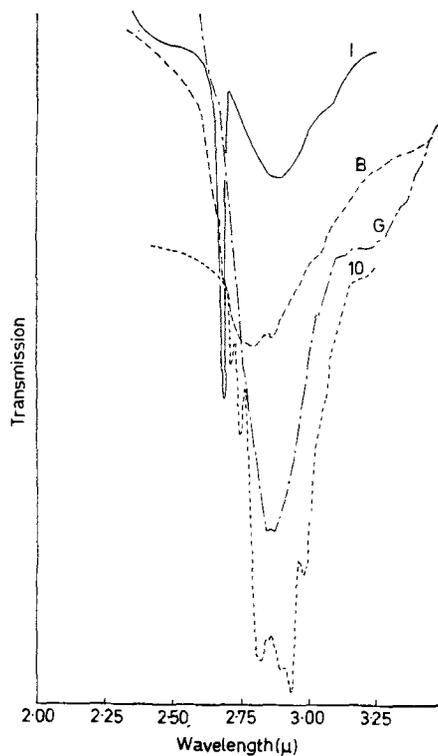


FIG. 4. Infrared absorption spectra in the 2.0–3.5  $\mu$  region for samples 1 (brucite), B (7.9 Å), G (7.6 Å) and 10 (mixture of bayerite, gibbsite and nordstrandite).

#### Chemical analyses

In view of the X-ray results, samples B, G and D were analysed because they represent the 7.9 Å phase, the 7.6 Å phase and an approximately 50 : 50 mixture. Table 4 gives the results along with the analysis of manasseite (Fronde!l, 1941) for comparison.

None of the samples had any cation exchange capacity. Small amounts of chloride remained after dialysis, probably because the chloride was not completely replaced by  $\text{CO}_3^{=}$  ions. The chloride is readily removed by washing with  $N$   $\text{NaNO}_3$  solution. Nitrate and carbonate ions are iso-structural and hence, if the structure can accommodate  $\text{CO}_3^{=}$  ions, it is also likely to accept  $\text{NO}_3^-$  ions. Roy *et al.* (1953) synthesized a compound thought to be the nitrate analogue of hydrotalcite, in which  $\text{NO}_3^-$  replaces the  $\text{CO}_3^{=}$  of hydrotalcite. Comparison of Fig. 1 with Fig. 6 shows that the maxima in the content of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and Cl measured chemically and the maximum in the content of synthetic hydroxycarbonates obtained from X-ray data, coincide.

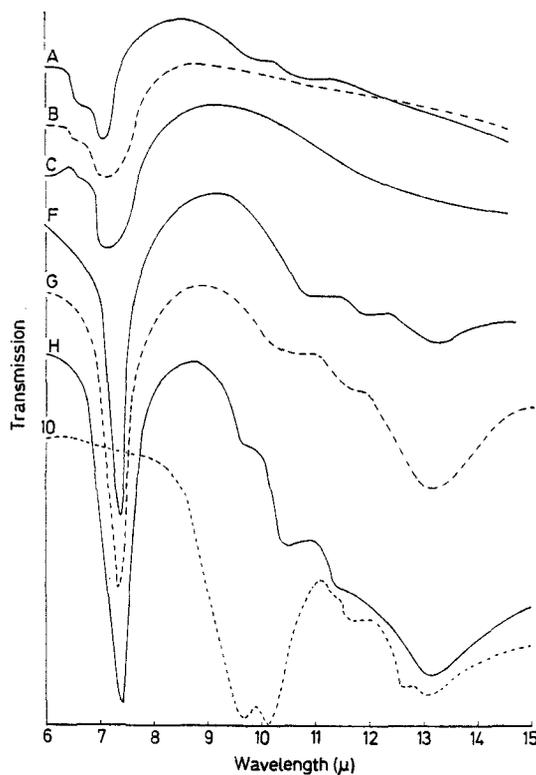


FIG. 5. Infrared absorption spectra in the 6–15  $\mu$  region for samples A (brucite), B and C (7.9 A), F, G and H (7.6 A), and 10 (mixture of bayerite, gibbsite and nordstrandite).

TABLE 4. Chemical analyses of synthetic Mg-Al hydroxycarbonates

	1	2	3	4	5	6	7
MgO	41.8	43.50	37.2	39.12	34.2	34.61	39.38
Al <sub>2</sub> O <sub>3</sub>	14.5	15.09	17.8	18.72	23.4	23.68	16.59
Fe <sub>2</sub> O <sub>3</sub>							0.21
CO <sub>2</sub>	8.7	9.05	7.0	7.36	7.6	7.69	7.48
H <sub>2</sub> O	31.1	32.36	33.1	34.81	33.6	34.00	36.34

1. Synthetic Mg-Al hydroxycarbonate, sample B (analyst, M. C. Gastuche).
2. Analysis 1, recalculated to 100%.
3. Synthetic Mg-Al hydroxycarbonate, sample D (analyst, M. C. Gastuche).
4. Analysis 3, recalculated to 100%.
5. Synthetic Mg-Al hydroxycarbonate, sample G (analyst, M. C. Gastuche).
6. Analysis 5, recalculated to 100%.
7. Manasseite, Snarum, Norway, recalculated to 100% (FrondeI, 1941).

## INTERPRETATION OF X-RAY POWDER PATTERN

Feitknecht & Gerber (1942) indexed the powder pattern of their materials on the basis of a rhombohedral lattice with  $a_H = 3.10 \text{ \AA}$ ,  $c_H = 23.8 \text{ \AA}$ . Feitknecht & Held (1944) remarked that the reflections were broadened, so that indexing may not be unequivocal.

The patterns of the 7.6 and 7.9  $\text{\AA}$  materials are so similar that it is sufficient to consider only one of these, the 7.6  $\text{\AA}$  phase. The reasons for the small differences between the patterns of the two materials will be discussed later.

Electron microscopy (Mortland & Gastuche, 1962; Gastuche, 1964) showed that the crystals were small hexagonal or pseudo-hexagonal plates about 1  $\mu$  in diameter. X-ray patterns of oriented specimens allowed the separation of the basal reflections, which are all sharp, from the non-basal reflections, of which some are very sharp and some are broad and diffuse. These features resemble those found in powder patterns of layer silicates in which two-dimensionally regular layers are stacked with some degree of disorder; the patterns of our synthetic materials can be explained in an analogous way.

*The basal reflections*

The basal spacing,  $d = 7.60 \text{ \AA}$ , and all the higher orders that can occur, can be seen on patterns of oriented flakes. This spacing clearly represents the thickness of the unit layer.\* A layer of this thickness will be made up of three superposed sheets\* of oxygens (at this stage  $\text{O}^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^-$  and  $\text{H}_2\text{O}$  are not distinguished) with the successive sheets more or less close packed.

*The non-basal reflections*

The presence of both sharp and diffuse reflections indicate a partially disordered structure and the pattern was interpreted on this basis.

First an attempt was made to find the ideal fully ordered structure(s) from which the real structure is derived by stacking faults. The hexagonal morphology suggested that the atomic arrangement in the plane of the layers was hexagonal. The non-basal reflection with  $d = 2.6 \text{ \AA}$  was, therefore, taken to be 100 (hexagonal indices), and from this and consideration of the 110 reflection,  $d = 1.524 \text{ \AA}$ , the value of  $a$  was found to be  $3.048 \text{ \AA}$ . Attempts were made to index the pattern on the basis of hexagonal cells with  $a = 3.048 \text{ \AA}$  and  $c = n \times 7.60 \text{ \AA}$ . No single value of  $n$  satisfied all the observed reflections but all except the very weak reflection with  $d = 4.57 \text{ \AA}$  could be indexed if  $n$  were allowed the values 2 and 3 (Table 5). The very sharp reflections,  $d = 1.524 \text{ \AA}$ ,  $1.493 \text{ \AA}$  and  $1.415 \text{ \AA}$  could be indexed  $11l$  with  $n = 1$  or  $2$  or  $3$ . The broad reflections, which are indexed  $hko$  on the above basis, correspond to the heads of  $hk$  bands from a turbostratic arrangement of layers and the subsequent broad maxima indicate a tendency to ordering with two- and three-layer sequences.

\* In this discussion a sheet is one atom thick; a layer is made up of several sheets, superposed in some regular way to form a unit of structure.

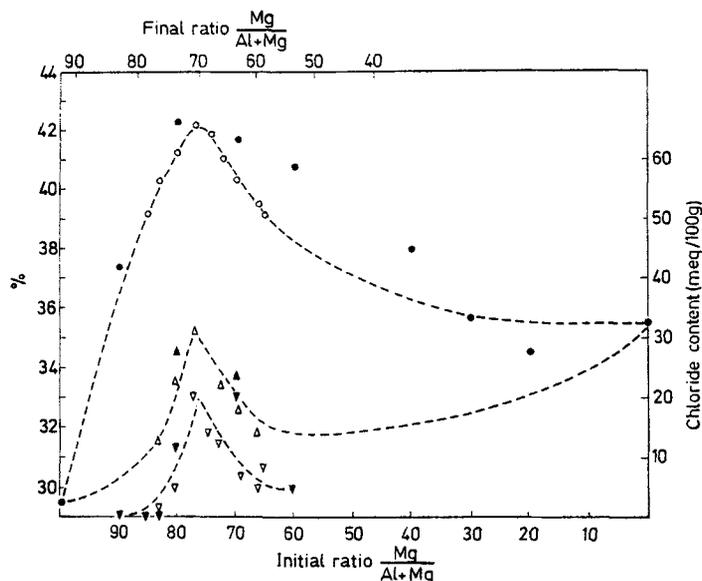


Fig. 6. Weight loss at 1000° C (O, ●), water content (Δ, ▲) and chloride content (▽, ▼) as a function of Mg/Mg + Al ratios in initial solutions. Filled symbols are for samples 1-10, open symbols for samples A-I.

Most of the features observed are explained if the structure consists of two-dimensionally regular hexagonal layers with  $a' = 3.048 \text{ \AA}$  and a layer thickness of  $7.6 \text{ \AA}$ . The layers are superposed with considerable stacking disorder but there is a tendency for two- and three-layer sequences to occur. No attempt was made to assess quantitatively the relative frequency of the two kinds of stacking or the size of the ordered sequences, but the line breadths indicate that only a few successive layers maintain any one stacking sequence.

The sharp reflections indicate a hexagonal sub-cell with  $a' = a/\sqrt{3} = 1.76 \text{ \AA}$  oriented so that the angle between  $a$  and  $a'$  is  $30^\circ$ . This is the fully-disordered sub-cell (see Kasper, Lucht & Harker, 1950) and arises from the indeterminate type of packing which does not follow exactly either a two-layer or a three-layer sequence. The shifts allowed between the sheets of oxygens are  $\pm n \times 1.76 \text{ \AA}$  ( $n \neq 3m$ ) along the directions of the traces of the 110 planes on the basal plane. Reflections from the fully disordered sub-cell are sharp; the other reflections are diffuse. Of the reflections within the Co  $K_\alpha$  powder sphere only 111 (large cell indices) reflections will be sharp and this agrees with the observed patterns.

There remains a broad very weak reflection,  $d = 4.57 \text{ \AA}$ , which cannot be accounted for on the basis of a unit layer with  $a = 3.048 \text{ \AA}$ , and a layer thickness of  $7.60 \text{ \AA}$ . It is probably the 100 reflection from a supercell having  $a'' = a\sqrt{3} = 5.28 \text{ \AA}$  and may be attributed to ordering or a tendency to ordering of the cations among the available sites in the brucite-like layer of the structure-determining oxygen framework.

TABLE 5. Indexing of powder pattern of synthetic hydroxycarbonate, sample 4; spacings in Å

1 <i>d</i> obs. sample 4	2 <i>d</i> calc.	3 <i>hkl</i>	4 <i>hkl</i>	5 <i>hkl</i>
7.63	7.60	003	002	001
4.57				
3.81	3.80	006	004	002
	2.640	100	100	100
	2.622	101		
2.60	2.601		101	
	2.572	102		
2.532	2.533	009	006	003
2.36	2.341		103	
2.26	2.285	105		
2.01	1.993		105	
1.91	1.937	108		
1.897	1.900	00, 12	008	004
1.523	1.524	110	110	110
	1.521	111		
	1.520	00, 15	00, 10	005
1.493	1.494	113	112	111
1.415	1.415	116	114	112
	1.320	200	200	200
	1.318	201		
1.317	1.317	10, 15	10, 10	105
1.300	1.315		201	
	1.311	202		
	1.306	119	116	113
	1.300	203	202	201
1.274	1.277		203	
	1.268	205		
1.262	1.267	11, 10; 00, 18	00, 12	006
	1.224		10, 11	
1.21	1.223	207		
	1.211		205	
	1.004	10, 21	10, 14	107
0.999	0.9977	210	210	210
	0.9967	211		
	0.9966	20, 15	20, 10	205
0.993	0.9955		211	
	0.9939	212		
0.979	0.9789		213	
0.972	0.9746	215		
	0.9741	11, 18	11, 12	116
0.9500	0.9500	00, 24	00, 16	008

1. Observed reflections from sample 4. Parentheses indicate the edges of bands.

2. Calculated spacings for hexagonal cells with  $a = 3.048$ ,  $c = 7.60$ ,  $15.20$  and  $22.80$  Å. Only reflections sufficiently close to be possible contributors to observed reflections are listed.

3, 4 and 5. Indices for reflections from cells with  $a = 3.048$  Å and  $c = 22.80$  Å,  $c = 15.20$  Å and  $c = 7.60$  Å, respectively.

The X-ray powder data show that there is no true unit cell but the unit of structure is the unit layer defined by the layer thickness and the length of the side of the hexagonal cell in the plane of the layers. The dimensions of the unit layer, determined accurately from their basal spacings and the spacing of the very sharp 110 reflections is  $a = 3.048 \text{ \AA}$ , layer thickness =  $7.60 \text{ \AA}$  for the Al-rich compound (G) and  $a = 3.072 \text{ \AA}$ , layer thickness =  $7.90 \text{ \AA}$  for the Al-poor compound (B).

## DISCUSSION

Our results show that the synthetic materials are magnesium-aluminium hydroxycarbonates. They resemble the natural minerals hydrotalcite and manasseite and also the magnesium aluminium double hydroxides and hydroxychlorides described by Feitknecht *et al.* (Feitknecht & Gerber, 1942; Feitknecht & Held, 1944). They differ from both of these groups of materials in some respects.

From initial solutions with Mg/Mg+Al ratios 0.83-0.67 two compounds characterized by X-ray powder data, are formed that have Mg/Al ratios of about 5:1 and 2:1. Their X-ray powder patterns are similar but distinct. They are layer structures and can be characterized by their basal spacings. The basal spacing of the 2:1 Mg-Al compound is  $7.6 \text{ \AA}$ , the 5:1 compound has a basal spacing of  $7.9 \text{ \AA}$ . The X-ray powder patterns show a considerable similarity to those of the minerals hydrotalcite and manasseite and also to that of the synthetic material prepared by Feitknecht.

The compounds have the same basic structure which consists of a partially disordered stacking of three-dimensionally regular unit layers. The synthetic materials resemble the minerals manasseite,  $a = 3.06 \text{ \AA}$ ,  $c = 2 \times 7.67 \text{ \AA}$  and hydrotalcite,  $a = 3.06 \text{ \AA}$ ,  $c = 3 \times 7.67 \text{ \AA}$  (Frondel, 1941) in the size of the unit layers and also in their tendency to form two-layer and three-layer stacking sequences.

Despite a strong chemical and structural similarity, the mineral hydroxycarbonates differ from the synthetic hydroxycarbonates in forming stacking-ordered structures, in having on Mg/Al ratio of 3:1, intermediate between those found for our materials, and in having structural parameters intermediate between those of the synthetic compounds.

The synthetic hydroxycarbonates also resemble the compounds described by Feitknecht *et al.* (Feitknecht & Gerber, 1942; Feitknecht & Held, 1944) as double hydroxides and hydroxychlorides of magnesium and aluminium. In the materials we studied  $\text{CO}_3^{2-}$  probably takes the place of  $\text{Cl}^-$  in Feitknecht's preparations. These were reported to have wide differences in Mg/Al ratios, without detectable differences in cell dimensions which were given as  $a = 3.09 \text{ \AA}$ ,  $c = 23.7 \text{ \AA} = 3 \times 7.9 \text{ \AA}$ . Our findings differ in that differences in  $d$  spacings are found that correlate with compositional differences. Infrared absorption spectra confirm the presence of carbonate and also indicate a trioctahedral hydroxide structure. Octahedral co-ordination of aluminium is also suggested by the wavelength of the Al  $K_\alpha$  X-ray fluorescent radiation.

The synthetic hydroxycarbonates are, therefore, new compounds but they have considerable chemical and structural resemblances to double hydroxides of

magnesium and aluminium and also to minerals of the pyroaurite group of which hydrotalcite and manasseite are the magnesium aluminium polymorphs.

An account of the structure and structural chemistry of the synthetic hydroxycarbonates and a general structural scheme, deduced from our findings, for a wide range of related minerals and compounds will be given in Part II (Brown & Gastuche, 1967).

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