

## MIXED MAGNESIUM-ALUMINIUM HYDROXIDES

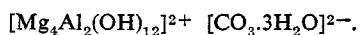
### II. STRUCTURE AND STRUCTURAL CHEMISTRY OF SYNTHETIC HYDROXYCARBONATES AND RELATED MINERALS AND COMPOUNDS

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**ABSTRACT:** A structural scheme is proposed for the synthetic Mg-Al hydroxycarbonates described in Part I (Gastuche, Brown & Mortland, 1967) based on chemical and X-ray powder data. The structure consists of positively-charged brucite-like layers in which Al replaces Mg up to a maximum of about one in three sites. The positive charge is balanced by an interlayer sheet containing carbonate groups and water molecules. The idealized structural formula for the Al-rich material is:



A similar structural scheme seems to apply to many other materials including the minerals of the pyroaurite group, the compound  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$  and the related mineral hydrocalumite, a nickeliferous magnesium hydroxide mineral described recently and to many synthetic products that have been referred to as double sheet structures.

Part I (Gastuche, Brown & Mortland, 1967) described the characterization of mixed Mg-Al hydroxycarbonates prepared in a dialysed system. The two compounds formed were shown to resemble minerals of the pyroaurite group and the double hydroxides of Mg and Al, but to differ significantly from both. In the first part of this paper the structure and structural formulae for the hydroxycarbonates deduced from chemical analysis and X-ray powder patterns by crystal chemical considerations are presented. The structural scheme found for the synthetic hydroxycarbonates is shown to apply to a wide range of natural and synthetic materials

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whose structures have not been satisfactorily explained before. The possible application of synthetic compounds of this kind to studies of layer silicates, particularly chlorites and chlorite-like minerals, is suggested.

## STRUCTURE OF SYNTHETIC HYDROXYCARBONATES

In Part I (Gastuche *et al.*, 1967) the unit of structure was shown to be a unit layer defined by the layer thickness and hexagonal axes in the plane of the layers, and the dimensions were given for the two modifications.

### *Contents of unit layer*

The structural chemistry can be considered on the basis of the unit layer. Assuming a density of 2.00 for the synthetic materials (the calculated density for the minerals hydrotalcite and manasseite which were shown to be very similar to the synthetic materials) the contents of the unit layer of samples B, D and G

TABLE 1. Unit layer contents of synthetic hydroxycarbonates

	Sample		
	B	D	G
Atom(s)			
Mg	0.841	0.736	0.632
Al	0.229	0.276	0.340
Mg + Al	1.070	1.012	0.972
C	0.159	0.126	0.128
H	2.808	2.934	2.782
O	2.907	2.869	2.789

Calculated assuming density = 2.00 and unit layer parameters given in Part I (Gastuche *et al.*, 1967) for B and G, and for D, layer thickness = 7.77 Å,  $a = 3.06$  Å.

(Table 1) were calculated from the chemical analysis given in Part I, Table 4 (Gastuche *et al.*, 1967). The assumption that the density of all three materials is the same is unlikely to be correct. Sample G, with the smaller structural unit, is probably more dense than B but the calculations, considered with the X-ray data, suffice to indicate the main structural features.

These are: (i) the unit layer contains one metal cation, i.e. Mg + Al is approximately equal to one; (ii) the unit layer contains three oxygens. This is what would be expected for a layer structure having a basal spacing of 7–8 Å and  $a = 3.1$  Å, approximately; (iii) the decrease in Mg/Al ratio from B to G is caused by increasing replacement of Mg by Al. This is paralleled by a decrease in  $a$  from 3.072 to 3.048 Å and a decrease in layer thickness from 7.9 to 7.60 Å.

A structure can be proposed by considering the contents of the unit layer, the structural information derived from the X-ray data, and the results of thermal

analysis, infrared absorption spectra, electron microscopy and X-ray fluorescence spectra. The content of the unit layer is consistent with a layer structure in which each layer is made up of three sheets of oxygens (or hydroxyls, etc.). Two of these sheets, probably made up of hydroxyls, are held together by the cations and form layers like those in brucite but having some of the  $\text{Mg}^{2+}$  replaced by  $\text{Al}^{3+}$ . This substitution leads to a positive charge on the octahedral layers which is balanced by a sheet containing anions taken up between the layers. In our materials the charge-balancing anions are mainly  $\text{CO}_3^{=}$  groups. In addition to  $\text{CO}_3^{=}$ , water molecules are taken up in the 3 Å thick interlayer sheet, ideally enough to fill the vacant sites in a close-packed hexagonal array, although the sheet may not be entirely filled in practice.

The following structural formula can be written for samples B (7.9 Å) and G (7.6 Å) in terms of a brucite-like layer and an interlayer sheet:

	Brucite-like layer	Interlayer sheet
<b>B</b>		
Composition	$(\text{Mg}_{0.841} \text{Al}_{0.159}) (\text{OH})_2$	$\text{C}_{0.159} \text{O}_{0.907} \text{H}_{0.808} \text{Al}_{0.070}$
Charge	+ 0.159	— 0.160
<b>G</b>		
Composition	$(\text{Mg}_{0.632} \text{Al}_{0.340}) (\text{OH})_2$	$\text{C}_{0.128} \text{O}_{0.789} \text{H}_{0.782}$
Charge	+ 0.284	— 0.284

All the analytical errors and errors introduced by assuming the same density, accumulate in the contents of the interlayer sheet. Taking account of these, the data seem to agree with the structural scheme proposed above.

Regular trioctahedral brucite-like layers with the Mg/Al ratios of B and G would have  $a = 3.08$  and  $3.04$  Å, respectively for  $\text{Mg-O} = 2.10$  Å and  $\text{Al-O} = 1.89$  Å. The observed values,  $3.072$  and  $3.048$  Å, do not agree in detail with the calculated values but errors in chemical analysis, differences in the bond lengths in the compounds from those taken for calculations and departures from regular octahedra may explain the small discrepancy. The difference in layer thickness of the two compounds is explained by the greater coulombic attractive force between the positively charged brucite-like layer and the negatively charged interlayer sheet for the material having more Al for Mg substitution.

The infrared absorption spectra and the X-ray emission spectra both indicate that the aluminium is octahedrally co-ordinated. Thus, the dimensions of the structural unit and the spectral evidence are consistent and strongly suggest that most, if not all, of the aluminium is in the brucite-like layer and not in the interlayer sheet, as proposed by Feitknecht.

The structure is, therefore, a layer structure made up of positively-charged brucite-like layers in which Al substitutes for some Mg, up to a maximum of about one in three sites. The positive charge on the structure-determining brucite-like layers is balanced by an interlayer sheet containing carbonate groups, the

plane of which is parallel to the plane of the layers. Most of the sites not occupied by anions in the interlayer sheet are occupied by water molecules. The weight losses and the d.t.a. curves support this interpretation. The weight loss associated with the first step in the curve amounts to about one-third of the total water content and is presumably caused by loss of water molecules from the interlayer sheet. The second weight loss, caused by evolution of  $\text{CO}_2$  and structural hydroxyls, occurs at a higher temperature.

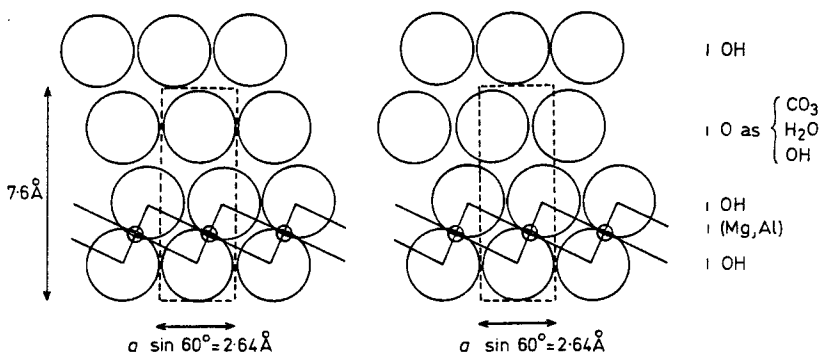
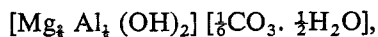


FIG. 1. Projection along  $a$  of idealized structures with two possible arrangements of the interlayer oxygens. The unit layer is outlined.

Fig. 1 shows idealized structures in which the interlayer oxygens have been arbitrarily sited in two sets of close-packed positions relative to the hydroxyls of the brucite-like layer. The basal spacing, 7.6–7.9 Å, indicates that the structure is not a completely close-packed one for which a basal spacing of about 7 Å would be expected. The ideal close-packed structures shown in Fig. 1 are likely to be modified by hydrogen bonding involving the hydroxyls of the aluminium-substituted brucite-like layer (cf. gibbsite, Bernal & Megaw, 1935) and the oxygens of the interlayer water molecules and carbonate groups. Stacking faults can readily arise at the interfaces between the brucite-like layers and the interlayer anion-water sheets and our synthetic hydroxycarbonates have irregular stacking sequences.

### IDEAL STRUCTURE

An ideal structural formula for the mixed Mg–Al hydroxycarbonate with maximum Al for Mg substitution can be written:



equivalent to  $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 9\text{H}_2\text{O}$ .

The analysis for our sample G and the analysis calculated from the ideal formula are compared in Table 2.

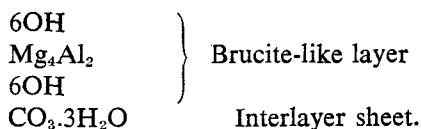
TABLE 2. Comparison of calculated and observed analysis of sample G

	1	2
MgO	34.36%	34.6%
Al <sub>2</sub> O <sub>3</sub>	21.73	23.7
CO <sub>2</sub>	9.38	7.7
H <sub>2</sub> O	34.53	34.0

1. Calculated from ideal formula 4MgO.Al<sub>2</sub>O<sub>3</sub>.CO<sub>2</sub>.9H<sub>2</sub>O.

2. Found for sample G.

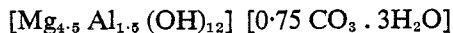
The ideal unit layer for an ordered arrangement of cations can be written schematically:



## RELATED COMPOUNDS

The structural scheme proposed above also applies to other synthetic and natural materials.

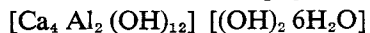
(i) Minerals of the pyroaurite group: the minerals that most resemble the synthetic Mg-Al hydroxycarbonates are the rhombohedral hydrotalcite for which Frondel (1941) reports a structural unit cell with  $a = 3.065 \text{ \AA}$ ,  $c = 23.075 \text{ \AA}$ , and the hexagonal manasseite with  $a = 3.060 \text{ \AA}$ ,  $c = 15.34 \text{ \AA}$ . These cells represent the ordered three-layer and two-layer stacking of layers  $7.68 \text{ \AA}$  thick. The ideal composition for hydrotalcite and manasseite according to Frondel is  $\text{Mg}_6\text{Al}_2(\text{OH})_{16} \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}$  and can be rewritten:



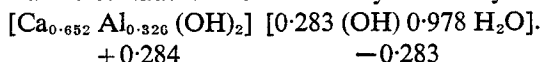
for comparison with our ideal formula. It seems, therefore, that hydrotalcite and manasseite are also composed of positively-charged brucite-like layers with carbonate ions and water molecules in the interlayer sheet. They differ from our materials in having a Mg/Al ratio of 3:1, a composition not found in our synthetic materials even though the Mg/Al ratios of the initial solutions and of our products bracketed it. The layer thickness,  $7.69 \text{ \AA}$  given by Frondel would be expected for Al for Mg substitution intermediate in amount between that of our samples B and G. The minerals stichtite and barbertonite, and pyroaurite and sjögrenite are also related. They have similar structural parameters to hydrotalcite and manasseite but differ in that  $\text{Cr}^{3+}$  in the former pair and  $\text{Fe}^{3+}$  in the latter replace the  $\text{Al}^{3+}$  of hydrotalcite and manasseite.

(ii) The compound that has been given the ideal formula  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$

(Roberts, 1957) and the related mineral hydrocalumite also resemble the synthetic hydroxycarbonates. The formula for  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$  can be recast:



or if recalculated from the ideal formula, the dimensions of the structural unit and the density given by Buttler, Dent Glasser & Taylor (1959) the contents of the unit layer equivalent to that found for the synthetic hydroxycarbonates are:



According to Buttler *et al.* (1959) this material has a layer structure with a layer thickness of 7.92 Å and a hexagonally based structure unit with  $a = 5.74$  Å. The structure is likely to be based on three superposed oxygen sheets as in our materials. The cell base corresponds to the cell base with  $a'' = 5.28$  Å detected for sample G and probably arises as in our materials from the ordering of the cations among the octahedral sites in the brucite-like layer.

This compound is therefore likely to have a structure in which octahedrally co-ordinated positively-charged layers of ideal composition  $[\text{Ca}_2 \text{Al}(\text{OH})_6]^{+1}$  are interstratified with sheets containing enough  $\text{OH}^-$  ions to balance the positive charge and water molecules to complete this sheet. The suggestion of Buttler *et al.* (1959) that the structure of hydrocalumite is derived from that of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$  by the substitution of a  $\text{CO}_3^{=}$  for  $2\text{OH}^- + 3\text{H}_2\text{O}$  cannot be taken as proved. The chemical analysis on which the suggestion is based is not accurate enough to disprove alternative suggestions such as the substitution of a  $\text{CO}_3^{=}$  for  $2\text{OH}^- + 1\text{H}_2\text{O}$ , which has the added attraction of replacing three oxygens with three oxygens.

(iii) The new nickeliferous magnesium hydroxide from Pennsylvania, U.S.A., described by Lapham (1965), also seems to be structurally and chemically related to the hydroxycarbonates. The chemical data are not good enough to warrant the calculation of a structural formula but the similarity in X-ray powder data suggest a structure in which brucite-like layers containing  $\text{Mg}^{2+}$  and some  $\text{Ni}^{3+}$  are interleaved with an anion sheet of hydroxyls and water molecules.

(iv) Many of the synthetic compounds prepared by Feitknecht and collaborators (Feitknecht, 1942, 1954), by Glemser & Einerhand (1950), and by Longuet-Escard (1951) also seem to be closely related structurally to the materials described above.

## DISCUSSION

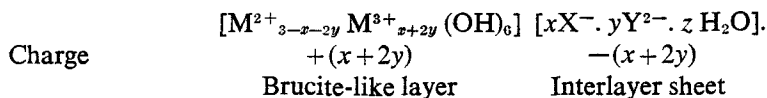
From the detailed work on the synthetic hydroxycarbonates and the consideration of structurally related compounds a general structural scheme that differs from the structures suggested before, can be proposed for the minerals and compounds already discussed and for the synthetic compounds referred to in (iv) above.

They will have layer structures with layers 7.5–8 Å thick. The layers will be composed of three sheets of anions. Two of these sheets of anions will be close packed hydroxyls\* held together by octahedrally co-ordinated divalent ( $\text{Mg}$ ,  $\text{Ni}^{2+}$ ,

\* Monovalent anions  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  can also form octahedrally co-ordinated layers with appropriate divalent cations and analogous structures based on layers of this kind may also form.

Ca,  $\text{Co}^{2+}$ , Zn,  $\text{Mn}^{2+}$ , Cd,  $\text{Fe}^{2+}$ ) and trivalent (Al,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Ni}^{3+}$ ) metal cations forming octahedrally co-ordinated hydroxide layers like those found in brucite. The substitution of trivalent for divalent metal cations leads to a positive charge on the brucite-like layer. This is balanced by sheets of anions ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) with water molecules in some or all of the sites remaining unoccupied by anions. The interlayer water molecules are easily removed without disrupting the structure. The upper limit of substitution of trivalent for divalent cations is probably about one trivalent to two divalent cations. This is the largest substitution found in our synthetic hydroxycarbonates. Forms with ordered and disordered arrangements of the cations among the sites in the brucite-like layer will be possible, and both ordered and disordered stacking sequences will be found. Because of the similar energies of the alternative stacking sequences, fully ordered forms will probably occur only under special conditions.

An ideal general structural formula for compounds of this type would be:



where  $\text{M}^{2+}$  are divalent cations,  
 $\text{M}^{3+}$  are trivalent cations,  
 $\text{X}^-$  are monovalent anions,  
 $\text{Y}^{2-}$  are divalent anions,  
 $x + 2y \leq 1$ ,

and the number of large atoms in interlayer sites is three ideally.

Differences in basal spacing are likely to be found that will result from changes in attractive forces caused by changes in the amount of trivalent for divalent substitution; larger amounts of substitution will give smaller basal spacings. This will be the main cause of changes in basal spacing for materials with interlayer sheets containing  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  and  $\text{H}_2\text{O}$ , but larger interlayer anions will also increase the basal spacing. Larger basal spacings will be obtained when anions larger than  $\text{OH}^-$  form the brucite-like layer. Analogous structures with larger anions in the interlayer sheet, e.g.  $\text{SO}_4^{2-}$ , are also possible. In these the basal spacings would be larger than 8 Å and the manner of packing the interlayer anion sheet between the brucite-like layers will also differ.

In the structure proposed above both divalent and trivalent cations are in the brucite-like layers, developing on them a positive charge that is balanced by interleaved anion-water sheets. This structure differs from those previously accepted for similar materials.

For compounds that have been ideally formulated  $\text{M}''(\text{OH})_2 \cdot \frac{1}{4} \text{M}''' \text{O.OH}$  or  $\text{M}''(\text{OH})_2 \cdot \frac{1}{4} \text{M}'''(\text{OH})_3$ , Feitknecht (see *Structure Reports*, Vol. 9, p. 281, for references) proposed a structure in which brucite-like  $\text{M}''(\text{OH})_2$  layers, containing the divalent cations only, are interleaved with disordered or amorphous molecular sheets, about 3 Å thick, containing the trivalent cations, oxygens and hydroxyls. In chloride-containing materials some of the interleaved hydroxyls were said to

be replaced by chloride ions. Glemser & Einerhand (1950), on the erroneous assumption that a disordered interlayer sheet would make no contribution to the intensities of X-ray reflections, proposed a structure for the compound  $\text{Ni}(\text{OH})_2 \cdot \frac{1}{4}\text{NiO} \cdot \text{OH}$  in which amorphous sheets of  $\text{NiO} \cdot \text{OH}$  are sandwiched between octahedrally co-ordinated  $\text{Ni}(\text{OH})_2$  layers. Lapham (1965) has accepted this structure for a new nickeliferous magnesium hydroxide mineral from Pennsylvania, believing the structure to be one in which disordered  $\frac{1}{4}(\text{Ni},\text{Fe})\text{O} \cdot \text{OH}$  sheets are interlaminated with  $\text{Mg}(\text{OH})_2$  layers, but gave no new supporting evidence.

These structures are unsatisfactory. It does not seem possible for the interlayer sheet to be structureless when it is only 3 Å thick and is sandwiched between ordered layers. The positions of the trivalent cations are not specified and it is difficult to suggest structurally reasonable sites. The differences in structural dimensions found for the synthetic hydroxycarbonates with different Mg/Al ratios, for sjögrenite and brugnatellite (see Frondel, 1941) and for different nickeliferous magnesium hydroxides reported by Lapham (1965), are not easily explained on the basis of the structure. Neither does it explain why compounds of this kind require some trivalent cations in addition to the divalent cations, nor why the ratio of trivalent to divalent seems to be limited at about 1:2.

The structure we have deduced for the synthetic hydroxycarbonates resolves these difficulties. Some trivalent cations are needed to develop the positive charge on the brucite-like layer. The interlayer anion sheet is necessary to neutralise the positive charge produced. The ratio of trivalent to divalent cations that can be incorporated into a trioctahedral layer is limited to about 1:2. This is set by the balance of forces between cation-cation repulsion across shared octahedral edges, anion-anion repulsion along the shared edges, and cation-anion bonds within octahedra (Radoslovich, 1963). Because  $\text{M}'''-\text{OH}$  bonds are shorter than  $\text{M}''-\text{OH}$  bonds, increasing substitution of trivalent for divalent cations causes a decrease in the *a* dimension of the brucite-like layer, which, being the most strongly bonded part of the structure, controls the dimensions of the entire structure. The decrease observed in layer thickness with increased substitution of trivalent for divalent cations is caused by the increased coulombic attractive force between the positively-charged brucite-like layer and the negatively-charged interlayer sheet. Finally, in our structure the interlayer sheet does not contain cations but is composed of a sheet of anions and water molecules arranged between the hydroxyl sheets of adjacent brucite-like layers.

The structural scheme we propose is likely to apply, with modification, to a wide range of materials. Precise parameters for the atoms cannot be obtained from our data. These and confirmation of the correctness of our structure can be obtained only by single crystal structure determinations.

#### RELEVANCE TO LAYER SILICATES

In addition to the compounds discussed above, the positively charged brucite-like octahedral layers found in the synthetic hydroxycarbonates is very similar to the brucite-like layer in chlorites. The charge-balancing anion-water sheet in our



materials is replaced in chlorites by the negatively-charged aluminosilicate talc-like layer. The charge on our materials,  $0.020/\text{\AA}^2$  for B and  $0.035/\text{\AA}^2$  for G, covers about the same range as the charge on the brucite-like layer in chlorites,  $0.02\text{--}0.04/\text{\AA}^2$ .

Synthetic compounds such as those described should prove useful as models for the study of the positively-charged brucite-like layer in the chlorite minerals, without the confusing effects of the octahedral layer in the talc-like layer. For example, the interpretation of infrared absorption bands given by chlorites may be assisted by the study of spectra of synthetic compounds in which not only the composition and degree of substitution of the brucite-like layer may be altered but also the nature of the intersheet anion may be varied independently.

#### REFERENCES

- BERNAL J.D. & MEGAW H.D. (1935) *Proc. R. Soc.* **A151**, 384.  
BUTTLER F.G., DENT GLASSER L.S. & TAYLOR H.F.W. (1959) *J. Am. ceram. Soc.* **42**, 121.  
FEITKNECHT W. (1942) *Helv. chim. Acta*, **25**, 555.  
FEITKNECHT W. (1954) *Kolloidzeitschrift*, **136**, 152.  
FRONDEL C. (1941) *Am. Miner.* **26**, 295.  
GASTUCHE M.C., BROWN G. & MORTLAND M.M. (1967) *Clay Miner.* **7**, 177.  
GLEMSER O. & EINERHAND J. (1950) *Zeit. anorg. allg. Chem.* **261**, 43.  
LAPHAM D.M. (1965) *Am. Miner.* **50**, 1708.  
LONGUET-ESCARD J. (1951) *Mém. Serv. chim. de l'Etat (Paris)*, **2**, 187.  
RADOSLOVICH E.W. (1963) *Am. Miner.* **48**, 76.  
ROBERTS M.H. (1957) *J. appl. Chem., Lond.* **7**, 543.

#### ADDENDUM

After the presentation of the results in Parts I and II at the joint meeting of the Groupe Belge des Argiles and the Clay Minerals Group of the Mineralogical Society in Brussels on 2 June 1967, Professor H. F. W. Taylor kindly sent us a typescript of a paper by Miss L. Hardman and Professor H. F. W. Taylor on *The Structure of Pyroaurite and Sjögrenite*\* determined by single crystal methods, which was read at the meeting. Professor Taylor also drew our attention to a paper by R. Allmann and H. H. Lohse (*N. Jb. Miner. Mh.* 1966, 161–181) on the same subject. Both determinations confirm the major features of the structural scheme outlined earlier (Mortland, M. M. & Gastuche, M. C. (1962) *C.r. hebdom. Séanc. Acad. Sci., Paris*, **225**, 2131 and Gastuche, M. C. (1964) *Clays Clay Miner.* **12**, 471) and presented in this paper. The single crystal structure determinations show that the interlayer oxygens are displaced from the approximately close-packed positions shown in Fig. 1 towards the adjacent hydroxyls of the brucite-like layers.

\* INGRAM L. & TAYLOR H.F.W. (1967) *Mineralog. Mag.* **36**, 465.