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Crystal structures of some double hydroxide minerals

H. F. W. TAYLOR

Department of Chemistry, University of Aberdeen, Scotland

SUMMARY. Three groups of minerals are discussed, which are typified by pyroaurite and sjögrenite, hydrocalumite, and ettringite. All show interesting structural features. In the pyroaurite–sjögrenite group, brucite-like layers carrying a net positive charge alternate with layers in which the oxygen atoms of carbonate groups and water molecules are statistically distributed on a single set of sites; other anions may replace the carbonate, especially in synthetic phases. Hydrocalumite and related synthetic phases also have layer structures in which positively charged main layers alternate with intermediate layers containing anions and water molecules; the anions occur in cavities and their nature can again vary widely. In the ettringite group, the structures are based on positively charged columns, between which occur channels containing anions and sometimes also water molecules. This group includes thaumasite, the only natural mineral known to contain silicon six-coordinated by oxygen that is not a high-pressure phase. The thermal dehydration behaviour in each group is briefly considered.

IN this lecture I shall deal with some minerals and synthetic phases that, while not of any major geological significance, are nevertheless interesting from a crystal-chemical point of view. Some are also of technical importance for cement, paper, or the corrosion of metals. In the title they are described, for brevity, as double hydroxides, but most contain also varying amounts of other anions, such as carbonate or sulphate.

Three groups will be considered, which are typified by pyroaurite and sjögrenite, hydrocalumite, and ettringite.

The pyroaurite–sjögrenite group

The members of this group form hexagonal, platy crystals. Pyroaurite and sjögrenite are two closely similar minerals to both of which the formula $Mg_6Fe_2(OH)_{16}(CO_3) \cdot 4H_2O$ has generally been assigned. In other members of the group, the Mg^{2+} may be replaced by other dipositive cations of similar size (e.g. Ni^{2+}), and the Fe^{3+} by suitable tripositive cations (e.g. Al^{3+} or Cr^{3+}). Most analyses seem to indicate that the $M^{2+}:M^{3+}$ ratio is fixed at 3:1, but recent work casts doubt on this and for the Mg–Al mineral,

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hydrotalcite, ratios of 3:1 and 2:1 have been reported for specimens from different localities. Early morphological work, confirmed by later unit-cell determinations, showed that two sub-groups could be distinguished, which would today be described as polytypes differing only in layer stacking; these are represented by pyroaurite and sjögrenite respectively. Table I gives the names and approximate compositions of the

TABLE I. *Some natural minerals of the pyroaurite-sjögrenite group*

Approximate composition	Name	
	3 <i>R</i> -polytype	2 <i>H</i> -polytype
$\text{Mg}_{3/4}\text{Fe}_{1/4}(\text{OH})_2(\text{CO}_3)_{1/8}(\text{H}_2\text{O})_{1/2}$	Pyroaurite	Sjögrenite
$\text{Mg}_{3/4}\text{Al}_{1/4}(\text{OH})_2(\text{CO}_3)_{1/8}(\text{H}_2\text{O})_{1/2}^*$	Hydrotalcite	Manasseïte
$\text{Mg}_{3/4}\text{Cr}_{1/4}(\text{OH})_2(\text{CO}_3)_{1/8}(\text{H}_2\text{O})_{1/2}$	Stichtite	Barbertonite
$\text{Ni}_{3/4}\text{Fe}_{1/4}(\text{OH})_2(\text{CO}_3)_{1/8}(\text{H}_2\text{O})_{1/2}$	Reevesite	—
$\text{Ni}_{3/4}\text{Al}_{1/4}(\text{OH})_2(\text{CO}_3)_{1/8}(\text{H}_2\text{O})_{1/2}^\dagger$	Eardleyite	—
Hexagonal cell parameters (approx.)	<i>a</i>	3·1 Å
	<i>c</i>	23·4 Å
		3·1 Å
		15·6 Å

* Some specimens have compositions near $\text{Mg}_{2/3}\text{Al}_{1/3}(\text{OH})_2(\text{CO}_3)_{1/6}(\text{H}_2\text{O})_{1/2}$.

† With some replacement of Ni by Zn. Evidence that this is a 3*R*-polytype is weak.

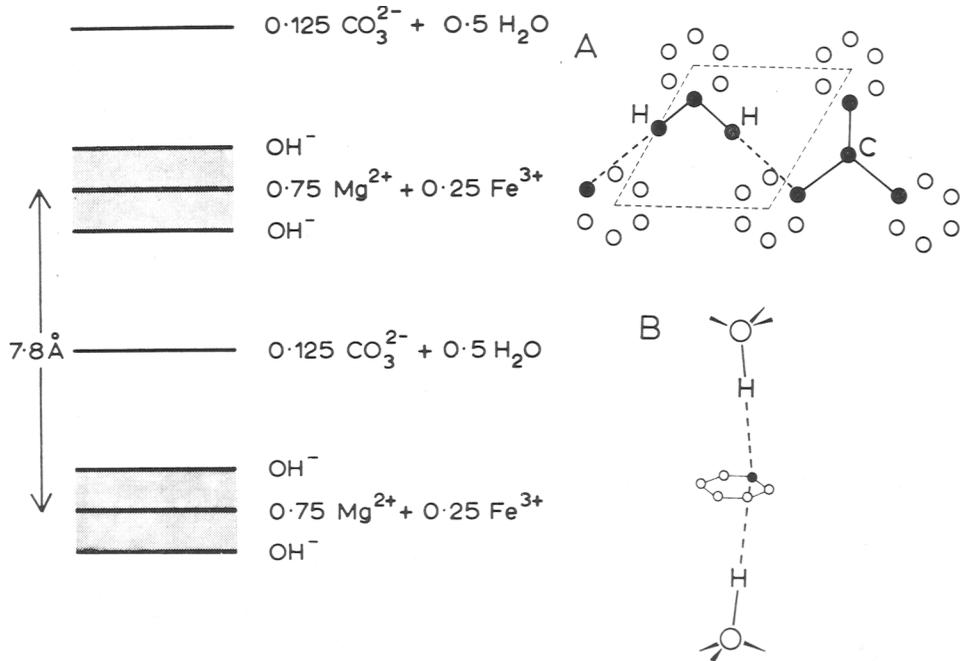
better-defined members of both sub-groups. Some less well-defined members have also been described (Jambor and Boyle, 1964; Lapham, 1965), as well as several minerals with related but distinctly different structures, metal corrosion products, and a wide range of synthetic phases; we shall consider some of these later.

The unit-cell studies made by Aminoff and Broomé (1930) and Frondel (1941) gave experimental results similar to those shown in Table I, and taken in conjunction with the space groups and other relevant information suggest that the structures for both sub-groups are based on structural elements that are hexagonal with $a = 3\cdot1$, $c = 7\cdot8$ Å approximately, and which have the atomic contents $M_{0\cdot75}^{2+}M_{0\cdot25}^{3+}(\text{OH})_2(\text{CO}_3)_{0\cdot125}(\text{H}_2\text{O})_{0\cdot5}$ if the formulae given in Table I are accepted. For the 2*H* and 3*R* sub-groups, there are respectively 2 and 3 elementary layers per unit cell. To avoid non-integral cell contents, both Aminoff and Broomé (1930) and Frondel (1941) postulated doubled values of *a* or *c* or both, but without experimental evidence.

The most detailed structure determinations on these minerals are those of Allmann and Lohse (1966), Ingram and Taylor (1967), Allmann (1968*a*), and especially Allmann (1969) on sjögrenite or pyroaurite, or both, and of Allmann and Jepsen (1969) on hydrotalcite. Less detailed studies were reported by Brown and Gastuche (1967) and Lea and Mackay (1967). The structures are all based on brucite-like layers alternating with what will be called inter-layers, one brucite layer and one inter-layer together making up an elementary layer (fig. 1). The cation sites in the brucite layers are occupied by both the di- and tripositive cations. For the crystals of sjögrenite, pyroaurite, and hydrotalcite used in the detailed structure determinations mentioned above, none of the investigators found any superlattice reflections, which would denote unit cells larger than those given in Table I, or effects of any kind that might indicate either ordering of cations among the octahedral sites or segregation

of the material into regions of differing composition. Some other crystals that have been examined show one or both of these characteristics, and I shall return to this later.

Adjacent brucite layers are stacked so that the hydroxyl groups on the lower surface of one layer are directly above those on the upper surface of the one below, as in gibbsite and not as in brucite. The $2H$ and $3R$ subgroups represent the two simplest



FIGS 1 and 2: FIG. 1 (left). Layer sequences in pyroaurite and sjögrenite. The brucite-like layers are shaded. FIG. 2 (right). The inter-layer of CO_3^{2-} ions and H_2O molecules in minerals of the pyroaurite-sjögrenite group. A: Plan view, showing arrangement of oxygen sites, assuming these to occur in groups of 6. Open circles represent empty sites. Typical situations of a CO_3^{2-} group (top) and of a H_2O molecule (bottom) are shown. Broken lines denote the unit cell or sub cell ($a = 3.1 \text{ \AA}$). B: Spatial relationship between any of the oxygen sites in the inter-layer and the OH^- groups above and below it, showing the possibility of hydrogen bonding to an occupied site.

sequences satisfying this condition. Between adjacent brucite layers are the inter-layers. These contain all the CO_3^{2-} ions and H_2O molecules in the structures, and perhaps the most interesting feature of these minerals is the way in which the oxygen atoms of both these groups are accommodated in a single set of sites. The main features of the inter-layers (fig. 2) are groups of oxygen sites distributed closely around those symmetry axes that pass through the hydroxyl ions of adjacent brucite layers. Within each group, these sites are so near together that, at the most, only one can be occupied. There was initially some doubt as to the number of sites in each group; Ingram and Taylor (1967) found 3 for sjögrenite and either 3 or 6 for pyroaurite, while Allmann and Lohse (1966) found 6 for sjögrenite and Allmann (1968*a*) an almost continuous ring for pyroaurite, but further refinements by Allmann (1969) indicated 6 in both cases.

Fig. 2 shows Ingram and Taylor's (1967) interpretation of the results for the inter-layer, assuming groups of 6. It is not essentially altered if the groups are of 3. If three oxygen sites from adjacent groups are occupied in a particular way, they are in exactly the right places to form a CO_3^{2-} group if a carbon atom (C) is placed between them. On the other hand, if an oxygen atom belongs to a water molecule, it can adopt a reasonably good tetrahedral environment by forming hydrogen bonds to other oxygen atoms in the inter-layer and to hydroxyl groups in adjacent brucite layers. Some of the groups of oxygen sites can be empty and the chemical analyses show that this is usually the case. Allmann (1968*a*, 1970) has also discussed the structure of the inter-layer, and has suggested that its constituents have a high degree of mobility.

Some crystals of these minerals show signs of cation-ordering or segregation into regions of differing chemical composition. Gastuche, Brown, and Mortland (1967) prepared a series of synthetic hydrotalcites of differing Mg:Al ratios. Their results indicated the existence of two phases, closely similar in structure, but differing in layer thickness and Mg:Al ratio. One had a layer thickness of 7.6 Å and a Mg:Al ratio of about 2:1, while the other had a layer thickness of 7.9 Å and a Mg:Al ratio of about 5:1; the two phases sometimes occurred together. I have observed a similar effect in some crystals of sjögrenite or pyroaurite, which show a splitting of X-ray reflections in the c^* -direction, indicating the existence of separately-diffracting regions with layer thicknesses similar to those in the synthetic Mg-Al phases (Taylor, 1969).

Gastuche, Brown, and Mortland (1967) also noted the occurrence of an X-ray powder reflection that could be attributed to a superlattice with an a -axial length $\sqrt{3}$ times the basic value of about 3.1 Å, while I have found crystals of pyroaurite and sjögrenite that give superlattice reflections corresponding to a -axial lengths of both $\sqrt{3}$ and $\sqrt{13}$ times the basic value (Taylor, 1969). The first of these probably indicates the existence of regions in which the Mg and Fe are ordered and in the ratio 2:1 and which have a layer thickness of 7.68 Å, while the second could possibly correspond to a Mg:Fe ratio of 12:1 and a greater layer thickness. One should, however, be cautious in deducing compositions from superlattice effects, because the occurrence of a superlattice does not exclude the possibility that sites are statistically occupied. Within individual crystals, regions can occur that differ in the type of layer stacking ($2H$ or $3R$), the layer thickness, the composition, and the pattern of superlattice reflections, these effects being on a scale that seems on occasion to be under 1 μm . I believe that no new names should be introduced to describe any of these varieties, the names pyroaurite and sjögrenite being applicable to the $3R$ and $2H$ forms of the Mg-Fe mineral irrespective of composition, layer thickness, and superlattice effects.

In sjögrenite-pyroaurite intergrowths examined by Allmann (1968*a*), the sjögrenite formed the core and the pyroaurite the outer regions. From this, and also because low-temperature syntheses give the $3R$ polytypes, he concluded that the latter are the low-temperature forms.

For all the phases of the pyroaurite-sjögrenite group, the general formula may be written as $[M_1^{2+}M_x^{3+}(\text{OH})_2](\text{CO}_3)_{x/2}(\text{H}_2\text{O})_{1-3x/2-\Delta}$ where Δ is below about 0.125 and x probably has a maximum value of 0.33. The minimum value of x is uncertain; in small regions of some crystals, it seems to approach zero (Taylor, 1969). The

reason for the apparently frequent occurrence of cation-disordered material with $x = 0.25$ remains unknown.

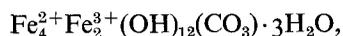
Related structures. Only the closest structural relatives of these minerals will be considered. Heddle (1879) described a specimen as igelströmite; it appears to have been similar to pyroaurite but with OH^- instead of CO_3^{2-} as the inter-layer anion. A specimen from the type locality examined by Rouxhet and Taylor (1969) contained CO_3^{2-} and was pyroaurite, but the actual specimen studied by Heddle could well have been different and there is no reason to doubt the correctness of his analysis. Several specimens similar to pyroaurite or sjögrenite have been called brugnatellite. Two of these, studied by Fenoglio (1938), were possibly sjögrenites with $\text{Mg}:\text{Fe} = 6:1$ and giving superlattice reflections corresponding to $a \approx \sqrt{3} \times 3.1 \text{ \AA}$, presumably attributable to ordered regions with $\text{Mg}:\text{Fe}$ of or near $2:1$; however, the analyses showed ratios of OH^- to $(\text{Mg}+\text{Fe})$ under 2, and this has not been satisfactorily explained.

Coalingite, of approximate composition $\text{Mg}_{10}\text{Fe}_2(\text{OH})_{24}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$, has a structure similar to that of pyroaurite, but with two brucite-like layers between each inter-layer instead of one; in the related coalingite-K, there are probably three brucite-like layers per inter-layer (Pastor-Rodriguez and Taylor, 1971). These structures are possibly formed in preference to a pyroaurite or sjögrenite of high $\text{Mg}:\text{Fe}$ ratio if the supply of water is restricted.

Wermlandite is a mineral similar to pyroaurite but with much more water and a little calcium; it has $a \approx 3 \times 3.1 \text{ \AA}$, and $c = 22.52 \text{ \AA}$ (Moore, 1971). The structure has not been determined, but the composition and crystal data suggest a 2-layer structure in which the elementary layer includes an additional sheet consisting largely of water molecules. It would seem unlikely that the large Ca ions occur in the brucite layers.

Pyroaurite-like structures also exist in which the inter-layer anion is not CO_3^{2-} ; the possibility of this in igelströmite has already been mentioned. Iowaite (Kohls and Rodda, 1967; Allmann and Donnay, 1969) is a pyroaurite-like mineral in which the inter-layer anion is chloride. Many synthetic phases have been described that resemble pyroaurite, in which the dipositive cations are Mg, Zn, Mn, Fe, Co, or Ni, the tripositive ones Al, Mn, Fe, Co, or Ni, and the inter-layer anions CO_3^{2-} , NO_3^- , OH^- , Cl^- , Br^- , or SO_4^{2-} . Many of these were first prepared by Feitknecht and his collaborators in Bern, and Allmann (1970) has listed them. Some of these compounds were assigned formulae of the type $4M^{2+}(\text{OH})_2 \cdot M^{3+}\text{O}(\text{OH})$, but the true formulae are almost certainly analogous to that of pyroaurite, with OH^- or CO_3^{2-} or both as the inter-layer anion.

Several metal corrosion products have structures related to those of the pyroaurite-sjögrenite group of minerals; thus Stampfl (1969) described a phase



closely analogous to pyroaurite, while the phases known as the green rusts (Bernal, Dasgupta, and Mackay, 1959) are of the same general family and may contain a variety of inter-layer anions.

One cannot help being impressed by the ease with which phases of this family form;

it seems to be necessary only to bring together appropriate di- and tripositive cations in the presence of water at a suitable pH at or little above room temperature, and any anions that are present are liable to be incorporated into the structure. Whether the presence of some anion other than OH^- is essential is, perhaps, not fully established. To settle this point it would be necessary to carry out synthetic experiments in which CO_2 was rigorously excluded.

Thermal decomposition. This was studied by Mumpton, Jaffe, and Thompson (1965) for coalingite, by Ross and Kodama (1967) for a synthetic hydrotalcite, and by Rouxhet and Taylor (1969) for sjögrenite and pyroaurite. Generalizing from these results, the molecular water is lost, reversibly, by about 200 °C. The crystallinity then deteriorates, there are d.t.a. effects and changes in infra-red absorption spectrum, and the layer thickness shrinks to around 5 Å; these changes seem to be largely completed before much hydroxyl water or CO_2 is lost, though for sjögrenite and pyroaurite this was not absolutely certain. Finally, dehydroxylation and CO_2 -loss occur and the crystalline, anhydrous products are formed: MgO and MgFe_2O_4 , topotactically, for sjögrenite and pyroaurite. If, as seems most likely, the lattice shrinkage really precedes dehydroxylation, there would appear to be some segregation into $\text{Mg}(\text{OH})_2$ and amorphous regions enriched in the tripositive cation after the molecular water has been lost.

The hydrocalumite group

The phases of this group resemble those of the last in forming hexagonal, platey crystals, and broadly also in composition, but the dipositive cation is Ca^{2+} . The only known natural mineral in the group is hydrocalumite (Tilley, Megaw, and Hey, 1934), the composition of which is approximately $\text{Ca}_2\text{Al}(\text{OH})_{6.75}(\text{CO}_3)_{0.125}(\text{H}_2\text{O})_{2.5}$, but there are many synthetic members, some of which are formed when Portland cement reacts with water. The general formula for the group is $\text{Ca}_2M^{3+}(\text{OH})_6X(\text{H}_2\text{O})_x$, where M^{3+} is typically Al, X denotes one formula unit of a singly-charged anion or equivalent amounts of more highly charged ones, and x is between 2 and 6 for materials that have not been partially or wholly dehydrated. An extremely wide range of anions can serve for X , of which OH^- , CO_3^{2-} , SO_4^{2-} , and Cl^- , or mixtures of these are the most important, and the layer thickness varies with the nature of this anion and the water content (Table II). The Al can be replaced by other tripositive cations, such as Fe, Cr, or Ga. Schwiete and Ludwig (1969) have reviewed these phases.

The structures are based on structural elements that are hexagonal with $a \approx 5.7$ Å (Feitknecht and Buser, 1951). For phases with at least two molecules of molecular water, the layer thickness is 7.4 to 10.7 Å; the structural element contains one unit of the general formula $\text{Ca}_2M^{3+}(\text{OH})_6X(\text{H}_2\text{O})_x$. Buttler, Dent Glasser, and Taylor (1959) noted that the a -axial length lay between the corresponding distances for $\text{Al}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$, and suggested that the structures were based on portlandite-like layers containing an ordered arrangement of Ca^{2+} and Al^{3+} in 2:1 ratio, together with intermediate layers containing water molecules and the X anions, and subsequent structure determinations have shown that this is essentially correct.

The first satisfactory structure determinations were carried out for a synthetic phase

TABLE II. *Some synthetic phases of the hydrocalumite group*

Composition	Layer thickness (Å)	Composition	Layer thickness (Å)
$[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH}) \cdot 6\text{H}_2\text{O}$	10.7	$[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$	7.9
$[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH}) \cdot 3\text{H}_2\text{O}^*$	7.9	$[\text{Ca}_2\text{Al}(\text{OH})_6](\frac{1}{2}\text{CO}_3) \cdot 2\frac{1}{2}\text{H}_2\text{O}$	7.6
$[\text{Ca}_3\text{Al}(\text{OH})_6](\text{OH}) \cdot 2\text{H}_2\text{O}$	7.4	$[\text{Ca}_2\text{Al}(\text{OH})_6](\frac{1}{2}\text{SO}_4) \cdot 3\text{H}_2\text{O}$	8.9
$[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH})$	5.8	$[\text{Ca}_2\text{Fe}(\text{OH})_6](\frac{1}{2}\text{SO}_4) \cdot 3\text{H}_2\text{O}$	8.9

* Some investigators have considered that the 7.9 Å phase contains $2\frac{1}{2}\text{H}_2\text{O}$ and that there is an 8.2 Å phase with $3\text{H}_2\text{O}$, but for CO_3^{2-} -free material the weight of the evidence is against this view. Hydrocalumite is related to the 7.9 Å phase with $3\text{H}_2\text{O}$ by replacement of some OH^- by CO_3^{2-} and loss of some molecular water; the layer thickness remains close to 7.9 Å. The 8.2 Å phase is probably $[\text{Ca}_2\text{Al}(\text{OH})_6](\frac{1}{4}\text{CO}_3)(\frac{3}{4}\text{OH})(3\text{H}_2\text{O})$; here some OH^- is replaced by CO_3^{2-} but the content of molecular water remains at $3\text{H}_2\text{O}$.

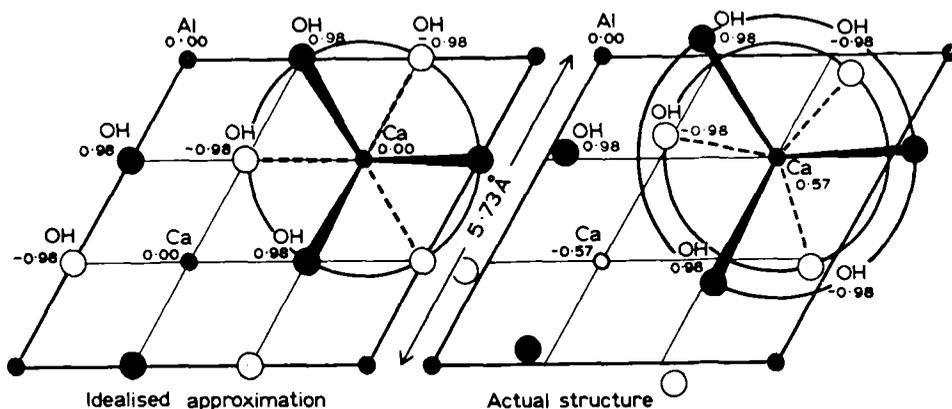


Fig. 3. Structure of a single principal layer of composition $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ in phases of the hydrocalumite group. Left: highly idealized approximation, consisting of a portlandite layer with ordered replacement of Ca by Al. Right: actual structure. Heights of atoms in the projections are in Å. Large circles indicate the distortion of the CaO_6 octahedron in the actual structure, which is sufficient to allow the coordination number of the Ca^{2+} ions to be raised to 7 by the approach of a water molecule (not shown) directly above or below them in the projection.

with a composition probably close to that of hydrocalumite (Ahmed and Taylor, 1967; Ahmed, Dent Glasser, and Taylor, 1969), and for the sulphate (Allmann, 1968*b*), bromide (Le Bel and Grasland, 1969), and iodide (Kuzel, 1969) derivatives. All gave essentially similar results. As in the pyroaurite-sjögrenite group, principal layers alternate with inter-layers, the principal layers having the composition $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and the inter-layers consisting of water molecules and anions. However, because of the difference in size between the Ca^{2+} and Al^{3+} ions, the $M^{2+}:M^{3+}$ ratio is fixed at 2:1 and their arrangement is ordered.

Fig. 3 shows the structure of one of the principal layers. It could be described as a considerably distorted portlandite layer. The distortion contains three components: the OH^- ions are drawn in towards the Al^{3+} ions, so that the layer could alternatively

be described as consisting of Ca^{2+} ions and isolated $[\text{Al}(\text{OH})_6]^{3-}$ octahedra; these octahedra are rotated around an axis normal to the plane of the layer; and the Ca^{2+} ions are displaced parallel to this axis, half of them in one direction, and half in the other. The net result of these distortions is to render the CaO_6 octahedra very open on one side, so that a water molecule from the inter-layer can bond to the Ca^{2+} , which thus becomes seven co-ordinated.

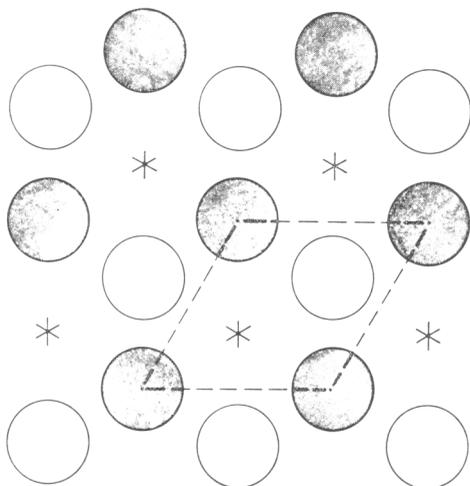


FIG. 4. Inter-layer material in phases of the hydrocalumite group, seen projected in the plane of the layers. Open and shaded circles denote respectively H_2O molecules attached to Ca^{2+} ions on the upper surface of the principal layer below and on the lower surface of the principal layer above. Asterisks denote centres of cavities, which can be occupied by additional H_2O molecules or anions. Broken lines outline the unit cell or sub cell ($a = 5.7 \text{ \AA}$).

The layer stacking in these phases is often complex, so that polytypism can occur and the true unit cells almost always contain a number of structural elements. However, the packing of adjacent layers is simple and is shown in fig. 4. The H_2O molecules attached to Ca^{2+} ions on the lower surface of one layer pack between those attached to Ca^{2+} ions on the upper surface of the one below. This leaves cavities, centred at points marked *, in which occur the inter-layer anions and, where space allows, additional water molecules. If the anions are more than singly-charged (e.g. SO_4^{2-}) their numbers will be insufficient to fill all the cavities, some of which may then contain additional water molecules; a cavity may also contain a hydroxyl ion and a water

molecule. If the anions are small, the layer thickness will be equal to or a little above a minimum value of 7.4 \AA , but if they are large, the layers move apart to provide the necessary space.

The arrangement of material in the cavities seems often to be disordered. For the crystals we studied, we concluded that 50 % of the cavities contained OH^- , 25 % ($\text{OH}^- + \text{H}_2\text{O}$), 12.5 % $2\text{H}_2\text{O}$, and 12.5 % CO_3^{2-} (Ahmed, Dent Glasser, and Taylor, 1969). There were no indications of ordering as regards the contents of the cavities, and where a cavity contained $2\text{H}_2\text{O}$ or ($\text{OH}^- + \text{H}_2\text{O}$), these were possibly statistically distributed among six positions within the cavity. Hydrocalumite is probably closely similar to this material in composition and thus in the contents of the cavities. However, the unit-cell parameters (Tilley, Megaw, and Hey, 1934) show that it is a different polytype and that there is a superlattice in the plane of the layers; this last observation suggests that there is some ordering as regards the contents of the cavities. For the sulphate derivative, Allmann (1968*b*) concluded that there was random occupancy of the cavities by SO_4^{2-} (50 %) and $2\text{H}_2\text{O}$ (50 %). The SO_4^{2-} groups were randomly distributed between two possible orientations.

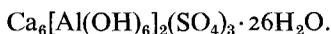
As in the pyroaurite-sjögrenite group, crystals of these phases are often found that show splitting of reflections corresponding to regions of different layer thickness, or superlattices in the plane of the layers, or both. The explanation is different, however; it cannot be connected with differences in $M^{2+}:M^{3+}$ ratio, because this is fixed at 2:1, and is instead related to segregation or ordering of the contents of the cavities. Many kinds and degrees of unmixing and ordering seem to occur, ranging from separate crystals of different phases, through regularly and possibly also randomly inter-stratified structures, to true solid solutions in which the variation occurs on a unit-cell scale.

The phases of this group can accommodate organic molecules between the layers (Dosch, 1967). It is also possible for a whole extra layer of water molecules to be present in each elementary layer; this happens in $[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH})(\text{H}_2\text{O})_6$, which has a layer thickness of 10.7 Å. Phases belonging to this group but containing also Na (Dosch and zur Strassen, 1967) or Mg (Sadran and Cottin, 1969) have been reported. In the latter case, the possibility of almost complete substitution of Ca by Mg was postulated; this is difficult to reconcile with the known structures.

When phases of this group are heated, the molecular water is first lost. At somewhat higher temperatures, the crystallinity deteriorates (Buttler, Dent Glasser, and Taylor, 1959; Ahmed, Dent Glasser, and Taylor, 1969). Some $\text{Ca}(\text{OH})_2$ can form from $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$ on heating at about 105 °C or on decomposition under the beam of the electron microscope. This recalls the behaviour in the pyroaurite-sjögrenite group mentioned earlier, and it seems certain in the present case that some segregation has occurred, to give regions enriched in the two different metal cations.

The ettringite group

Ettringite occurs as a natural mineral and has the formula



In its qualitative composition it thus resembles members of the previous group, but, unlike any of the phases hitherto described, it forms prismatic crystals, which are of hexagonal cross-section. It can readily be synthesized, and is formed as a hydration product of Portland cement. Under the name 'Satin White', it is also made as a coating material for paper. It is trigonal, with $a = 11.23$, $c = 21.44$ Å.

Several phases have been synthesized that resemble ettringite but contain other anions instead of the sulphate; partial or complete replacement appears to be possible by, among other ions, CO_3^{2-} , CrO_4^{2-} , Cl^- , IO_3^- , and even para-nitrobenzoate. These ions vary widely in size and charge and, as with the previous group, there is an interesting crystal-chemical problem in how the structure can accommodate them. The Al can be replaced by tripositive Ti, Cr, Mn, Fe, or Ga, and the Ca by Sr. Schwiete and Ludwig (1969) discussed some of these phases in the review mentioned earlier.

Minerals are also known that resemble ettringite in varying degrees but which contain tetrapositive cations in place of the Al^{3+} (Table III). Two of them (thaumasite and jouravskite) have compositions and a -axial lengths quite close to those of ettringite, but the other three (*despujolsite*, *schaurteite*, and *fleischerite*) contain much less water and have $a = 8.5\text{--}8.9$ Å.

The first structure determination to be reported for these minerals was made on thaumasite by Welin (1956). He found a structure based on columns, in which SiO_4^{4-} tetrahedra alternated with groups of Ca^{2+} ions and H_2O molecules, and between which occurred the SO_4^{2-} and CO_3^{2-} ions. The structure was unsatisfactory in that some of the H^+ ions could not be properly accounted for; Welin suggested that they were attached to the SO_4^{2-} ions. The first fully satisfactory determination was that of jouravskite, by Granger and Protas (1966, 1969). The structure was very broadly similar to that proposed for thaumasite by Welin, but contained $\text{Mn}(\text{OH})_6^{2-}$ octahedra

TABLE III. *Natural minerals of the ettringite group*

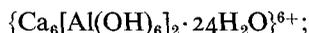
Ettringite	$\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	} $a = 11.0-11.7 \text{ \AA}$
Thaumasite	$\{\text{Ca}_6[\text{Si}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}(\text{SO}_4)_2(\text{CO}_3)_2$	
Jouravskite	$\{\text{Ca}_6[\text{Mn}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}(\text{SO}_4)_2(\text{CO}_3)_2$	} $a = 8.5-8.9 \text{ \AA}$
Despujolsite	$\{\text{Ca}_3[\text{Mn}(\text{OH})_6] \cdot 3\text{H}_2\text{O}\}(\text{SO}_4)_2$	
Schaurteite	$\{\text{Ca}_3[\text{Ge}(\text{OH})_6] \cdot 3\text{H}_2\text{O}\}(\text{SO}_4)_2$	
Fleischerite	$\{\text{Pb}_3[\text{Ge}(\text{OH})_6] \cdot 3\text{H}_2\text{O}\}(\text{SO}_4)_2$	

in place of the SiO_4^{4-} tetrahedra; all atoms could be satisfactorily placed. The structure of ettringite was then solved, by Courtois, Dusausoy, Laffaille, and Protas (1968) and by Moore and Taylor (1968, 1970). We were ignorant of the French work and used Welin's structure of thaumasite as a starting point. Finally, the structure of thaumasite was redetermined, by Edge and Taylor (1969, 1971) and Laffaille and Protas (1970).

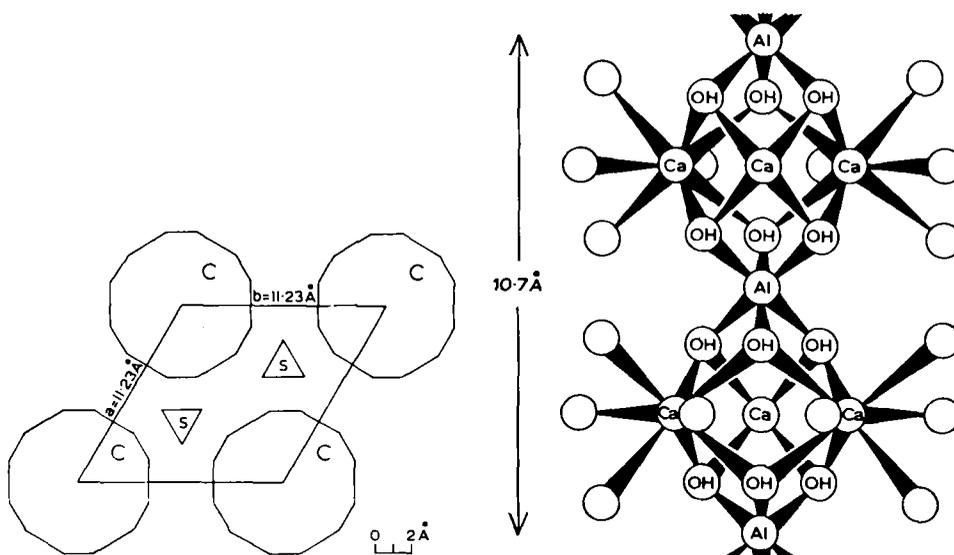
All these structures are closely similar to each other, and we will consider that of ettringite in more detail. The most important feature is the arrangement of columns and channels, both running parallel to the prism axis (fig. 5). The composition of the columns is $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$ and that of the material in the channels is $[(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}]^{6-}$, per half unit cell in each case. Here we have the basis of an explanation of the existence of phases similar to ettringite but containing other anions instead of SO_4^{2-} ; assuming these can satisfy the coordination requirements of whatever atoms form the surfaces of the columns, the separation of the latter could be readily altered in accordance with the differing sizes of the anions.

Fig. 6 shows the structure of a single column, seen now from one side. $\text{Al}(\text{OH})_6^{3-}$ octahedra alternate with groups of three Ca^{2+} ions arranged around a symmetry axis; each Ca is linked to four OH^- groups of $\text{Al}(\text{OH})_6^{3-}$ octahedra above and below it and to four H_2O molecules, and is thus eight-coordinated. The configuration of the Ca polyhedron may be described as a trigonal prism, with its main axis parallel to the column direction, and having two additional vertices outside the centres of two of the prism faces. The resulting column is of nearly cylindrical shape, and its surface is composed entirely of H_2O molecules, or more accurately by the H atoms that these contain. For the atoms within the columns, Pauling's electrostatic valency rule is exactly obeyed, and it is probably correct to think of the net positive charge of the columns as being distributed, more or less evenly, over these H atoms.

In the channels, there are four potential anion sites per unit of



three of these are occupied by SO_4^{2-} and one by approximately 2 H_2O molecules distributed over 3 positions. The columns are linked to the material in the channels by hydrogen bonds. There are possibilities of twinning and disorder associated with occupancy of the anion sites, which I shall not discuss here. The structures of the derivatives containing singly-charged anions, such as Cl^- , deserve further study, since there must be more anions than there are sites for them in ettringite; presumably anion sites in the channels are more closely spaced in these cases.



FIGS. 5 and 6: FIG. 5 (left). Broad features of the ettringite structure, projected along the prism axis. The polygons C represent the columns, of empirical formula $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{3+}$, while the triangles S represent the SO_4^{2-} ions and groups of H_2O molecules present in the channels. FIG. 6 (right). Ettringite: part of a single column projected on $(11\bar{2}0)$. Unmarked circles represent H_2O molecules. For clarity, H_2O molecules attached to Ca ions lying in the central vertical line of the figure are omitted, as are all the H atoms.

Jouravskite has a structure almost identical with that of ettringite but with $\text{Mn}(\text{OH})_6^{2-}$ in place of $\text{Al}(\text{OH})_6^{3-}$ and for every four anion sites in the channels it contains two SO_4^{2-} and two CO_3^{2-} ions instead of three SO_4^{2-} ions and a group of water molecules. Thauamasite is isostructural with jouravskite, with $\text{Si}(\text{OH})_6^{2-}$ in place of $\text{Mn}(\text{OH})_6^{2-}$. It is of interest in being the only substance in which the octahedral $\text{Si}(\text{OH})_6^{2-}$ group has been shown to exist. Even before the recent X-ray structure determinations had been carried out, Moenke (1964) concluded from an infra-red investigation that the Si in thauamasite was six-coordinated. It is probably fair to say that this report made little impact in mineralogy at the time, and Moenke's interpretation was disputed (Kirov and Poulieff, 1968), but the X-ray work showed that it was correct.

Until recently it was widely supposed that six coordination of silicon by oxygen occurred only in phases formed under high pressure. However, thauamasite can be

synthesized at ordinary pressure and in view of its low density (1.88 g cm^{-3}) is most unlikely to be stable at high pressures. In point of fact, octahedral coordination of silicon by oxygen occurs in other compounds formed at ordinary pressure. Coordination compounds have long been known in which there is chemical evidence for it (Dilthey, 1903; Rosenheim, Raibmann, and Schendel, 1931), while Levi and Peyronel (1935) showed by a structure determination that one polymorph of SiP_2O_7 contained octahedral silicon. More recently, this has been found true for other polymorphs of this compound (Bissert and Liebau, 1969; Liebau and Hesse, 1969). It seems that six coordination of silicon by oxygen can be achieved by either of two methods: application of high pressure, or attaching some other atom to the oxygen that is sufficiently electronegative to draw electrons out of the silicon-oxygen bonds, thereby allowing the silicon to form six relatively long bonds ($1.73\text{--}1.83 \text{ \AA}$) instead of four of a more normal length ($1.57\text{--}1.67 \text{ \AA}$). These other atoms are H in thaumasite, P in the SiP_2O_7 polymorphs, and C in the coordination compounds which I have mentioned. I do not want to imply that, when such atoms are attached to the oxygen, six coordination of the silicon always occurs, but only that it can occur. What further conditions have to be satisfied do not seem to be understood.

If ettringite is heated at 110°C most of the molecular water is lost and lattice shrinkage occurs in directions normal to the prism axis; the product has $a = 8.4 \text{ \AA}$ (Bannister, Hey, and Bernal, 1936). This behaviour forms an interesting contrast to that of the lamellar groups of minerals. The structure of the dehydration product has not been determined, but it is probably similar to those of despujolsite, schaurteite, and fleischerite. The structure of despujolsite was determined by Gaudefroy, Granger, Permingeat, and Protas (1968). It is similar to those of ettringite, thaumasite, and jouravskite, but most of the molecular water is missing and those water molecules that remain are shared between adjacent columns, which have thus come closer together to give the shorter a -dimension. Schaurteite, fleischerite, and also their strontium analogue have been synthesized (Otto, 1968).

All the minerals and synthetic phases of the ettringite group are characterized by hexagonal structural elements with $c = 10.3\text{--}11.1 \text{ \AA}$, the doubled c -axis in ettringite being merely a consequence of the ordering of the material in the channels. The structural element always contains six large cations (typically Ca^{2+} , Sr^{2+} , or Pb^{2+}) and two $M(\text{OH})_6$ octahedra, where M is typically Al^{3+} , Fe^{3+} , Si^{4+} , Ge^{4+} , or Mn^{4+} . The length of the a -axis varies. Where the water content is high, as in ettringite, it is $11.0\text{--}11.7 \text{ \AA}$ in those cases for which it has been determined, though larger values are possible, at least in theory, if larger anions can be placed in the channels. Where the water content is low, as in despujolsite, the a -axial length is $8.4\text{--}8.9 \text{ \AA}$.

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