

MIXED-VALENCE HYDROXIDES AS BIOORGANIC HOST MINERALS

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Abstract. A range of naturally occurring divalent-trivalent metal cation hydroxides and modified artificial analogs have been synthesized and characterized. Structural and chemical properties of these minerals, determining their capability to selectively concentrate, order and alter molecules of prebiotic interest, include their anion exchange capacity and specificity, photochemical reactivity, production of nascent hydrogen, and catalytic efficiency. Properties relevant to these functions have been investigated and are discussed.

Introduction

A commonly employed working hypothesis assumes that oligomeric macromolecules, functionally similar to RNA, initiated replication and mutation in a carbon based system. Consequently a central theme in related studies of biomolecular evolution concerns the generation of simple aldehydes and nitrogen bases, and their arrangement into reactive configuration, together with monomeric or condensed phosphate. It has been pointed out (Arrhenius *et al.* 1989) that these proto-RNA components are anions (CN^- , PO_4^{3-} , CO_3^{2-}) or polar molecules (HCN, formaldehyde hydrate). In the need for selective concentration, ordering and reaction of these components, naturally occurring catalytically active minerals with exchange capability for anions and polar molecules were therefore proposed by these authors as reaction systems to be investigated.

Following the original suggestion by Bernal (1949, 1951, 1967), considerable attention has in the past been given to the exploration of clay minerals in similar capacities. The seminal proposal was made by Cairns-Smith (1966, 1975, 1982) that clay mineral complexes with organic molecules could have constituted the first organisms, capable of self-assembly, replication and mutation, and that carbon based life may have gradually evolved from such an organic-inorganic hybrid state.

Since aluminosilicate surfaces carry excess negative charge, their basal faces form bonds only with cations and polar molecules; anion sorption is limited to crystal edges where the interrupted lattice exposes excess positive charge. Much of the earlier work has involved sorption and attempted oligomerization of amino acids on clay minerals. The only study of nucleic acid reactions catalyzed by clay mineral surfaces, of which we are aware, is the successful cyclization of sorbed AMP by diaminosuccinonitrile, formed at oxidation of diaminomaleonitrile by hydrated ferric

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ion, incorporated in the structure of the magnesium aluminosilicate montmorillonite (Ferris, 1987; Ferris and Hagan, 1986; Ferris *et al.*, 1982, 1986, 1988).

In view of the perceived potential of the mixed-valence hydroxide (pyroaurite type) minerals for the bioinductive functions discussed, we have synthesized a representative series of these minerals and investigated some of their properties, relevant in this context. One member of this group, Fe(2)Fe(3) hydroxide, is represented in nature by the green rust minerals and by their alteration products, magnetite and iron silicates. Because of the special significance of the Fe(2)Fe(3) hydroxide complexes in Archean ocean sedimentation (Arrhenius, 1984, 1986, 1987) and in reactions involving cyanides, phosphates and aldehydes, these ferroferric members of the pyroaurite family of minerals are being investigated in further detail and are discussed in a separate paper. An extended study of the interaction of

TABLE I

Some naturally occurring $M^{2+} M^{3+}$ hydroxide sheet structures with exchangeable interlayer anions. Alternative stacking sequences of the hydroxide sheets give rise to either rhombohedral or hexagonal symmetry, the latter generally favored by high crystallization temperature.

| Mineral name | | | | Interlayer | |
|--------------------------|----------------------------|----------|----------|-----------------|---------------------------------------|
| <i>Rhombohedral</i> | <i>Hexagonal</i> | M^{2+} | M^{3+} | Anion | Generic Name |
| Hydrotalcite | Manasseite | Mg | Al | CO_3^{2-} | MgAl hydroxide carbonate ^a |
| Stichtite | Barbertonite | Mg | Cr | CO_3^{2-} | MgCr hydroxide carbonate |
| Pyroaurite | Sjögrenite | Mg | Fe | CO_3^{2-} | MgFe hydroxide carbonate |
| Iowaite | | Mg | Fe | Cl^- | MgFe hydroxide chloride |
| Chlormagaluminitite | | Mg,Fe | Al | $Cl^-CO_3^{2-}$ | Mg-FeAl hydroxide chloride-carbonate |
| | Hydrocalumite ^b | Ca | Al | OH^- | CaAl hydroxide |
| Green rust 1 | Green rust 2 | Fe | Fe | CO_3^{2-} | Ferroferric hydroxide carbonate |
| Berthierine ^c | | Fe | Fe | SiO_3^{2-} | Ferroferric hydroxide silicate |
| | Takovite | Ni | Al | CO_3^{2-} | NiAl hydroxide carbonate |
| Reevesite | | Ni | Fe | CO_3^{2-} | NiFe hydroxide carbonate |
| Honessite | | Ni | Fe | SO_4^{2-} | NiFe hydroxide sulfate |
| Eardlyite | | Zn,Ni | Al | CO_3^{2-} | Zn-NiAl hydroxide carbonate |
| 8.85Å SO_4 | 8.85Å SO_4 | Mg | Al | SO_4^{2-} | MgAl hydroxide sulfate |
| hydrotalcite 3R | hydrotalcite 2H | | | | |

^a) To specify the rhombohedral or hexagonal form, Drits *et al.* (1987) propose the suffixes 3R and 2H respectively, as in the MgAl hydroxide sulfates discovered by them; they also include in the mineral name the value for the c' spacing. Their proposal also includes a limit to the proliferation of trivial mineral names. The suggestion is to use a standard name for each general species, regardless of stacking order, anion- or partial cation substitution, and to add modifiers indicating the structural and chemical variations. An example is given by the hydrotalcite sulfates in the last line of the table.

^b) At low temperature monoclinic-pseudohexagonal; $\beta=111^\circ$.

^c) A variety of ferroferric hydroxide silicates with 1:1 serpentine structures (e.g. greenalite (Baily, 1980); minnesotaite (Ahn and Buseck, 1989), occur as important iron ore minerals in the Archean iron formations; they are probably metamorphic (dehydrated-dehydroxylated and partially ordered) green rust silicates.

M(2)M(3) hydroxides with ortho- and polyphosphates and with nucleic acids and RNA has been carried out by Gedulin (1989), and Gedulin *et al.* (1989).

Pyroaurite type structures

The most common hydrous minerals with structural, exchangeable anions are the members of the pyroaurite group. Of these the green rust (ferroferic hydroxide with various exchangeable structural anions) must have been one of the most abundant authigenic minerals in the anoxic Archean ocean. As such it is likely to have given rise to the extensive deposits of its spontaneous auto-oxidation product, magnetite (ferroferrispinel; $\text{FeO-Fe}_2\text{O}_3$), and of iron silicates, in the banded iron formation.

The pyroaurite minerals are mixed valence cation hydroxides, which can be regarded as derived from the brucite type structure (C6) (Fig. 1). A fraction of the divalent cations in the relatively strongly hydrogen bonded metal hydroxide sheets are in the pyroaurite structure replaced by trivalent metal cations such as Fe^{3+} , Al^{3+} or Cr^{3+} . This substitution introduces excess positive charge on the sheets, weakening the bond between them, and permitting admission to the interlayer of counteranions. An overview of the properties of synthetic compounds of this type, as well as related minerals has been given by Allmann (1968a, 1970), Brindley and Bish (1976), and Bish (1980). Their occurrence in ocean sediments and evaporites has been reported by Drits *et al.* (1985, 1987); Arrhenius *et al.* (1989) have suggested that the ferroferric member (green rust) is the progenitor of magnetite, hematite and ferroferrisilicate in the widespread Precambrian banded iron formations. In the work reported here a series of pyroaurite type structures of topical interest have been synthesized and studied with particular attention to the anion exchange properties of the interlayer.

Phases observed as natural minerals are listed in Table 1 together with structural information and provenance. Phases synthesized as a part of the present work are arranged in Table 2 in increasing order of atomic number of the divalent cation.

Experimental procedures

Except as noted in Table 2, the mixed valence hydroxide chlorides were prepared by diluting 50 ml of 100 mM aqueous solutions of the metal chlorides to slightly less than the ultimate volume (mostly 1,000 ml), alkalizing the solution to the pH indicated (in most cases 8.2-9.0) with NaOH and completing the volume with water. Annealing of the precipitate was carried out from one day to one week at temperatures ranging from 2 to 220°C, as indicated. The solids were separated by filtration, dried over silica gel at room temperature and analyzed. In cases where precautions were needed to prevent oxidation of the M^{2+} ion, solutions were purged and blanketed with nitrogen or argon, or reducing anions such as SO_3^{2-} introduced in the interlayer.

Structural properties were determined by x-ray and electron diffraction, and by electron microscopy, the latter two using a Hitachi H500 instrument, generally at an acceleration potential of 100 keV. For x-ray powder diffraction we used a

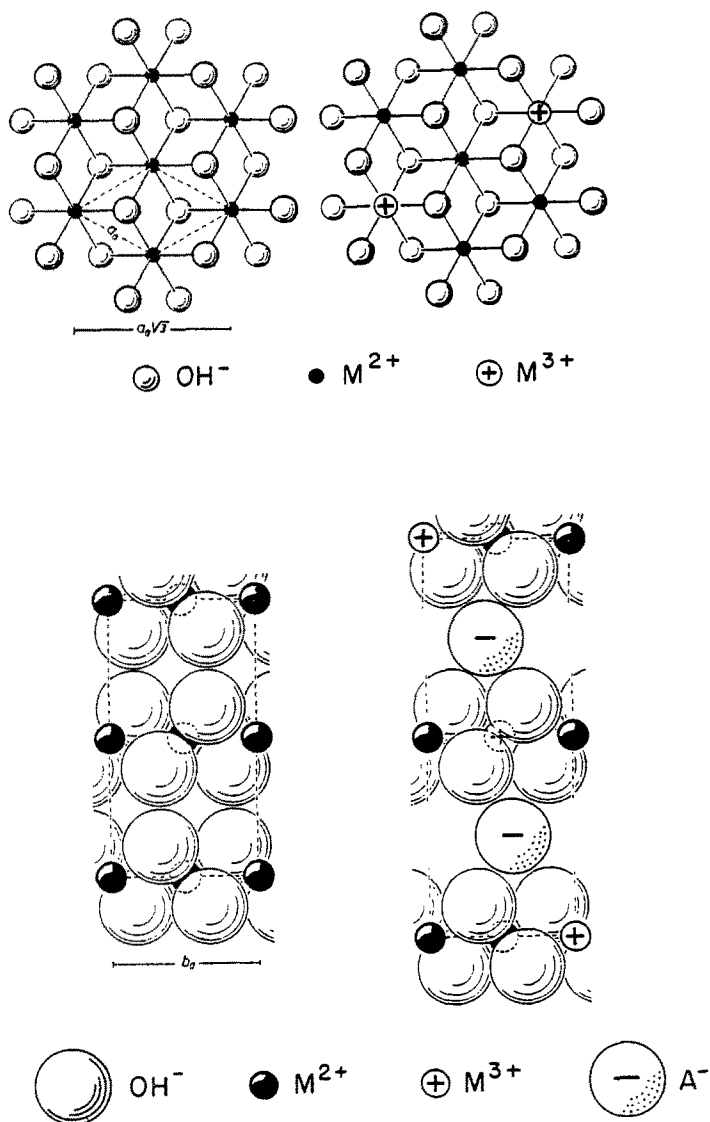


Fig. 1. Schematic representation of divalent metal hydroxides with brucite ($\text{Mg}(\text{OH})_2$)-type structure (left hand diagrams), and mixed (II, III) valence structure of pyroaurite type (right). The top graphs show projection on the basal sheet plane (001), and the lower graphs a section (100) through the stack of sheets.

The lower right graph illustrates how partial substitution of M^{3+} for M^{2+} introduces excess positive charge on the sheets, which separate and attract anions or polar molecules from solution into interlayer position.

Expandable mixed-valence hydroxide sheet structures of this type, with interlayer anion sorption properties include the common hydrous minerals pyroaurite with ($\text{Mg}^{2+} \text{Fe}^{3+}$), hydrotalcite ($\text{Mg}^{2+} \text{Al}^{3+}$) and green rust with ($\text{Fe}^{2+} \text{Fe}^{3+}$) as hydroxide sheet cation pairs. Magnetite, $\text{Fe}^{2+}\text{O}\cdot\text{Fe}_2^3+\text{O}_3$ forms spontaneously by auto-oxidation of green rust and occurs massively in sedimentary deposits from the Archean Ocean.

General Electric XRD-5 diffractometer modified for automated input and data processing; radiations employed were cobalt and copper $K\alpha$, monochromatized with an AMR graphite crystal focusing monochromator, and measured with a Philips scintillation counter.

Surface area measurements were made by three different techniques; BET nitrogen adsorption, x-ray diffraction line broadening and geometric measurement of individual crystals in electron micrographs.

Standard anion exchange tests were carried out by dispersing 20 mg of the silica gel - vacuum dried hydroxide-chloride crystals in 10 ml of 2.5-1,000 mM solutions of the sodium salts of the anions in question, mostly between pH 6.5 and 9. Ion exchange was normally carried out at room temperature for 24 hours. The extent of sorption and exchange was measured by analysis of the supernatant solution and/or of the crystalline solid. For phosphate determination the phosphomolybdate complex was measured spectrophotometrically, after reduction with ascorbic acid. Nucleic acids were determined by measurement of the ultraviolet absorption by the nitrogen bases at 260 nm. For these analyses we used a Perkin-Elmer Lambda 3b UV-visible light spectrophotometer.

Structurally controlling interlayer sorption of anions, differing in size from the original Cl^- (Table 3), was established by measurement of the layer separation in the crystalline hydroxides; as examples, shown in Fig. 5, diagnostic expansion of the interlayer from 8 Å into the range 19 to 32 Å takes place at exchange of chloride ion against adenosine monophosphate or dodecyl sulfate.

Calcium-aluminum hydroxide chloride and derivatives

Because of their importance in cement technology, extensive research has been devoted to the double-layer calcium aluminates with exchangeable interlayer anions; discussion of this group has been given by Allmann (1968b; 1970; 1977). The chloride- and chloride-hydroxide interlayer forms, which in the present work were used as starting materials for exchange, were first synthesized and studied by Feitknecht and Gerber (1942), Feitknecht and Buser (1951) and Kuzel (1966).

TABLE II
Synthesis conditions and products

| Sample number | Composition | | M(2) to M(3) ratio in source solution | Precipitation conditions | | | Annealing time days | X-ray diffraction | | |
|---------------|-------------|------|---------------------------------------|--------------------------|---------|------|---------------------|-----------------------------|------------------------------|----------------|
| | M(2) | M(3) | | Conc. mM | Temp °C | pH | | Products | Basal spacing c' d(001), Å | rel. intensity |
| 4000.1 | Mg | Al | 3:1 | 100 | 25 | 10.0 | | M(2)M(3) ^a | 8.1 | w |
| 4000.2 | | | | | 130 | | 1 | M(2)M(3) | 8.0 | vs |
| 4404.1 | Mg | Al | 3:1 | 100 | 25 | 10.0 | | n-cryst ^b | | |
| 4004.2 | | | | | 130 | | 2 | M(2)M(3) | 8.0 | vs |
| 5016 | Mg | Fe | 3:1 | 50 | 20 | 9.0 | | M(2)M(3) | 8.2 | w |
| 4038 | Mg | Al | 1:0 | 100 | 25 | 10.0 | | Mg(OH) ₂ | | |
| 4040.1 | | | | | 100 | 8.5 | | n-cryst | | |
| 4040.2 | | | | | 130 | | 3 | γ -AlOOH | | |
| 4050 | Ca | Al | 3:1 | 100 | 25 | 12.0 | | M(2)M(3) | 8.1 | m |
| 4054 | Ca | Al | 3:1 | 5 | 2 | 12.4 | | n-cryst | | |
| 4055 | Ca | Al | 3:1 | 100 | 23 | 12.7 | | M(2)M(3) | 8.0 | w |
| 4056 | Ca | Al | 3:1 | 100 | 2 | 12.5 | | M(2)M(3) | 8.0 | w |
| 4057 | | | | | 100 | 8.1 | | n-cryst | | |
| 4058 | Ca | Al | 1:2 | 100 | 25 | 8.2 | | n-cryst | | |
| 4059 | Ca | Al | 2:1 | 100 | 25 | 8.4 | | n-cryst | | |
| 4060.1 | Ca | Al | 3:1 | 100 | 25 | 12.5 | | n-cryst | | |
| 4060.2 | | | | | 130 | | 1 | M(2)M(3) | 7.8 | s |
| 4063 | Ca | Fe | 3:1 | 100 | 25 | 12.3 | | CaCO ₃ + n-cryst | | |
| 4064.1 | Ca | Y | 3:1 | 100 | 25 | 12.5 | | M(2)M(3) | 8.1 | w |
| 4064.2 | | | | | 130 | | 1 | M(2)M(3)? | 7.7 | w |
| 4064.3 | | | | | 130 | 12.5 | 3 | M(2)M(3)?+ | 7.7 | w |
| 4067.1 | Ca | Y | 4:1 | 100 | 25 | 12.5 | | Ca(OH) ₂ | | |
| 4067.2 | | | | | 130 | | 1 | M(2)M(3)?+? | 7.6 | w |

a) refers to divalent-trivalent cation hydroxide layer structure of pyroaurite-sjögrenite type, or of the closely related hydrocalumite type.

b) nanocrystalline (crystallites with thickness of the order of \approx 1–50 nm and hence with sufficient broadening of c' and other reflections to preclude identification).

Table II. Continued.

| Sample number | Composition | | M(2) to M(3) ratio in source solution | Precipitation conditions | | | Annealing time days | X-ray diffraction | |
|---------------|-------------|------|---------------------------------------|--------------------------|---------|------|---------------------|---|----------------------------------|
| | M(2) | M(3) | | Conc. mM | Temp °C | pH | | Products | Basal spacing c' d(00 l), Å |
| 4069.1 | Ca | Y | 2:1 | 100 | 25 | 12.5 | 1 | n-cryst | |
| 4069.2 | | | | | 130 | | | M(2)M(3)?+ | 7.6 w |
| 4071 | Ca | | 1:0 | 5 | 22 | 12.5 | | Ca(OH) ₂ | |
| 4072 | Ca | | 1:0 | 5 | 2 | 13.1 | | Ca(OH) ₂ | |
| 4100 | Mn | Al | 2:1 | 100 | 25 | 8.7 | | M(2)M(3) | 7.8 w |
| 4101 | Mn | Al | 3:1 | 100 | 25 | 8.6 | | M(2)M(3) | 7.9 w |
| 4102.1 | Mn | Al | 1:1 | 100 | 25 | 8.7 | | M(2)M(3)+ | 7.8 s |
| | | | | | | | | Al(OH) ₃ ? | |
| 4103.1 | Mn | Al | 2:1 | 100 | 80 | 8.5 | | M(2)M(3) | 7.8 s |
| 4103.2 | | | | | 130 | | 2 | M(2)M(3)+ | 7.9 vs |
| | | | | | | | | γ -AlOOH+ | |
| | | | | | | | | MnCO ₃ | |
| 4111.1 | Mn | Al | 2:1 | 80 | 80 | 8.5 | | n-cryst | |
| 4111.2 | | | | | 130 | | 3 | M(2)M(3)+ | 7.9 vs |
| | | | | | | | | γ -AlOOH+ | |
| | | | | | | | | MnCO ₃ | |
| 4135.1 | Mn | Al | 2:1 | 100 | 25 | 8.7 | | n-cryst | |
| 4135.2 | | | | | 200 | | 1 | M(2)M(3)+ | 8.0 s |
| | | | | | | | | γ -AlOOH | |
| 4136.1 | Mn | Al | 2:1 | 100 | 80 | 8.5 | | n-cryst | |
| 4136.2 | | | | | 220 | | 1 | M(2)M(3)+ | 8.0 w |
| | | | | | | | | γ -AlOOH | |
| 4137.1 | Mn | Al | 1:1 | 100 | 25 | 8.6 | | n-cryst | |
| 4137.2 | | | | | 130 | | 1 | M(2)M(3)+ | 7.9 vs |
| | | | | | | | | γ -AlOOH | |
| 4139.1 | Mn | Fe | 2:1 | 100 | 25 | 8.8 | | n-cryst | |
| 4139.2 | | | | | 130 | | 2 | Mn(OH) ₂ + MnFe ₂ O ₄ | |
| 4141.1 | Mn | Fe | 3:1 | 100 | 25 | 9.0 | | Mn(OH) ₂ | |

Table II. Continued.

| Sample number | Composition | | M(2) to M(3) ratio in source solution | Precipitation conditions | | | Annealing time days | X-ray diffraction | |
|---------------|-------------|------|---------------------------------------|--------------------------|---------|------|---------------------|---|---------------------------------|
| | M(2) | M(3) | | Conc. mM | Temp °C | pH | | Products | Basal spacing c' $d(00l)_s$ Å |
| 4141.2 | | | | | | | 1 | Mn(OH) ₂ MnFe ₂ O ₄ | |
| 4143.1 | Mn | Y | 3:1 | 100 | 25-80 | 8.8 | 3 | ? | |
| 4143.2 | | | | | 130 | | | | |
| 4144.1 | Mn | Y | 3:1 | 100 | 80 | 8.2 | 1 | Mn(OH) ₂ + α -Y(OH) ₃ | |
| 4144.2 | | | | | 130 | | | | |
| 4148.1 | Mn | In | 2:1 | 100 | 25 | 8.5 | 1 | Mn(OH) ₂ + n-cryst | |
| 4148.2 | | | | | 130 | | | | |
| 4151.1 | Mn | In | 3:1 | 100 | 25 | 8.6 | 1 | In(OH) ₃ n-cryst | |
| 4151.2 | | | | | 130 | | | M(2)M(3)+ In(OH) ₃ | 8.0 w |
| 4154.1 | Mn | In | 4:1 | 100 | 25 | 8.6 | 5 | M(2)M(3) | 8.0 w |
| 4154.2 | | | | | 130 | | | M(2)M(3)+? | 7.9 m |
| 4156.1 | Mn | Ga | 2:1 | 100 | 25 | 8.5 | 1 | M(2)M(3)+? | 7.6 w |
| 4156.2 | | | | | 130 | | | M(2)M(3)+? | 7.4 w |
| 4158.1 | Mn | Ga | 3:1 | 100 | 25 | 8.9 | 1 | M(2)M(3) | 7.9 m |
| 4158.2 | | | | | 130 | | | M(2)M(3) | 7.9 s |
| 4162.1 | Mn | | 1:0 | 100 | 25 | 8.8 | 3 | n-cryst Mn(OH) ₂ | |
| 4162.2 | | | | | 130 | | | M(2)M(3) | 7.9 w |
| 4200.1 | Fe | Al | 2:1 | 100 | 25 | 8.6 | 2 | Fe ₃ O ₄ + γ -AlOOH | |
| 4200.2 | | | | | 130 | | | M(2)M(3) | 7.8 w |
| 4202.1 | Fe | Al | 2:1 | 100 | 80 | 8.6 | 2 | Fe ₃ O ₄ + γ -AlOOH | |
| 4202.2 | | | | | 130 | | | M(2)M(3) | 7.8 w |
| 4205 | Fe | Al | 3:1 | 100 | 50 | 8.5 | | ? | |
| 4250.1 | Co | Al | 2:1 | 100 | 25 | 11.1 | 1 | M(2)M(3) | 7.8 w |
| 4250.2 | | | | | 130 | | | M(2)M(3) | 8.0 vs |

Table II. Continued.

| Sample number | Composition | | M(2) to M(3) ratio in source solution | Precipitation conditions | | | Annealing time days | X-ray diffraction | | |
|---------------|-------------|------|---------------------------------------|--------------------------|---------|------|---------------------|---|---|----------------|
| | M(2) | M(3) | | Conc. mM | Temp °C | pH | | Products | Basal spacing c' $d(00D), \text{\AA}$ | rel. intensity |
| 4263.1 | Co | Al | 3:1 | 100 | 25 | 11.1 | 1 | M(2)M(3) | 8.0 | w |
| 4263.2 | | | | | 130 | | | M(2)M(3) | 8.0 | s |
| 4265.1 | Co | Al | 2:1 | 100 | 25 | 11.1 | 1 | M(2)M(3) | 8.0 | vs |
| 4265.2 | | | | | 220 | | | M(2)M(3) | 8.0 | vs |
| 4268.1 | Co | Al | 1:1 | 100 | 25 | 11.0 | 1 | M(2)M(3)+ γ -AlOOH | 7.9 | vs |
| 4268.2 | | | | | 130 | | | M(2)M(3) | 7.9 | w |
| 4300.1 | Ni | Al | 2:1 | 100 | 25 | 8.8 | 1 | M(2)M(3) | 7.8 | m |
| 4300.2 | | | | | 130 | | | M(2)M(3) | 7.8 | w |
| 4303.1 | Ni | Al | 3:1 | 100 | 25 | 8.8 | 2 | M(2)M(3) | 7.9 | vs |
| 4303.2 | | | | | 130 | | | M(2)M(3) | 7.8 | w |
| 5028.1 | Ni | Fe | 3:1 | 200 | 25 | 9.0 | 7 | M(2)M(3)? | 7.8 | w |
| 5028.2 | | | | | 130 | | | M(2)M(3) | 8.0 | vs |
| 4350.1 | Cu | Al | 2:1 | 100 | 25 | 8.6 | 1 | Cu(OH) ₃ Cl+ CuO+ | 7.8 | w |
| 4350.2 | | | | | 130 | | | γ -AlOOH | 7.8 | w |
| 4353.1 | Cu | Al | 3:1 | 100 | 25 | 8.9 | 1 | M(2)M(3) | 7.7 | w |
| 4353.2 | | | | | 130 | | | Cu ₂ (OH) ₃ Cl+ CuO+ | 7.7 | w |
| 4355.1 | Cu | Al | 2:1 | 100 | 25 | 8.9 | 1 | γ -AlOOH | 7.8 | w |
| 4355.2 | | | | | 130 | | | M(2)M(3) | 7.8 | w |
| 4357.1 | Cu | Al | 2:1 | 100 | 25 | 8.9 | 1 | M(2)M(3)? | 6.1 | s |
| 4357.2 | | | | | 80 | | | M(2)M(3) | 6.1 | vs |
| 4357.3 | | | | | 130 | 9.0 | 2 | M(2)M(3) | 7.6 | vs |
| 4357.4 | | | | | 50 | 8.2 | 1 | M(2)M(3) | 7.9 | m |
| 4400.1 | Zn | Al | 2:1 | 100 | 25 | 8.9 | 1 | M(2)M(3) | 7.8 | vs |
| 4400.2 | | | | | 130 | | | M(2)M(3) | 7.9 | m |
| 4405.1 | Zn | Al | 3:1 | 100 | 25 | 8.9 | 1 | M(2)M(3) | 7.9 | m |
| 4405.2 | | | | | 130 | | | M(2)M(3) | 7.8 | vs |

TABLE III
 Interlayer spacings in pyroaurite type mixed layer hydroxides with sorbed complex anions, and chloride

| Sample | main layer cations | | Interlayer separation, <i>c</i> (in Å), by intercalated anion | | | | | | | | | | | |
|--------|--------------------|------|---|------|--|--|--|----------|-------------------------|---------|-------------------------------|-------------------------------|--------------------------------|-----------------------------------|
| | M(2) | M(3) | Cl | AMP | dodecyl SO ₄ ²⁻ | dodecyl SO ₃ ²⁻ | dodecyl PO ₄ ³⁻ | benzoate | 4-methyl- salicylate | acetate | SO ₄ ²⁻ | CO ₃ ²⁻ | MoO ₄ ²⁻ | Fe(CN) ₆ ⁴⁻ |
| 4000.2 | Mg | Al | 8.1 | | 23.5 | | | | | | | | | |
| 4004.2 | Mg | Al | 8.1 | 19.6 | 28.3 | 23 | 30 | | | | 11.0 | 7.8 | 11.3 | 10.9 |
| 4050 | Ca | Al | 8.1 | | 30 | | | | | | | | | |
| 4106 | Mn | Al | 7.9 | 17.9 | 24.2 | | | | | | | | | |
| 4111 | Mn | Al | 7.9 | | 24.2 | 23 | 26.8 | 15.4 | 16.9 | 13.1 | 11.0 | | 11.3 | 10.7 |
| 5028 | Ni | Fe | 8.0 | | 27.5 | | | | | | | | | |
| 4400.1 | Zn | Al | 7.8 | 19.3 | 26.8 | | | | | | | 7.8 | | |
| 4303.2 | Ni | Al | 7.9 | 17.0 | 25.2 | | | | | | | 7.6 | | |

Due to the large size of the Ca^{2+} ion, it is in these structures displaced about 0.57 Å from the $Z = 1.00$ Å position, normally occupied in the pyroaurite structure.¹ The inequality of the M(2) and M(3) positions (occupied by Ca^{2+} and Al^{3+}) leads, in contrast to the situation in the normal pyroaurite structures, to ordering of the cations in the main layer. Due to the increased interaction of the displaced M(2) ion with the interlayer anions and water molecules, these are more highly ordered than in pyroaurite structures in the strict sense. The resulting calcium aluminum hydroxide structure is hexagonal with space group $R\bar{3}$ or $R\bar{3}c$; at low temperature and small interlayer anion size it becomes slightly deformed (pseudohexagonal-monoclinic; $2/c$) (Allmann, 1970; 1977). With CO_3^{2-} and $(\text{OH})^-$ forming the interlayer anions, the structure occurs naturally as the mineral hydrocalumite.

In the present work, syntheses of this group of compounds were carried out at Ca:Al ratios of the chloride solutions of 0.5:1 and 2:1 at pH 8.2-8.4, and 3:1 at pH 12-12.7 (Table 2). Well crystallized calcium aluminum hydroxide chloride hydrate formed only under the latter conditions, particularly when combined with annealing at 130°C. A layer spacing c' of 7.8 Å was observed compared to 7.9 Å reported for the synthetic phase by Kuzel (1968) and 7.8 in the mineral hydrocalumite (Tilley, 1934; Tilley, Megaw and Hey, 1934; Butler *et al.* 1959; Ahmed and Taylor, 1967).

Synthesis at increased pH (sample #4055; pH 12.7; Table 2) or at low temperature (2°C; #4056) predictably resulted in smaller crystallite size with increased external surface to mass ratio; similar effects are observed in the synthesis of calcium hydroxyphosphate, apatite (Kuma *et al.*, 1989).

Among the eight pyroaurite type structures investigated, the calcium aluminum hydroxide chloride hydrate was found to be the most efficient sorbent of phosphate ion (Arrhenius and Gedulin, 1988).

In contrast to most other double layer hydroxides analyzed (Table 2), the calcium-aluminum structures do not show internal sorption of phosphate under the exchange conditions employed. However, sorption of alkyl anions such as dodecyl sulfate takes place readily, expanding the interlayer spacing c' to 30 Å.

In order to study the effect of coupling the large size of the Ca^{2+} ion to an increase in size also of the M(3) ion, synthesis was attempted of the previously unknown $\text{Ca}^{2+} \text{Y}^{3+}$ hydroxide chloride hydrate. At source ratios of calcium to yttrium 3:1 a nanocrystalline phase formed, structurally similar to the double layer Ca-Al hydroxide, and with $c' = 8.0$ Å. Annealing at 130°C led to crystallization of an unidentified phase with strongest reflection at 7.6 Å, similar to the pyroaurite structures; however, the lack of expansion with dodecylsulfate makes it likely that this is not an analogous structure. Increasing the source ratio Ca/Y to 4:1 resulted in the crystallization of $\text{Ca}(\text{OH})_2$, portlandite.

¹) This term, in a strict sense referring to Mg-Al hydroxyde carbonate (Table 1), is used here to include also the closely related Ca-Al double layer hydroxides, and, with regard to interlayer substitution, any anion species.

Magnesium aluminum- and magnesium ferrihydroxide

The magnesium-aluminum hydroxide is represented by minerals (Table 1) in the two characteristic stacking forms (hydrotalcite and manasseite), mainly observed with carbonate and sulfate as interlayer ions, singly or in mixed layer sequences (Ingram and Taylor, 1967; Allmann, 1968c; 1969; 1970; Allmann and Jepsen, 1969; Drits *et al.* 1987; Pausch *et al.* 1986). It is probably the most extensively investigated pyroaurite type phase, both as synthetic material (Miyata and Okada, 1977) and as mineral. Many of the latter have fallen prey to the desire to assign separate, trivial names to minerals with slightly different isomorphous substitutions, as indicated in Table 1. The sulfate form, and mixed layer carbonate-sulfate phases have been shown by Drits *et al.* (1985, 1987) to occur commonly as authigenic products in evaporite deposits and in marine volcanogenic sediments. Their presence was also forecast by the demonstration by Thomassin and Touray (1979; 1982) and Grovisier *et al.* (1983) that Mg-Al hydroxide carbonate forms in the laboratory as a hydrothermal reaction product of basalt and seawater. Drits *et al.* (1987) proposed a rational scheme, followed here in abbreviated form, for generic naming of all double layer hydroxide minerals based on composition of the main hydroxide layer, the interlayer composition, the periodicity of the stacking and symmetry of the structure (cf. Table 1).

In their chloride forms, the Mg-Al and Mg-Fe (3) hydroxides have a characteristic c' spacing of 8 Å, and can be readily crystallized in the rhombohedral form at room temperature (Fig. 2); annealing at 120 °C for a day leads to crystal growth to the order of 0.5 µm in the a-b direction (Fig. 3, 4). Species with interlayer chloride (Table 1) also occur as the minerals iowaite [MgFe(3) hydroxide main layer] (Kohls and Rodda, 1967; Allmann and Donnay, 1968) and koenenite [MgAl hydroxide] (Berdesinski, 1952; Allmann *et al.*, 1968), the latter with a complex anionic interlayer of the composition $[\text{Na}_4(\text{Ca},\text{Mg})_2\text{Cl}_{12}]^{4-}$.

Large alkyl anions are readily intercalated, such as dodecyl sulfate ($c' = 25$ Å) (Fig. 5), and dodecyl phosphate ($c' = 30$ Å). Sulfate intercalation leads to expansion of the chloride form to $c' = 8.8$ Å in the lowest state of hydration, and a discrete higher hydration state at 11 Å. Orthophosphate, pyrophosphate, and polyphosphate (P_6O_{18}) expand the interlayer and bond strongly (Gedulin *et al.*, 1989); the isotherm for PO_4^{3-} indicates the capacity of this mineral group to effectively concentrate phosphate species from dilute solution (Arrhenius and Gedulin, 1988). Molybdate, chromate and vanadate expand the basal spacing into the range 11 to 12 Å (Table 3). Similar results are reported in the literature dealing with the use of hydrotalcite complexes for industrial catalysis (Reichle, 1986; Kwon *et al.*, 1988; Drezdson, 1988; Chibwe and Jones, 1989). AMP and ADP are readily sorbed with interlayer expansion up to 24 Å; the interlayer nucleotides are released in exchange with carbonate or bicarbonate ion (Gedulin *et al.*, 1988). In contrast, ATP in corresponding concentrations (3 mM) does not enter the interlayer in exchange for chloride ion, at noticeable rates under the exchange conditions used.

FILE: MGAL1 09-29-1987 CoK α 40 KVP 8 MA
 Mg: A1=3: 1, pH10 25oC

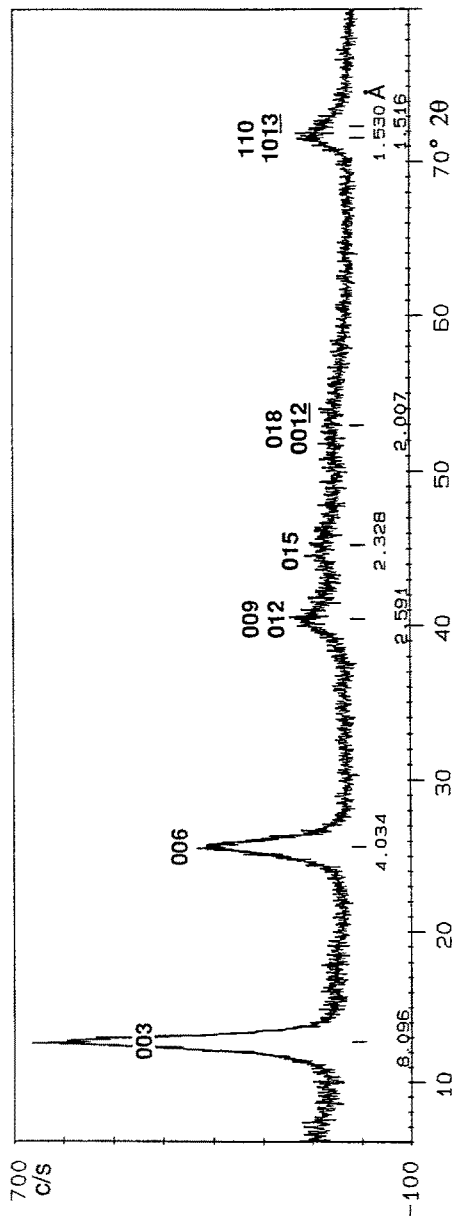


Fig. 2. X-ray diffractogram of magnesium aluminum hydroxide chloride. This is the chloride form of the mineral hydrotalcite, a common pyroaurite type product of alteration of submarine basalt by seawater. The mineral analog was synthesized at 25 °C, resulting in small crystallites (~50–100 nm) and correspondingly weak and broadened diffraction maxima in comparison to the same material annealed hydrothermally (Figs. 3, 4).

In this and following diffraction diagrams the power (intensity) of diffraction in counts per second is indicated on the y-axis, and the Bragg angle of diffraction 2θ on the x-axis. The angular position of diffraction maxima is marked, and the corresponding interplanar spacing in ångström units indicated. The radiation employed (in this case K α radiation from cobalt) is shown in the upper right together with acceleration potential in kVp, and tube current in mA.

The most notable variable in the structures, illustrated by this and following figures, is the basal spacing c' (003) and its overtones (006...00n), representing the separation of the hydroxide layers by the intercalated anions, and thus indicating their size and orientation in the interlayer between the cation-carrying main sheets of the mineral structure.

In the synthetic phases used for the present study, chloride was initially introduced as an easily exchangeable interlayer anion; the rate and extent of exchange with other anions can then be followed by measurement of the discrete change in basal spacing, in addition to other properties such as chemical composition, infrared absorption, etc.

The c' spacings, given in the text and the tables, are calculated from the value of the highest order reflection observed (e.g. in this figure from (006); in Fig. 5 from (0018)), since the error in calculated interplanar distance c' decreases with increasing Bragg angle 2θ .

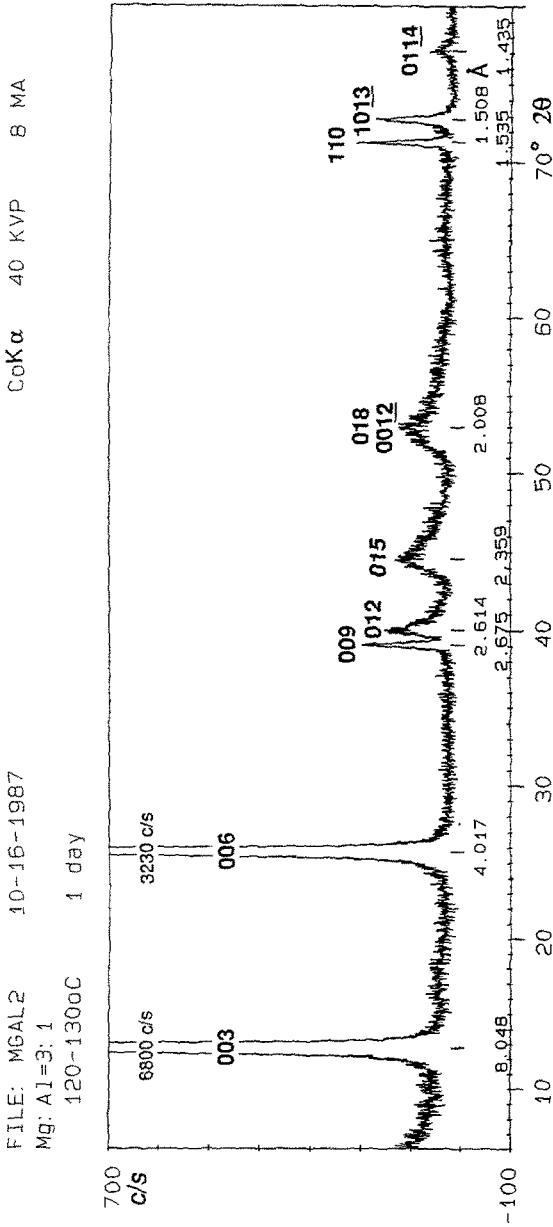


Fig. 3. X-ray diffractogram of synthetic magnesium aluminum hydroxide chloride (sample no. 4004, Table 2), annealed hydrothermally. Because of their platy habit (cf. Fig. 4), the crystals are preferentially oriented, resulting in strong enhancement of the basal reflections and commensurate suppression of (hk0) type reflections. The opposite situation arises in electron diffraction with the beam normal to the flat crystal (Fig. 4c); in this case only (hk0) reflections are recorded.

The crystalline perfection, achieved by growth at annealing, is indicated by the tenfold enhancement of diffracted power from the basal planes over the 25 °C preparation (Fig. 2). The asymmetry of the (0kl) diffraction profiles suggests turbostratic stacking disorder, further shown by electron diffraction, and by the rounded outline of the nominally hexagonal crystal plates (Fig. 4).

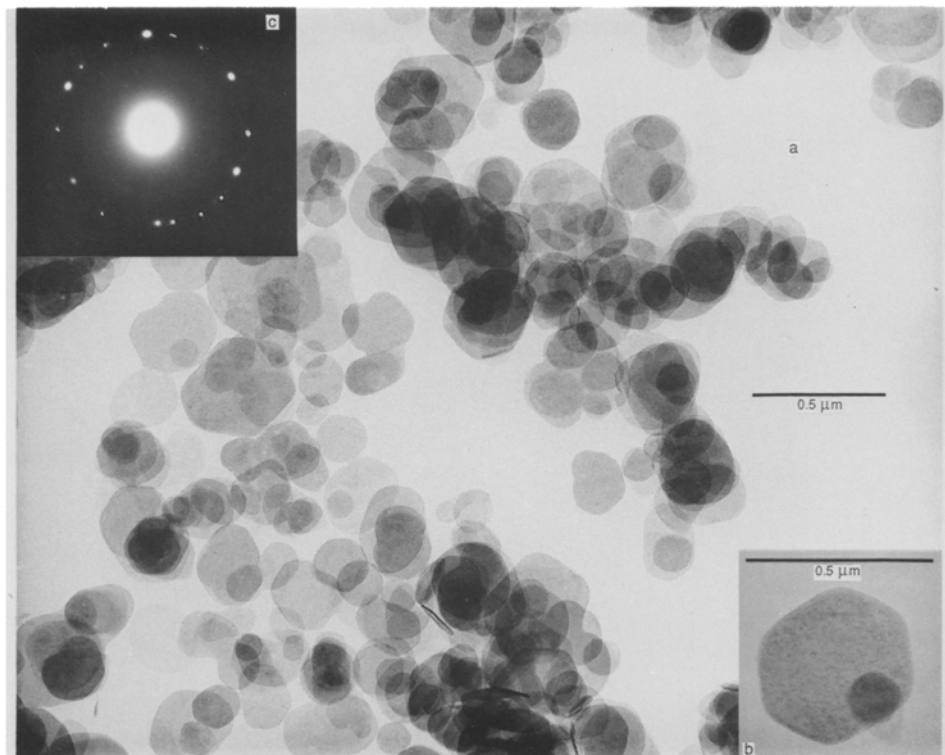


Fig. 4a, b. *Electron micrographs, and (c) electron diffractogram, of magnesium aluminum hydroxide chloride (hydrotalcite chloride) from Fig. 3.* The crystals show a high degree of perfection in the *c*-direction (normal to the hydroxide sheets and to the plane of the photograph), indicated by the sharpness of the (003) basal reflections in Fig. 3, but angular offset between successive sheets or sheet packs (turbostratic structure) shown by asymmetric (0*kl*) reflections in Fig. 3 and multiple hexagonal spot sets (Fig. 4c). These spots are diffracted from the prism planes (110), parallel to the *c*-axis in the isolated single crystal in Fig. 4b. This twist in registry between the layers results from the relatively weak bonding between the main sheets and the interlayer ions, and probably causes the rounding of the hexagonal form of the crystals. With increasing size of the sorbed interlayer ions, vanishing layer registry is suggested by the weakening of reflections (*hk*0) and (0*kl*), such as in Fig. 5. This situation typically arises with interlayer arrays of nucleoside phosphates such as AMP and ADP, ferrocyanide- and carboxylate ions.

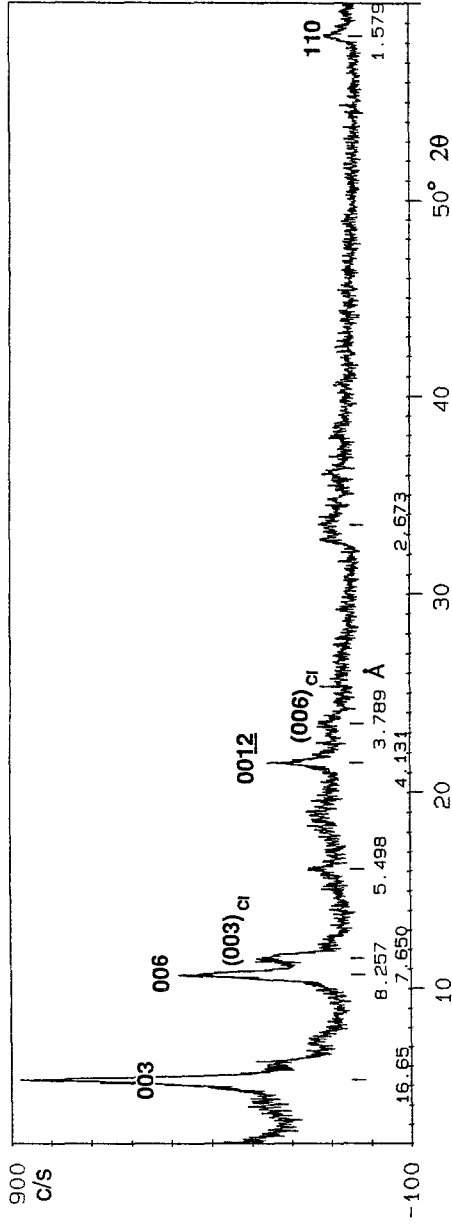
The crystals are frequently seen to have grown epitactically from small seeds, characteristic of the low temperature source material (Fig. 2).

Ferrocyanide- and ferricyanide ions are sorbed, with *c'* expansion to 11 Å. Ferrocyanide ion sorption was first demonstrated by Miyata and Hirose (1976; 1978), see also Miyata (1980; 1983).

In the low-temperature experiments reported here, the rhombohedral $R\bar{3}m$ phase with stacking order of the positions A, B and C of the threefold axis, -BC-CA-AB-BC- is consistently formed; the hexagonal form with space group $P6_3/mmc$ and stacking sequence -BC-CB-BC- is in all likelihood, and in analogy with the Mg-Fe³⁺ hydroxide carbonates (pyroaurite - sjögrenite), the stable form at higher temperatures (Allmann, 1970). Magnesium ferrihydroxide chloride, corresponding

FILE: 2236AMP2 04-27-1989 CuK α 40 KVP 20 MA

MnAl hydroxide - AMP, 40C, 2 days



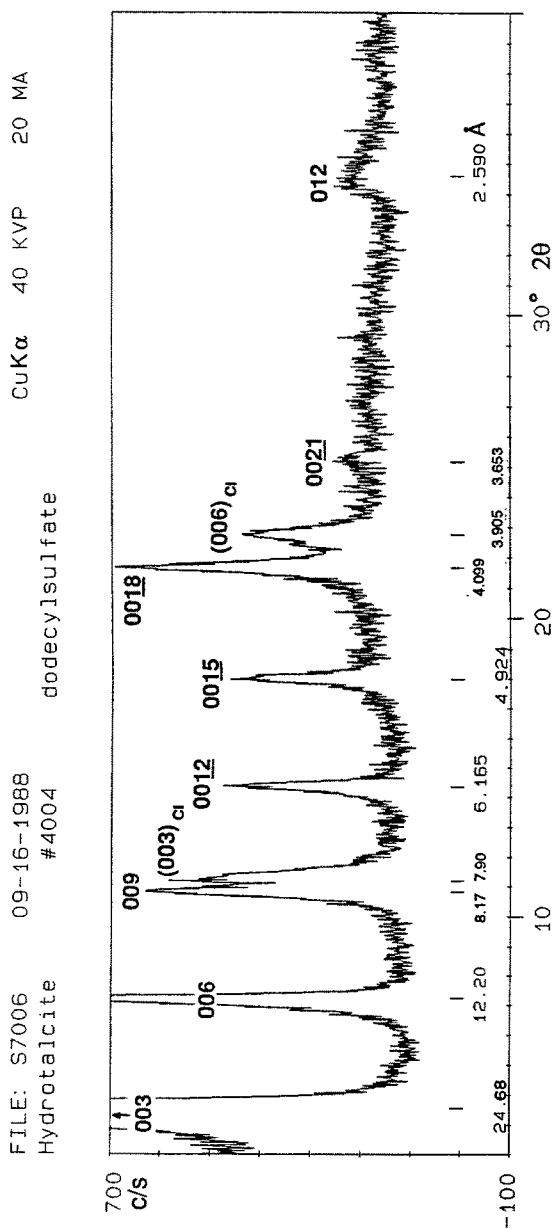


Fig. 5. X-ray diffractograms showing structural effects of concentration and ordering of large organic anions by intercalation between the molecular metal hydroxide sheets: a) AMP; b) dodecylsulfate.

AMP was, in this case, sorbed from 0.002 M solution, displacing the chloride ions occupying the interlayer and converting the mineral to a stoichiometric manganese aluminum hydroxide-adenosine monophosphate hydrate complex. The AMP ions are oriented with their polar axes normal or near-normal to the metal hydroxide sheets to which the phosphate groups are loosely attached. The intercalation of this double layer array of AMP ions expands the distance between the hydroxide sheets from 7.7 to 16.7 \AA , as evidenced by the fundamental c' (003) reflection, and higher orders. Catalytic reactions of manganese hydroxide with ADP as substrate are discussed by Gedulin (1989).

Dodecylsulfate (Fig. 5b) provides an example of an ionic, long-chain hydrocarbon compound, intercalating with molecular orientation similar to that of ADP. However, in this case the basal spacing is expanded to 25 \AA because of the larger size of the substrate molecule. Each pair of metal hydroxide sheets, with its double interlayer of opposing, polarized alkyl sulfate ions, forms an amphiphilic bilayer with a highly lipophilic environment in the midplane of the double alkyl sulfate interlayer. The high degree of order along the axis normal to the molecular sheets of the mineral-adduct complex results in the appearance of a large number of higher order reflections ($n > 1$ in $n\lambda = 2d \sin \theta$; the Bragg angle θ relationship to the interplanar spacing d at fixed wavelength λ); up to the seventh-order basal reflection (0021) of the fundamental (003) is seen in Fig. 5b. A small fraction of the sample remains unexpanded, as shown by the residual first and second order reflections of the original chloride complex, marked (003)_{Cl} and (006)_{Cl} in 5a and b.

to the type mineral pyroaurite (Fron del, 1941), was synthesized at a ratio Mg/Fe 3/1 and pH 9. The basal spacing c' was found to be 8.2 Å, similar to the value, 8.0, found by Kuzel (1968); variations in spacing may be due to differences in the hydration of the interlayer.

Manganese(2) aluminum hydroxide

This phase, which has not yet been reported as a mineral, formed optimal crystals when the reactant solution contained an excess of aluminum (Mn:Al=2:1-1:1), resulting in the formation of a major amount of MnAl-hydroxide chloride and the excess aluminum crystallizing as γ -AlOOH. Aqueous annealing at 130 °C led to increased crystal perfection and size (Fig. 6-7), and at 220° resulted in partial conversion of the MnAl-hydroxide to Mn(OH)₂ and γ -AlOOH. It is sensitive to oxidation, already at room temperature leading to topotactic growth of hausmannite (Mn₃O₄).

The interlayer chloride ion can be readily exchanged against a variety of mono- or polyvalent anions, with expansion of the basal spacing c' with alkyl sulfate and -phosphate to 26 Å, with salicylate, trichloroacetate, benzoate and acetate to 17, 16, 15 and 13 Å respectively (Table 3). Sulfate, orthophosphate and molybdate substitution in the interlayer expanded this to c' about 11 Å. Introduction of carbonate ion led to conversion of the MnAl-hydroxide to MnCO₃ and an undefined aluminous phase; 0.1-0.2 M pyrophosphate and hexametaphosphate dissolved the solid at pH 7.9 and 7.0 respectively. AMP and ADP were efficiently sorbed from 2.5-5 mM solution and gave well ordered complexes with c' in the range 17-24 Å, while no interlayer sorption or expansion was observed with 3 mM ATP. Breaking of the glycosidic bond, liberating adenine, was found to be strongly enhanced catalytically in ADP, presumably by partially oxidized manganese in the manganese aluminum hydroxide (Gedulin, 1989).

Mn²⁺ M³⁺ hydroxides with Fe³⁺, Y³⁺, Ga³⁺ and In³⁺

Synthesis was attempted of the previously unknown Mn²⁺M³⁺ hydroxides with Fe³⁺, Y³⁺, Ga³⁺ and In³⁺ as trivalent ions, in order to explore the stability of the M(2)M(3) hydroxides over a range of electronic structures. At a source ratio 2:1 of Mn:Fe an unidentified nanocrystalline material is formed, which at aqueous annealing at 130 °C crystallizes as Mn(OOH), possibly due to accidental partial oxidation, together with manganese-iron spinel Mn²⁺O·Fe₂³⁺O₃. At increase of the ratio to 3/1, Mn(OH)₂ (pyrochroite) appears in the low temperature precipitate, and persists, in addition to the spinel, at 130 °C annealing.

Substitution with Y³⁺ yielded Mn(OH)₂, Mn(OH)₃ and δ -Y(OH)₃ as separate hydroxide phases, while crystallization with Ga³⁺ and In³⁺, together with unidentified compounds, gave phases of pyroaurite type with c' 7.9 Å for the MnGa-hydroxide chloride and 8.2 Å, for the MnIn phase. These structures, which have previously not been reported, remain to be studied in detail. The MnGa-pyroaurite phase persisted and grew at 130 °C while the MnIn hydroxide chloride formed at 25°,

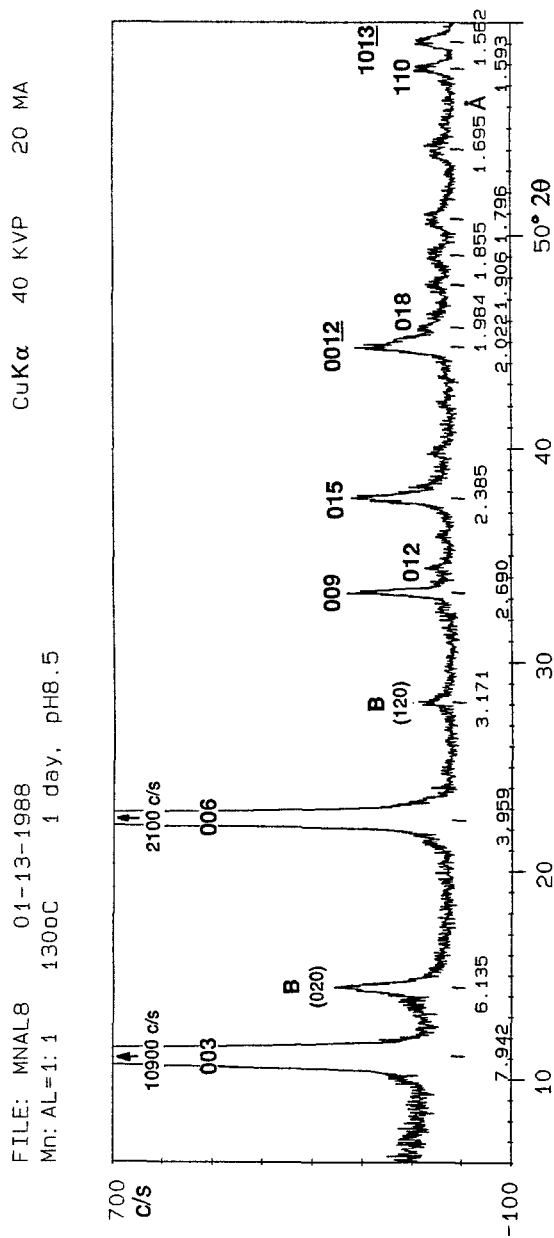


Fig. 6. *Pyocaurite* type structure with manganese as divalent- and aluminum as trivalent cation in the main hydroxide sheet, and chloride as anion in the hydrated interlayer.

This double layer hydroxide is among those that most readily exchange interlayer anions such as chloride for oxyanions such as molybdate and phosphate or large organic anions, including AMP, ADP, acetate, alkyl sulfate and sulfonate (see Table 3). It catalyzes breakage of the glycosidic bond in ADP (Gedulin, 1989).

The product shown in this X-ray diffractogram was prepared with an excess of Al^{3+} , leading to the formation of γ - $AlOOH$ (boehmite) as a second phase, indicated by the reflections B (020) and B' (120).

An electron micrograph of the material is shown in Fig. 7.

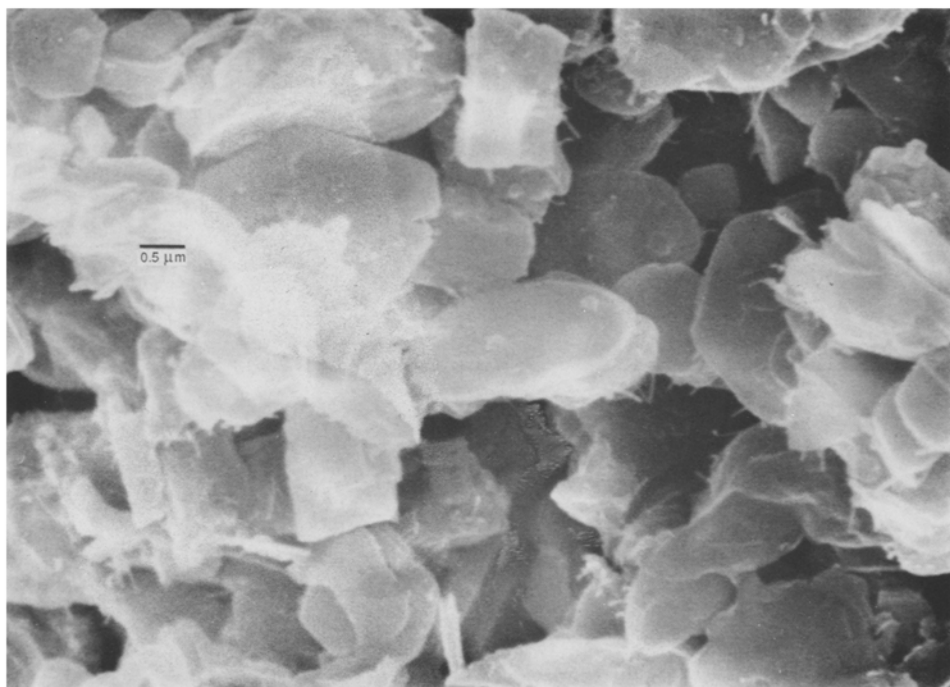


Fig. 7. Scanning electron micrograph of manganese aluminum hydroxide crystals with dodecylsulfate anion interlayer (cf. structure; Fig. 6). The metal hydroxide- and interlayer sheets are in the planes of the crystal plates, which, particularly when the interlayer consists of large, organic anions such as here, also are planes of easy cleavage and gliding.

The small fibrous overgrowths are crystals of γ -AlOOH (boehmite) from excess Al^{3+} above saturation of the pyroaurite structure with this ion at about Mn:Al 2:1.

decomposed into an unidentified phase or assemblage at elevation of the temperature to 130° . The intercalated sheet structure of the manganese-aluminum hydroxide is confirmed by the fact that it readily sorbs dodecyl sulfate into the interlayer, expanding the basal spacing c' to 24 \AA .

Iron (2) aluminum hydroxide

This pyroaurite analog (in chloride form) was readily synthesized at room temperature; the a_0 lattice parameter is closely similar to that of analogous structures with Mn^{2+} , Co^{2+} , and Ni^{2+} as divalent components of the main hydroxide layer. The Fe^{2+} phase differs, however, both with regard to stability and hydrogen bonding of the hydroxide sheets. At 130° hydrous annealing it decomposes to spinel (magnetite, $\text{Fe}^{2+}\text{O}\cdot\text{Fe}_2^{3+}\text{O}_3$) and γ -AlOOH (boehmite), and even a highly polar anion such as dodecyl sulfate is not capable of separating the hydroxide sheets and entering into the interlayer under the exchange conditions employed. The instability against auto-oxidation to spinel is characteristic also for the pyroaurite type $\text{Fe}^{2+}\text{Fe}^{3+}$ hydroxide (green rust) (Schrauzer and Guth, 1976), which, however, has

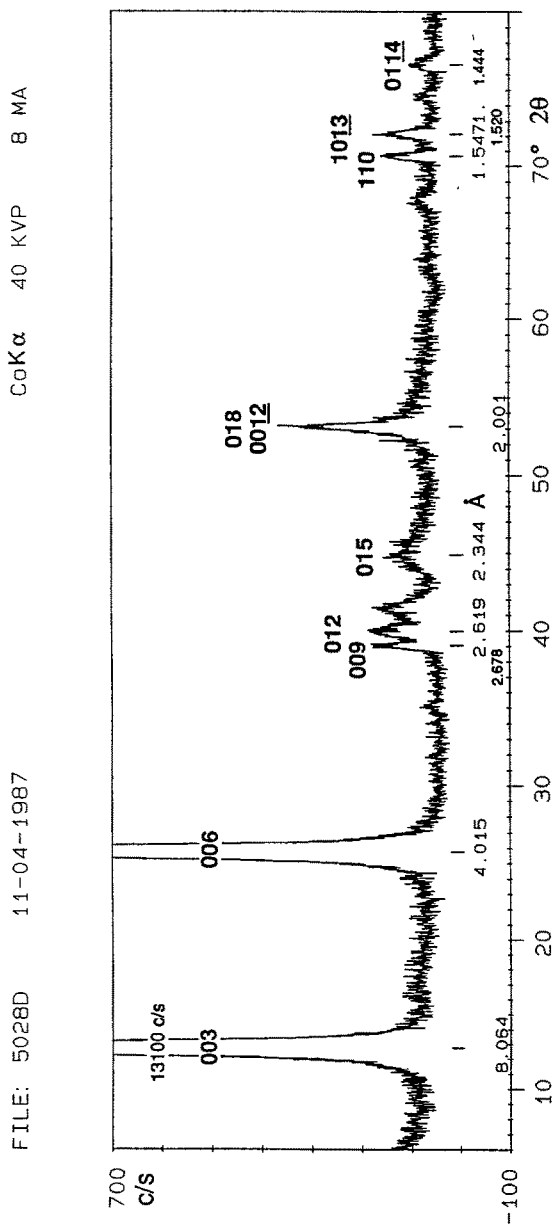


Fig. 8. X-ray diffractogram of synthetic chlorite analog of the mineral reevesite, nickel iron(3) hydroxide with varying anion species (Table 1). The use of this mineral for reactions with organic anions of biogenic importance is of particular interest since both of the main sheet cations are transition metal ions, yet the divalent ion is stable against oxidation, a feature shared also by the Co(2)Fe(3) hydroxides. Reevesite is found to concentrate ADP and ATP, as well as inorganic orthophosphate and condensed phosphates particularly effectively by adsorption (Gedulin, 1989).

an anion-accessible, expandable interlayer.

Cobalt (2) aluminum hydroxide

This M(2)M(3) hydroxide was first prepared with OH⁻ as interlayer ion by Ribi (1948) and with Cl⁻, Br⁻ and NO₃⁻ by Feitknecht (1953). We found the chloride to form readily at room temperature, to develop exceptional crystalline perfection at 130° and, as expected from the high oxidation potential of the couple Co²⁺/Co³⁺, to show stability against oxidation and spinel formation at elevated temperature (≤ 130C). It readily sorbs AMP, polyphosphate and complex metal anions such as molybdate, chromate, vanadate, ferro- and ferricyanide (Table 3).

Nickel aluminum- and nickel iron (3) hydroxide

With the divalent/trivalent cations in proportion 3/1 both of these compounds were found to crystallize with pyroaurite type structure, highly perfected at 130° annealing (Table 2.4). Both phases are known as minerals (Table 1) with names such as eardleyite (Ni-Zn, Al) and reevesite (Ni, Fe(3) hydroxide (Jambor and Boyle, 1963; Lapham, 1965). The synthesis of the NiAl-phase was first reported by Feitknecht (1942) and the Ni Fe(3) hydroxide in the present study (Fig. 8). Both phases sorb alkylsulfate, AMP, and orthophosphate in the interlayer with corresponding expansion of the main hydroxide sheet separation (Table 3).

Copper aluminum hydroxide

The structure of Cu(2)M(3) hydroxides differs from other transition metal analogs, presumably due to Jahn-Teller crystal field distortion. This tends to destabilize the pyroaurite type double layer structure when chloride ion is used as the interlayer anion, resulting in a three-dimensional network, lacking the anion exchange capability, characteristic of the pyroaurite type sheet structure.

Our experiments indicate that the pyroaurite-type double layer hydroxide chloride may form at room temperature (experiments 4350 and 4353; Table 2), although with a weak and broadened c' reflection (Fig. 9a) indicating crystal imperfection or small crystallite size. Aqueous annealing at 130°, however, leads to decomposition of the low temperature structure with the formation of the three-dimensional hydroxide trichloride (para-atacamite) together with cupric oxide (tenorite) and γ-AlOOH (boehmite) (exp. 4351 and 4354; Fig. 9b).

It was reported by Wells (1986) that bromide as the interlayer anion stabilizes the Cu(2)Al(3) sheet structure. Replacement of chloride- with bromide ion in the synthesis and in the annealing solution indeed resulted in formation of a structure with features similar to the double layer hydroxides (exp. 4357). Annealing at higher temperatures, 80 and 130 °, caused contraction of the c' spacing from 7.57 to 6.07 and 6.05 Å respectively, and the appearance of new phase indicating instability, also the bromide substituted structure, at elevated temperature.

The bromide substituted hydroxide structure (samples 4357 and 4360) resisted week-long attempts to replace the interlayer anion content and expand the structure

FILE: CUAL1 11-17-1987
 Cu: Al=2: 1 250c pH8.5

CoK α 40 KVP 8 MA

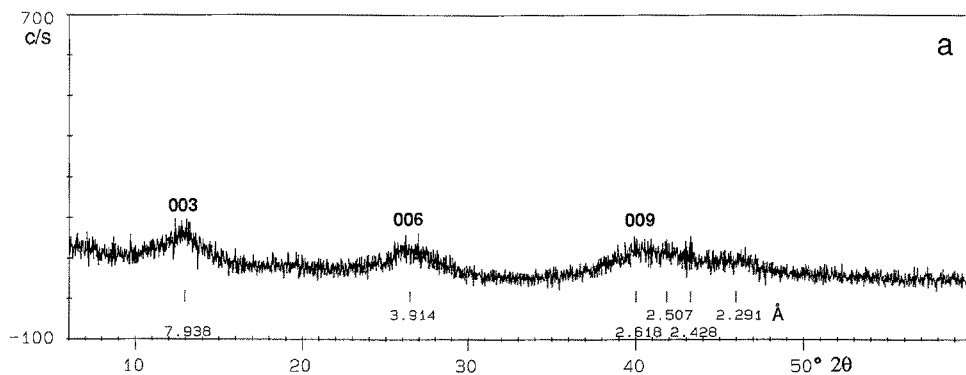


Figure 9a.

FILE: CUAL1A 11-17-1987
 1300C 1 day,
 (Cu: Al=2: 1)

CoK α 40 KVP 8 MA

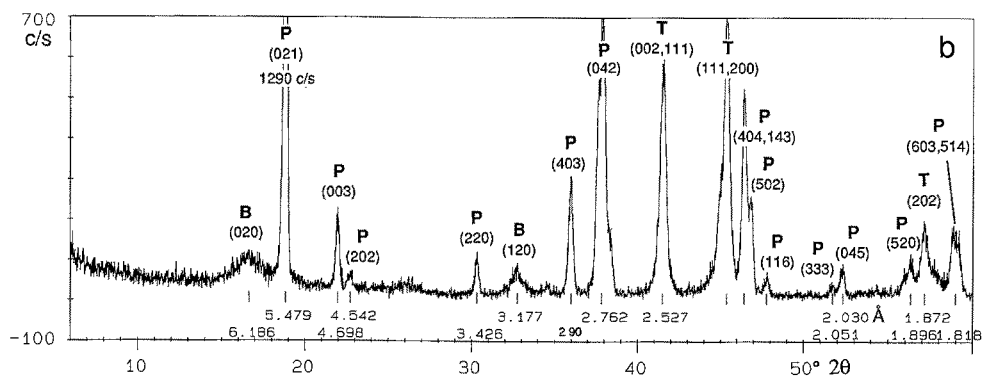


Figure 9b.

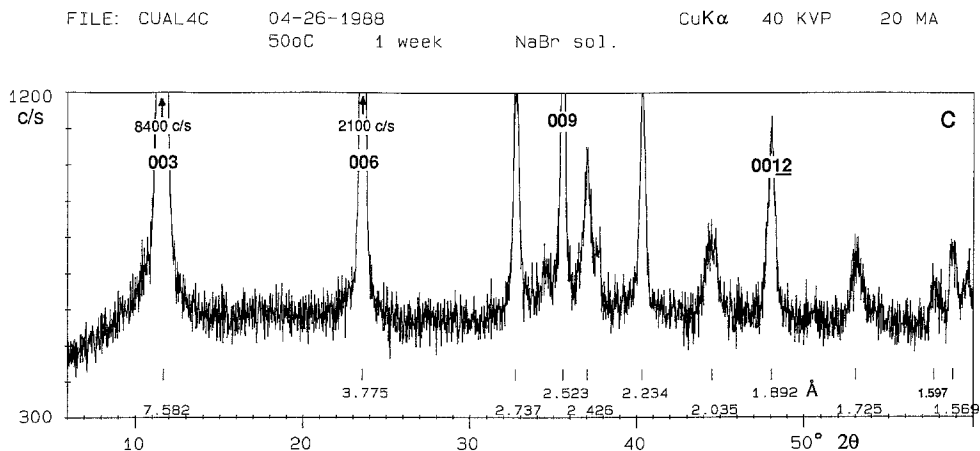


Figure 9c.

Figs. 9a-c. *Structural features of copper aluminum hydroxide.*

a. Chloride form, crystallized at 25 °C. The broad, low intensity diffraction maxima indicate a layer structure with crystallite size \lesssim 50 nm and/or low degree of long range order.

b. The structure in *a* is unstable at elevated temperature and decomposes at or below 130° into γ -AlOOH (boehmite, B), $\text{Cu}_2(\text{OH})_3\text{Cl}$ (para-atacamite, P) and CuO (tenorite, T), whose reflections are marked with respective Miller indices (hkl) in the graph.

c. Replacement of chloride ion with bromide in the interlayer, and in the surrounding aqueous solution stabilized the layer structure, incipient in *a*, and perfect it at hydrothermal annealing. The detail relationship between this structure and the pyroaurite type is however not yet clear, since reflections, except those tentatively assigned to basal planes, have not been indexed. The copper aluminum hydroxide bromide, like the low-temperature chloride also resists exchange and intercalation even with highly polar anions such as alkylsulfates.

with dodecylsulfate.

Zinc aluminum hydroxide

This member of the double layer hydroxide group was investigated early by Feitknecht (1942) and made the subject of yet another metal hydroxide thesis at Bern (Siegfried, 1955), substituting the OH^- interlayer with Cl^- , Br^- , NO_3^- and SO_4^{2-} . Our experiments (4400–4406) showed the structure to be stable and developing crystalline perfection at 130° , and to readily sorb dodecyl sulfate and AMP with characteristic interlayer expansion from $c' 7.82 \text{ \AA}$ to 26.8 and 19.2 \AA respectively.

The zinc aluminum hydroxide was used extensively as a host structure for nucleotide- and phosphate sorption in the experiments by Gedulin (1989), yielding further information on its ion exchange properties.

Discussion

The various M(2)M(3) double layer hydroxides differ considerably with regard to properties potentially important in prebiotic molecular chemistry such as thermal stability; disproportionation with auto-oxidation and hydrogen formation; interlayer anion exchange; steric configuration and internal mobility of sorbed interlayer anions and polar molecules. The ferroferric- (green rust) (Arrhenius *et al.* 1989) together with manganese and magnesium aluminum- and ferric compounds, with carbonate, chloride and silicate as interlayer anions suggest themselves as the most abundant species in the Archean ocean, green rust presumably being the precursor mineral for magnetite in the banded iron formation. Other pyroaurite type structures could have been of importance because of their specific properties and local concentration – they may also enter into solid solution in more abundant species.

Of the phases investigated, the Fe(2)Fe(3) hydroxide is most unstable toward decomposition to spinel (magnetite) by disproportionation of Fe(2), accompanied by reduction of water (Schrauzer and Guth, 1976; Jingkun *et al.*, 1984), and is thus providing a potentially important, continuous source of nascent hydrogen in the primordial ocean. This is further enhanced by photochemical oxidation of the solid (Schrauzer and Guth, 1976; Arrhenius, 1987), similar to the reaction described for dissolved Fe^{2+} and $[\text{Fe}(\text{OH})_2]^0$ (Cairns-Smith, 1982; Braterman *et al.*, 1983; Mauzerall and Borowska, 1988). The conversion of green rust to magnetite is rapid in the presence of cyanide ion, and less rapid when ferrocyanide ion is introduced in the interlayer; both the ferroferricyanide product and the ferrocyanide substituted green rust could, in the Archean ocean, have formed reservoirs of concentrated cyanide of potential significance for production of hydrogen cyanide oligomers and derivatives such as nitrogen bases (Arrhenius *et al.*, 1989).

In general, pyroaurite type structures with Fe^{2+} as the M(2) ion are unstable against auto-oxidation leading to spinel formation; Mn^{2+} with higher oxidation potential forms a stable pyroaurite structure with Fe^{3+} at low temperature but converts to Mn-Fe spinel at 130°C .

Understandably then, divalent cations with filled *s* shells such as Mg^{2+} and Ca^{2+} , or filled *d*-shells such as Zn^{2+} show thermal stability up to temperatures in the 300–500° range where dehydroxylation ultimately leads to phase transformation. Co^{2+} also stabilizes the M(2)M(3) hydroxide structure due to the high intrinsic oxidation potential for the couple Co^{2+}/Co^{3+} , and the inability of OH as a ligand to lower the potential substantially; introduction of cyanide ion in the interlayer could however conceivably destabilize the structure by formation of cobalt complex pairs with lower oxidation potential.

The Cu(2)M(3) hydroxides provide an interesting case, where the instability of the chloride complex probably is determined by electron configuration anisotropy at the formal M(2) valence state of the cation; the stabilization by Br^- and I^- is probably caused by their enhanced electron donor properties over Cl^- , and increase of the covalent character of the bond.

The strength of bonding of anions and polar molecules in the interlayer of the pyroaurite type hydroxide sheet structures changes markedly both with anion type and with the nature of the metal cations in the main hydroxide layer. Sorption isotherm determinations with different anions has been carried out by Miyata *et al.* (1983), using magnesium aluminum hydroxide as the host structure with nitrate as leaving anion in the interlayer. These data indicate the strong sorption preference for anions with high charge density; in exchange reactions against NO_3^- the planar carbonate ion was most strongly sorbed, followed by SO_4^{2-} , OH^- , F^- , Cl^- , Br^- , and I^- .

The strong carbonate ion interlayer bond is reflected in the prevalence of carbonate substituted M(2)M(3) hydroxides in nature; other interlayer anions such as sulfate and chloride, impressed by mass action, are found in M(2)M(3) hydroxides, grown in saline environment (Allmann and Lohse, 1966; Allmann *et al.*, 1968; Kohls and Rodda, 1967; Drits *et al.*, 1987). Silicate ion in $10^{-3}M$ concentration is effectively sorbed by green rust (Karim, 1986); this affinity is reflected by the relatively common ore grade occurrence, in the Archean, of layer structure ferroferric hydroxide silicates (Table 1). These are presumably derived by diagenetic alteration (mainly dehydration) of green rust silicate.

The bond strength of carbonate and hydrogen carbonate ion has been used by Gedulin (1989) to displace into solution nucleotides, introduced into the interlayer, and their reaction products. The capability of different anions in displacing chloride ion from the interlayer in a variety of M(2)M(3) hydroxides is indicated in the discussion of the individual hydroxide phases above and in Table 3. The displacement is here evidenced by the change in interlayer spacing, reflected by the *c'* parameter (Table 2).

A diagnostically useful result is the finding of highly stable complexes forming with alkyl anions such as dodecyl sulfate and -phosphate. The sorbed interlayer structures are probably similar to those obtained with long-chain alkyl ammonium cations in sheet structure minerals with excess negative framework charge such as the smectite minerals, e.g. montmorillonite (Walker, 1967), and in the manganates

(Paterson, 1981; Arrhenius and Tsai, 1981). The efficient expansion yields large Lorentz-polarization- and structure factors, and thus high diffraction intensities. This effect provides a potentially useful tool for identifying and measuring pyroaurite type minerals in complex micro- or nanocrystalline phase mixtures such as sediments and weathering products, where they are easily masked by clay minerals and are likely to be overlooked. The layer spacing obtained at intercalation of the M(2)M(3) hydroxides with dodecyl sulfate varies between 24 and 31 Å (Table 3). The stacking dimensions of the complex indicate that the alkyl anions are oriented normal or near-normal to the hydroxide sheet planes, with the ionic ends bound to the hydroxide sheets and with the non-ionic ends from opposite layers meeting or partially overlapping. As pointed out by Boyd *et al.* (1988) for an analogous arrangement of alkyl cations in smectite minerals, this generates a hydrophobic environment along the midplane of the interlayer, permitting the entry of lipids and lipid soluble molecules. This property of the alkane containing pyroaurite type minerals gives them the characteristic of lipid bilayer membranes, stabilized and protected by the laterally infinite molecular sheets of metal hydroxide, and suggests their possible importance in early membrane evolution (cf. Oró *et al.*, 1978).

Of the phases investigated in this work, only three show sufficiently strong hydrogen bonding across the main hydroxide sheets to resist intercalation and expansion with dodecyl sulfate under the conditions utilized; these are the Fe(2)Al(3), the Ca(2)Y(3) and the Cu(2)Al(3) structures.

The catalytic activity of the M(2)M(3) hydroxides, established by their interaction with ADP, is now being investigated in contexts relevant to biomolecular evolution (Gedulin, 1989).

Acknowledgments

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