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NEW MEMBERS OF THE HYDROTALCITE-MANASSEITE GROUP

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Abstract—Several new minerals, structurally and chemically similar to the hydrotalcite-manasseite group, have been found in the saline deposits of the central pre-Caspian depression and in those of Middle Asia. Their structures consist of layers of $(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_2$ plus interlayers of anions and molecular water. In addition to manasseite itself, $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{CO}_3) \cdot 3\text{H}_2\text{O}]$, having unit-cell parameters of $a = 3.042$, $c = 2 \times 7.56 = 15.12 \text{ \AA}$ and a calculated density of $D_c = 2.15 \text{ g/cm}^3$, other varieties were identified whose interlayers contain alternately SO_4^{2-} or SO_4^{2-} and CO_3^{2-} anions. The following new phases were recognized: (1) an 8.85- \AA phase having the composition $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{SO}_4) \cdot 3\text{H}_2\text{O}]$, subcell dimensions of $a' = 3.04$, $c' = 8.85 \text{ \AA}$, and $D_c = 1.96 \text{ g/cm}^3$; (2) an 11- \AA phase having the composition $[(\text{Mg}_{3.96}\text{Fe}_{0.06}\text{Al}_{1.98})(\text{OH})_{12}][\text{Na}_{0.56}(\text{SO}_4)_{1.30} \cdot 7.3\text{H}_2\text{O}]$, hexagonal unit-cell parameters of $a = \sqrt{3} \times 3.042 = 5.28 \text{ \AA}$, $c = 11.16 \text{ \AA}$, and $D_c = 1.90 \text{ g/cm}^3$; (3) a 16.5- \AA mixed-layer phase having the composition $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{SO}_4)_{0.5}(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}]$ and an ordered ABAB . . . alternation of 7.56- \AA layers (i.e., a brucite-like layer + a CO_3^{2-} -containing interlayer) and 8.94- \AA layers containing SO_4^{2-} anions in interlayers; this phase has unit-cell dimensions of $a' = 3.05$, $c' = 16.5 \text{ \AA}$ and $D_c = 2.06 \text{ g/cm}^3$; and (4) an 18.5- \AA ordered mixed-layer phase having the ideal composition $[(\text{Mg}_8\text{Al}_4)(\text{OH})_{24}][\text{M}^{+0.5}(\text{SO}_4)_{1.25}(\text{CO}_3)_{1.0} \cdot 9\text{H}_2\text{O}]$ and an alternation of 7.56- \AA , CO_3 -containing layers and 11- \AA layers having SO_4^{2-} anions and Na and Mg cations in interlayers ($\text{M}^{+0.5}$ corresponds to interlayer cations). This last phase has unit-cell dimensions of $a = 3.046$, $c = 3 \times 18.54 = 55.62 \text{ \AA}$ and $D_c = 1.99 \text{ g/cm}^3$. Some of the varieties containing SO_4^{2-} in the interlayers swelled with ethylene glycol or glycerol.

For this diverse family of minerals whose structures are based on brucite-like layers of the composition $(\text{R}^{2+}_{1-x}\text{R}^{3+}_x)(\text{OH})_2$, a unifying system of nomenclature is offered for consideration. In describing these brucite-like structures intercalated with anion- and cation-containing interlayers, the composition of the hydroxide sheet and the interlayers, the periodicity of the layers, and the mixed-layer nature of the material should be described. By means of symbols, a single term might be used to describe the crystal chemistry of any member of the group having a given cation composition for the brucite-like layers, for example, manasseite, a 2H polytype of hydrotalcite that has a repeat distance of 7.56 \AA and CO_3 -containing interlayers, might be designated as 7.56- \AA CO_3 -hydrotalcite-2H.

Key Words—Carbonate, Hydrotalcite, Interlayer, Nomenclature, Sulfate, X-ray powder diffraction.

Резюме—В соленосных отложениях центральной части Прикаспийской впадины и Средней Азии обнаружен ряд новых минералов, структурно близких к минералам группы гидроталькит-манассейта. Основу структур этих минералов составляют положительно заряженные бруситоподобные слои состава $(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_2$, между которыми располагаются анионы и молекулы воды. Помимо собственно манассейта состава $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{CO}_3) \cdot 3\text{H}_2\text{O}]$ с параметрами элементарной ячейки $a = 3.042$, $c = 2 \times 7.56 = 15.12 \text{ \AA}$ и рассчитанной плотностью (D_p) = 2.15 г/см³, установлены следующие разновидности, межслоевые промежутки которых содержат анионы SO_4^{2-} или SO_4^{2-} и CO_3^{2-} : (1) 8.85- \AA фаза состава $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{SO}_4) \cdot 3\text{H}_2\text{O}]$ с параметрами $a' = 3.04$, $c' = 8.85 \text{ \AA}$ и $D_p = 1.96 \text{ г/см}^3$; (2) 11- \AA фаза состава $[(\text{Mg}_{3.96}\text{Fe}_{0.06}\text{Al}_{1.98})(\text{OH})_{12}][\text{Na}_{0.56}(\text{SO}_4)_{1.30} \cdot 7.3\text{H}_2\text{O}]$ с параметрами гексагональной ячейки $a = \sqrt{3} \times 3.042 = 5.28$, $c = 11.16 \text{ \AA}$, и $D_p = 1.90 \text{ г/см}^3$; (3) 16.5- \AA смешанослойная фаза состава $[(\text{Mg}_4\text{Al}_2)(\text{OH})_{12}][(\text{SO}_4)_{0.5}(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}]$, в которой упорядоченно по закону АВ АВ . . . чередуются 7.56- \AA слои (бруситоподобный слой + CO_3 -содержащий межслой) и 8.94- \AA слои с анионами SO_4^{2-} в межслоях; параметры элементарной ячейки $a' = 3.05$, $c' = 16.5 \text{ \AA}$, и $D_p = 2.06 \text{ г/см}^3$; (4) 18.5- \AA упорядоченная смешанослойная фаза состава $[(\text{Mg}_8\text{Al}_4)(\text{OH})_{24}][\text{M}^{+0.5}(\text{SO}_4)_{1.25}(\text{CO}_3)_{1.0} \cdot 9\text{H}_2\text{O}]$, в которой по закону АВ АВ . . . чередуются 7.56- \AA , CO_3 -содержащие слои и 11- \AA слои, содержащие анионы SO_4^{2-} и катионы Na и Mg в межслоях ($\text{M}^{+0.5}$ соответствует межслоевому катиону). Параметры элементарной ячейки этой фазы $a = 3.046$, $c = 3 \times 18.54 = 55.62 \text{ \AA}$, и $D_p = 1.99$. Некоторые разновидности, содержащие в межслоях анионы SO_4^{2-} , обладают способностью к внутрикристаллическому набуханию при обработке их этиленгликолем и глицерином.

Предлагается унифицированная система номенклатуры для всего многообразного семейства минералов, основу структур которых составляют слои состава $(\text{R}^{2+}_{1-x}\text{R}^{3+}_x)(\text{OH})_2$. Для обозначения этих бруситоподобных структур, интеркалированных межслоевыми анионами и катионами, необходимо указать состав гидроокисных слоев и межслоев, период повторяемости слоев, смешанослойную природу минерала. На основании предлагаемой символики можно использовать только одно наименование, чтобы описать любой член группы, имеющий данный состав бруситоподобных слоев. Например, манассейт-2H, помимо гидроталькита, который имеет период повторяемости 7.56 \AA и CO_3 -содержащие межслои, может быть обозначен как 7.56- \AA CO_3 -гидроталькит-2H.

INTRODUCTION

Hydrotalcite and manasseite are rhombohedral and hexagonal polytypes having the composition $[\text{Mg}_x\text{Al}_{2-x}(\text{OH})_{12}][\text{CO}_3 \cdot 3\text{H}_2\text{O}]$. Both minerals are relatively rare and have never been reported from sedimentary rocks. Most occurrences of hydrotalcite and manasseite are associated with serpentinites (Kurnakov and Chernykh, 1926; Černý, 1963; Scaini *et al.*, 1967). As a rule, the two polytypic modifications form submicroscopic intergrowths (Aminoff and Broome, 1930). Hydrotalcite without admixed manasseite was described by Černý (1963) in a quartz-oligoclase pegmatite in a serpentinite in western Moravia, Czechoslovakia, and by Scaini *et al.* (1967) at the contact of a basaltic intrusion and Triassic limestones near Tonessa, Italy. Isolated samples from Snarum, Norway, have been reported to contain deformed masses of manasseite without hydrotalcite (Ivanova and Moskaleva, 1970; Frondel, 1941).

In the course of investigating the saline deposits of the central pre-Caspian depression and of Middle Asia, several new materials were discovered whose X-ray powder diffraction patterns and chemical compositions are close to those of members of the hydrotalcite-manasseite group. Their structures appear to consist of layers of $(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_2$ and anion-containing interlayers. In addition to manasseite itself, which contains only CO_3 in its interlayers, several other materials containing interlayer SO_4 or SO_4 and CO_3 anions were found. The present paper describes these minerals as new members of the hydrotalcite-manasseite group and discusses the overall crystal chemistry and nomenclature of this group of layered minerals and of closely related synthetic phases.

CRYSTAL CHEMICAL BACKGROUND

As noted above, minerals having the general composition $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{2+}[(\text{CO}_3)_x \cdot n\text{H}_2\text{O}]^{2-}$ occur in two polytypic modifications—rhombohedral hydrotalcite and hexagonal manasseite. The value of “ x ” in the formula ranges from 0.25 to 0.33 (Taylor, 1973). The structure of these minerals consists of positively charged brucite-like layers and CO_3 anions and water molecules in interlayer positions. Minerals containing octahedral cations other than Mg and Al are also known: Mg, Fe—pyroaurite, sjögrenite (Allmann, 1968, 1969; Allmann and Lohse, 1966; Aminoff and Broome, 1930; Ingram and Taylor, 1967; Taylor, 1969); coalingite and coalingite-K (Mumpton *et al.*, 1965; Jambor, 1969; Pastor-Rodriguez and Taylor, 1971); Mg, Cr—stichtite, barbertonite (Frondel, 1941; Read and Dixon, 1933; Ulrych, 1966; Tatarinov *et al.*, 1985); Mg, Mn—desautelsite (Dunn *et al.*, 1979); Ni, Al—takovite (Bish and Brindley, 1977; Maksimovic, 1957, 1968, 1970, 1974); Ni, Fe—reevesite (Calanchi, 1978; DeWaal and Viljoen, 1971; White *et al.*, 1967; Wilson *et al.*, 1976).

All these minerals generally contain only CO_3 in their interlayers; however, a Cl-containing variety $[(\text{Mg}, \text{Fe}^{2+})_4\text{Al}_2(\text{OH})_{12}][(\text{Cl}, 0.5\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]$ was described by Feoktistov *et al.* (1978) from iron-rich skarns in the southern Siberian platform and referred to as “chlormagaluminite” by Kashaev *et al.* (1982). Kohls and Rodda (1967) described iowaite, a magnesium-ferric iron oxychloride having the composition $\text{Mg}_4(\text{OH})_8\text{FeOCl} \cdot \text{H}_2\text{O}$. Koritnig and Süssé (1975) described a hydrotalcite containing OH instead of CO_3 anions in the interlayers having the composition: $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]^{2+}[(\text{OH})_2 \cdot 4\text{H}_2\text{O}]^{2-}$.

Minerals containing SO_4 or SO_4 and CO_3 anions in interlayers also have been described, e.g., carrboydite, a Ni-Al-sulfate mineral (Nickel and Clark, 1976); honessite, a Ni-Fe³⁺-hydroxy sulfate mineral (Bish and Livingstone, 1981; Heyl *et al.*, 1959); hydrohonessite, a hydrated form of honessite (Bish and Livingstone, 1981; Nickel and Wildman, 1981); motukoreaite, a Mg-Al-carbonate-sulfate mineral (Rodgers *et al.*, 1977; Brindley, 1979; Hudson and Bussell, 1981); wermlandite, a Mg-Al-Fe³⁺-sulfate mineral (Moore, 1971; Rius and Allmann, 1978, 1984); mountkeithite, a Mg-Fe³⁺-hydroxy sulfate mineral, containing exchangeable MgSO_4 (Hudson and Bussell, 1981); woodwardite, a Cu-Al-sulfate mineral (Nickel, 1976); and SO_4 -exchanged takovite (Bish, 1980).

Closely related to the hydrotalcite-manasseite group is the mineral koenenite whose structure consists of regularly alternating layers of $(\text{Mg}_{1-x}\text{Al}_x)(\text{OH})_2$ and $(\text{Na}_{1-x}\text{Mg}_x)\text{Cl}_2$. Allmann *et al.* (1968) suggested that the structure of koenenite consists of two trigonal sublattices having different a and b parameters and different periodicities of the two kinds of layers along the c axis. Koenenite has been found only in saline deposits, e.g., the Zechstein potash zones (Kühn, 1951, 1961) and in some carnallite- and sylvite-bearing rocks of the Devonian Prairie Evaporite Formation of Saskatchewan (Wardlaw and Schwerdtner, 1963). The alteration product of koenenite was named chlormanasseite by Allmann and Lohse (1966), as it is a $2H$ polytype that contains Cl in the interlayers instead of CO_3 .

Several papers have described the synthesis of similar crystalline compounds consisting of brucite-like layers and various anions and water molecules in the interlayers. Thomassin and Touray (1979, 1982) and Croviesier *et al.* (1983), for example, synthesized CO_3 -hydrotalcite by reacting basaltic glass with sea water. Miyata (1975, 1980) and Miyata and Okada (1977) used low-temperature alkali synthesis to obtain a hydrotalcite-like compound containing SO_4 and CO_3 anions in the interlayers. They also described similar synthetic compounds containing monovalent anions, such as Cl^- , NO_3^- , and CrO_4^- . Bish (1980) and Miyata (1983) reported the ease of anion exchange within the interlayers of these phases.

EXPERIMENTAL

Three samples were studied in detail. Sample 1, from the pre-Caspian depression, was collected from a clay lens within a boron-potassium-magnesium salt body. Samples 2 and 3, from Middle Asia, were the insoluble residues from halite and sylvite-containing halite bodies, respectively. The new minerals were separated from these samples as follows: A 0.05–0.07-mm size fraction of each sample was separated into density fractions using the stratification method of Katz and Dolgopolskaya (1979) at intervals of 0.01–0.02 g/cm³. The density fractions were examined optically and by X-ray powder diffraction (XRD) and scanning electron microscopic (SEM) techniques.

A Cambridge Stereoscan-600 electron microscope was used for the SEM examination. Samples were covered with a carbon film about 200 Å thick and then by a gold film about 100 Å thick. XRD patterns were recorded on a DRON-3 diffractometer using CuK α radiation and a scanning speed of 1°2 θ /min. The slit provided a width of the source image in the sample plane of 1.8 mm. Samples 20 mm high and 5 mm wide were partly irradiated as high as 40°2 θ . These conditions were taken into account in calculations by using a Lorentz polarization factor for monocrystal-like form for the given angular range. Unoriented samples containing a single structural entity were used to produce full XRD patterns if sufficient material was available. These full patterns were used to define the unit-cell parameters of each polytypic variety.

Due to lack of sufficient material, complete chemical analyses were not possible for each sample; consequently some samples were analyzed for SO₃ and CO₂ only. The amount of SO₃ and CO₂ was determined gravimetrically. For SO₃, the sample was first treated with a 2% solution of HCl, the insoluble residue was separated, and R₂O₃ was precipitated from the solution and separated. BaSO₄ was then precipitated from the solution with a few drops of a 3–5% solution of BaCl₂. CO₂ was determined by decomposition of the sample in 10% H₂SO₄ in a Knopp-Fresenius apparatus.

NOMENCLATURE

The following terminology is used to describe the newly discovered members of the hydrotalcite-manasseite group:

1. A phase containing interlayers filled with SO₄ anions and molecular H₂O and for which the brucite-like layer + interlayer thickness, c' , is 8.85 Å is herein called an 8.85-Å SO₄-hydrotalcite-2H phase or an 8.85-Å SO₃-hydrotalcite-3R phase, depending on whether it has 2- or 3-layer periodicity. If the mode of stacking is disordered or difficult to establish, such a phase is called an 8.85-Å SO₄-hydrotalcite or, simply, an 8.85-Å phase.
2. A phase containing interlayers filled with SO₄ anions, cations, and molecular H₂O, but for which the brucite-like layer + interlayer thickness is 10.8–11.2 Å is herein called an 11-Å SO₄-hydrotalcite (or simply an 11-Å phase). Its composition is expressed $[Mg_{1-x}Al_x(OH)_2][M^{+}_y(SO_4)_{(x+y)/2} \cdot nH_2O]$, where M⁺ indicates interlayer cations.
3. A phase consisting of regularly alternating 7.56-Å layers (i.e., a brucite-like layer + a CO₃-containing interlayer) and 8.94-Å layers (i.e., a brucite-like layer + an SO₄-containing interlayer) is herein called a 16.5-Å ordered, mixed-layer phase, or simply a 16.5-Å mixed-layer phase. Its composition is expressed as $[Mg_{1-x}Al_x(OH)_2][(SO_4)_{x/4}(CO_3)_{x/4} \cdot nH_2O]$.
4. A phase consisting of regularly alternating 7.56-Å layers (i.e., a brucite-like layer + a CO₃-containing interlayer) and 11-Å layers (i.e., a brucite-like layer + an SO₄-containing interlayer) is herein called an 18.5-Å ordered, mixed-layer SO₄-CO₃-hydrotalcite or simply, an 18.5-Å phase. Its composition is expressed as $[Mg_{1-x}Al_x(OH)_2][M^{+}_y(SO_4)_{(x+2y)/4}(CO_3)_{x/4} \cdot nH_2O]$.

MINERALOGIC AND PETROGRAPHIC RESULTS

In addition to minerals of the hydrotalcite-manasseite group, the >0.01-mm size fractions of samples from the Lower Permian rocks of the pre-Caspian depression contain quartz, chalcedony, chlorite, biotite, oxylepidomelane, zircon, garnet, sphene, anhydrite, kieserite, langbeinite, and various borate minerals. The <0.01-mm fractions contain “hydrated talc” (kerolite), serpentine, and disordered chlorite/swelling chlorite. The new minerals in the salt deposits of Middle Asia coexist with authigenic quartz, chalcedony, anhydrite, and magnesite. The finest size fractions contain Mg-chlorite and authigenic illite, as well.

The new minerals occur in a pyramidal-prismatic habit (Figure 1) and typically display the hexagonal prism and hexagonal pyramid-hexagonal prism forms. The trigonal prism form was noted rarely. Some crystals display combinations of dihexagonal prisms and several hexagonal pyramids. The platy crystals cleave readily, prism faces are typically striated, and crystal faces are pitted. The lowest density fractions (1.83–2.09 g/cm³) contain crystals displaying chiefly hexagonal and dihexagonal prism forms; pyramid-prismatic forms are more common on crystals from the denser fractions. Many crystals are deformed and display split and corroded sides. Crystals in the 2.17–2.25-g/cm³ density fractions are intensely overgrown by quartz.

The newly discovered minerals are optically positive (Ng||c), with negative elongation. The refractive index varied from 1.528–1.538 to 1.490–1.493 in a period of 15–25 min within a single section of the same grain (sample 1). Measured immediately after preparation, the optical constants were: sample 1—Ng = 1.532–

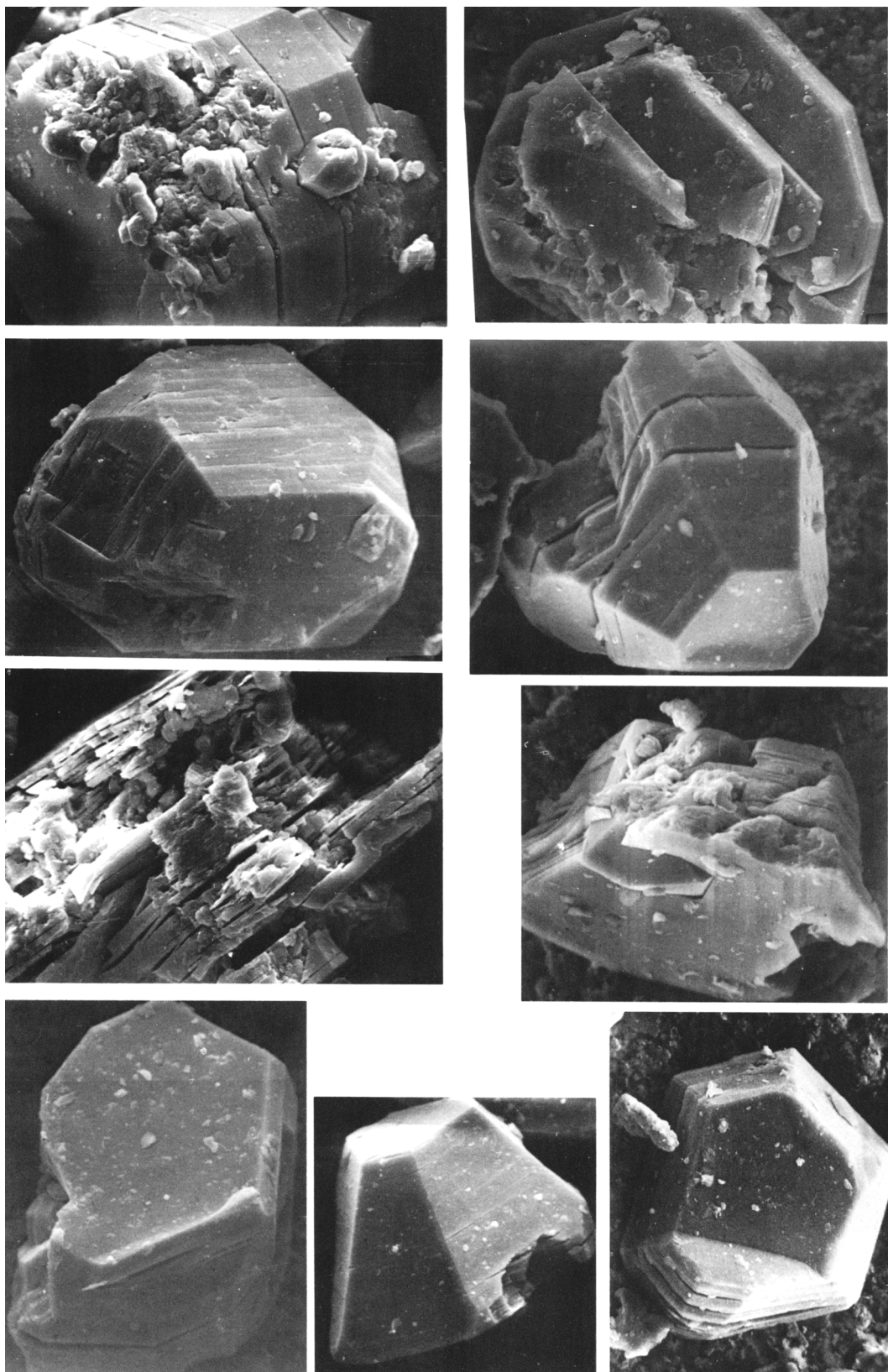


Figure 1. Scanning electron micrographs of crystals under study; >0.05-mm fraction.

Table 1. Indices of reflections, calculated (d_c) and observed (d_o) spacings for the studied minerals.

CO ₃ -manasseite $a = 3.042, c = 2c' = 15.12 \text{ \AA}$			11- \AA phase $a = 5.293, c = c' = 11.16 \text{ \AA}$			18.54- \AA phase $a = 3.046, c = 3c' = 55.62 \text{ \AA}$		
<i>hkl</i>	d_c	d_o	<i>hkl</i>	d_c	d_o	<i>hkl</i>	d_c	d_o
002	7.56	7.56	001	11.16	11.16	003	18.54	18.54
004	3.78	3.78	002	5.58	5.58	006	9.27	9.27
101	2.597	2.598	100	4.584	4.576	009	6.18	6.18
006	2.52	2.519	101	4.24	4.23	00,12	4.635	4.64
102	2.486	2.486	003	3.720	3.72	00,15	3.708	3.708
103	2.334	2.332	102	3.543	3.539	00,21	2.648	2.649
104	2.160	2.161	004	2.790	2.790	012	2.626	2.629
105	1.987	1.988	110	2.646	2.644	104	2.591	2.592
008	1.890	1.888	111	2.574	2.574	107	2.504	2.505
106	1.821	1.821	112	2.391	2.396	018	2.466	2.461
108	1.536	1.536	201	2.245	2.245	10,10	2.384	2.386
110	1.521	1.521	005	2.232	2.234	10,13	2.246	2.246
112	1.490	1.491	113	2.156	2.158	10,19	1.960	1.961
109	1.416	1.412	202	2.120	2.122		1.869	
114	1.410	1.411	203	1.951	1.954	10,22	1.825	1.827
200	1.316	1.312	114	1.920	1.922	01,23	1.783	1.784
10,10	1.311	1.311	006	1.860	1.867	10,25	1.701	1.704
			115	1.706	1.708	01,26	1.662	1.661
			205	1.599	1.598	110	1.523	1.523
			300	1.528	1.528	116	1.503	1.503
			301	1.514	1.516	119	1.479	1.479
			117	1.365	1.369			

1.528, $N_p = 1.520$ – 1.513 ; sample 2— $N_g = 1.546 \pm 0.002$, $N_p = 1.534 \pm 0.002$ for the 11- \AA phase still within the halite and $N_g = 1.508$ – 1.505 , $N_p = 1.489$ – 1.488 after the salt had been dissolved away.

X-RAY POWDER DIFFRACTION AND CHEMICAL RESULTS

Observed and calculated d -values and Miller indices of the new minerals are listed in Table 1. XRD patterns of oriented and unoriented samples are shown in Figures 2 and 3, respectively. Figures 5 and 7 show XRD patterns of air-dry, ethylene glycol-saturated, and glycerol-saturated samples from two density fractions. Calculated and experimental XRD patterns of the new minerals are shown in Figure 6. Calculated and observed intensities of the basal reflections of these phases are compared in Table 3. The technique of Drits and Sakharov (1976) was used to compute XRD patterns for comparison with those recorded for the minerals. Chemical compositions and densities of near monomineralic samples of these minerals are listed in Table 2, along with empirical formulae calculated from these data. The chemical data and published structural information were used to construct the models of these minerals shown in Figure 4.

DISCUSSION

7.56- \AA CO₃-hydrotalcite-2H

XRD patterns of oriented samples of the densest fractions (2.17–2.18 g/cm³) showed a series of basal reflections having d -values of 7.56, 3.78 \AA , etc. (Figure 2A). The 2.14–2.15-g/cm³ fraction (Figure 2B) contains

a small amount of the 16.5- \AA phase, and the 2.11–2.12- and 2.07–2.09-g/cm³ fractions (Figures 2C and 2D, respectively) contain small amounts of the 18.5- \AA phase. A more complete pattern of the 2.17–2.18-g/cm³ fraction is shown in Figure 3A. The experimental and calculated XRD patterns of the principal phase in these samples indicate that it is a 2H polytype of the CO₃-containing member of the hydrotalcite-manasseite group with unit-cell parameters of $a = 3.042$ and $c = 15.12 \text{ \AA}$. From the chemical analyses (Table 2), the formula of this material is $[\text{Mg}_{3.95}\text{Al}_{2.05}(\text{OH})_{12}][(\text{CO}_3)_{0.91}(\text{SO}_4)_{0.12} \cdot 3\text{H}_2\text{O}]$. The small amount of SO₄ is probably contained in the 16.5- and 18.5- \AA phases. If so, the ideal formula of the material under examination would be $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3) \cdot 3\text{H}_2\text{O}]$.

For different samples, the layer thickness (c') of this mineral ranges from 7.56 to 7.61 \AA . For a c' value of 7.56 \AA , the calculated density is 2.147 g/cm³, in accord with the measured density of this fraction.

8.85- \AA SO₄-hydrotalcite

XRD patterns of oriented material from the least dense fractions of sample 1 commonly showed several distinct series of basal reflections, corresponding to different structural varieties. One series of d -values of 8.85, 4.42 \AA , etc. (Table 3) was predominant. Miyata and Okada (1977) listed a value of $d(003) = 8.83 \text{ \AA}$ for synthetic SO₄-hydrotalcite, and Bish (1980) and Bish and Livingstone (1981) reported practically the same c' value for SO₄-exchanged takovite and honessite, respectively. Allmann (1977) reported the same value for the compound $[\text{Ca}_2\text{Al}(\text{OH})_6]^{+}[(0.5\text{SO}_4 \cdot 3\text{H}_2\text{O})]^{-}$.

Table 2. Chemical composition of the studied samples (0.05–0.07-mm fractions).

Density (g/cm ³)	Pre-Caspian depression						Middle Asia					
	Sample 1		Sample 2		Sample 3		Sample 1		Sample 2		Sample 3	
	2.15 ≦ D _n ≦ 2.16	2.14 ≦ D _n ≦ 2.15	2.10 ≦ D _n ≦ 2.12	2.12 ≦ D _n ≦ 2.14	2.14 ≦ D _n ≦ 2.15	2.09 ≦ D _n ≦ 2.11	2.14 ≦ D _n ≦ 2.15	2.12 ≦ D _n ≦ 2.14	2.14 ≦ D _n ≦ 2.15	2.09 ≦ D _n ≦ 2.11	2.11 ≦ D _n ≦ 2.13	
	Composition of phases											
	(CO ₂ -muscovite (+16.5-Å phase))											
SiO ₂	25.11	4.37	3.12	3.03	10.06	3.61	10.06	3.99	10.06	3.61	4.07	
TiO ₂	0.18	0.20	0.09	0.09	0.10	0.05	0.10	0.14	0.10	0.05	0.05	
Al ₂ O ₃	15.34	20.27	15.71	15.71	14.39	19.16	14.39	14.71	14.39	19.16	18.95	
Fe ₂ O ₃	1.55	0.19	no	0.71	0.74	1.04	0.74	2.03	0.74	1.04	1.01	
FeO	no	no	no	no	no	no	no	no	no	no	no	
MnO	0.01	no	no	no	no	no	no	no	no	no	0.01	
CaO	no	no	no	0.08	0.56	no	0.56	0.51	0.56	no	0.03	
MgO	24.17	31.38	31.77	24.61	22.74	30.16	22.74	23.17	22.74	30.16	30.12	
P ₂ O ₅	no	no	no	0.08	0.09	no	0.09	3.00	0.09	no	0.18	
Na ₂ O	0.08	0.08	0.08	2.70	2.43	0.36	2.43	0.36	2.43	0.36	0.34	
K ₂ O	0.23	0.21	0.12	0.11	0.30	no	0.30	0.36	0.30	no	0.56	
H ₂ O ⁺	32.81	32.13	31.41	37.02 ¹	32.70 ¹	32.25 ¹	32.70 ¹	20.93	32.70 ¹	32.25 ¹	31.70 ¹	
H ₂ O ^{...}	0.84	1.77	1.77	14.74	14.74	no	14.74	14.74	14.74	no	no	
C	no	0.06	no	no	no	no	no	0.09	no	2.84	2.49	
CO ₂	7.77	7.08	7.08	15.86	15.89	10.43	15.89	16.14	15.89	10.43	10.49	
SO ₃	1.84	1.84	3.16	no	no	no	no	no	no	no	no	
	Chemical formulae											
Al ^{IV}	2.02	2.07	1.98	1.98	1.97	1.97	1.97	1.94	1.97	1.97	1.96	
Fe ³⁺	3.98	3.93	0.06	0.06	0.06	0.07	0.06	0.17	0.06	0.07	0.07	
Mg	no	no	3.96	3.96	3.97	3.96	3.97	3.89	3.97	3.96	3.97	
Na	no	no	0.56	0.56	0.55	0.55	0.55	0.65	0.55	0.55	0.55	
Ca	no	no	no	no	0.07	0.07	0.07	0.01	0.07	0.34	0.30	
CO ₃	0.90	0.83	no	no	no	no	no	0.01	no	0.34	0.30	
SO ₄	0.12	0.20	1.27	1.27	1.38	0.68	1.38	1.36	1.38	0.68	0.69	
H ₂ O	9.30	9.13	13.24	13.24	12.67	9.4	12.67	13.31	12.67	9.4	9.29	

no = not detected.

Analysis were made in the chemical laboratory of the Geological Institute of the U.S.S.R. Academy of Sciences, by K. A. Stepanova.

¹ Calculated to 100% total.

Table 3. Comparison of calculated (I_c) and experimental (I_o) intensities of basal reflections.

8.85-Å phase			11-Å phase				16.5-Å phase			18.4-Å phase			
d(001)	I_c	I_o	d(001)	Model I I_c	Model II I_c	I_o	d(001)	I_c	I_o	d(001)	Model I I_c	Model II I_c	I_o
8.85	100	100	11.16	100	100	100	16.5	—	1.5	18.4	10	23	20
4.42	97	89	5.58	41	46	47	8.25	100	100	9.20	100	100	100
2.95	0.1	—	3.72	50	55	56	5.50	19	17	6.13	45	43	40
2.21	0.2	—	2.79	0.4	1.1	—	4.125	88	88	4.60	21	13	11
1.77	0.1	—	2.23	1.5	3.9	—	3.30	9	8	3.68	75	80	81
1.475	0.4	—	1.860	0.6	3.2	—	2.73	2	1	3.06	2	0	—
1.264	0.8	—	1.594	0.1	0.2	—	2.357	2	1	2.63	3	3.2	—
			1.395	2.5	—	—	2.063	0.5	—	2.30	0.2	4	—
			1.240	3.9	—	—	1.833	0.8	—	1.840	4.1	3.5	—
							1.650	0.1	—				

These data suggest that the principal mineral in these samples is a SO_4 -containing member of the hydrotalcite-manasseite group. Such a mineral, having the formula $[\text{Mg}_{3.96}\text{Al}_{1.98}(\text{OH})_{12}][(\text{SO}_4)_{1.02} \cdot 7.3\text{H}_2\text{O}]$ and $a = 3.04$ and $c = 26.55$ Å (i.e., 3×8.85 Å) was recently reported by Lisitzina and Drits (1985) from pores and fissures in basalt fragments and the volcano-sedimentary rocks that cover basaltic sea mounts in the North Atlantic.

The structural model shown in Figure 4b for this material is similar to that proposed by Allmann (1977) for $[\text{Ca}_2\text{Al}(\text{OH})_6][0.5\text{SO}_4 \cdot 3\text{H}_2\text{O}]$. SO_4 tetrahedra in the interlayers are equally probable in either of two orientations; the oxygens of the SO_4 tetrahedra in close proximity to hydroxyls of the brucite-like layers apparently form hydrogen bonds. Figure 4b shows the z coordinates and the composition of the atoms that correspond to each z value. The satisfactory correspondence between the calculated and experimental XRD intensities (Table 3) supports this model for the material examined here. The same interlayer structure was reported by Bish (1980) for SO_4 -exchanged takovite.

For a c' value of 8.85 Å, the calculated density is 1.962 g/cm³, slightly less than the observed density of 1.98–2.04 g/cm³, because the separated crystals of this mineral are overgrown with quartz.

11-Å SO_4 -hydrotalcite

The XRD pattern of oriented sample 2 shows a $d(001)$ value of 11.16 Å (Figure 5). The $d(001)$ values ranged from 10.8 to 11.16 Å for different samples of this material, and in some samples, two phases were apparently present and gave rise to two slightly different values of $d(001)$. Unit-cell parameters of $a = 5.28$ Å ($\sqrt{3} \times 3.052$ Å) and $c = 11.16$ Å were determined from the XRD pattern of an unoriented sample (Figure 3C). An oblique-texture electron diffraction pattern confirmed a one-layer periodicity and the enlarged a parameter, which is probably due to ordering of SO_4 anions in the interlayer.

We originally concluded that this sample (i.e., sample 2, Table 2, $D = 2.10$ – 2.12 g/cm³) consisted of the 11-Å SO_4 -hydrotalcite phase admixed with 3.03% SiO_2

and 6.10% Na_2SO_4 . On the basis of the chemical analysis, the formula for this mineral would be $[\text{Mg}_{3.96}\text{Fe}^{3+}_{0.06}\text{Al}_{1.98}(\text{OH})_{12}][(\text{SO}_4)_{1.02} \cdot 7.3\text{H}_2\text{O}]$. These data suggest that the 11-Å SO_4 -hydrotalcite phase is a new mineral, which, like the 8.85-Å phase (*vide supra*) accommodates SO_4 anions between the brucite-like layers. The increase in layer thickness compared with the 8.85-Å phase could be explained by its greater water content in the interlayers.

To test this conclusion, several structural models were considered. One model assumed bonds between the basal oxygens of the SO_4 tetrahedra and the OH groups of brucite-like layers, similar to those in the 8.85-Å phase. In this model, the positions of the SO_4 tetrahedra are fixed with respect to the OH groups of the brucite-like layer, leading to an extremely large distance between the apical oxygens of the SO_4 tetrahedra and the basal surface of the brucite-like layer. Water molecules between the OH surface of the brucite-like layers and the apical oxygens of the SO_4 tetrahedra probably facilitate the effective transfer of charges to achieve electrical neutrality in the structure. The best agreement between the experimental and calculated reflection intensities (Figure 6a, Table 3) was achieved for the positions and the content of water molecules shown in Figure 4c (model I).

Comparing the interlayer composition determined from model I (Figure 4c) with that calculated from the chemical analyses revealed a significant difference in the number (n) of H_2O molecules per unit cell ($n = 10$ and 7.3, respectively). This difference suggests that Na_2SO_4 is not an admixed phase in this sample, but that Na cations are present in the interlayers of the structure. On this basis, the formula is: $[\text{Mg}_{3.96}\text{Fe}^{3+}_{0.06}\text{Al}_{1.98}(\text{OH})_{12}][\text{Na}_{0.56}(\text{SO}_4)_{1.30} \cdot 7.3\text{H}_2\text{O}]$. We then used model II (Figure 4d) to evaluate the structure of the 11-Å phase. Model II is based on the structure of werm-landite, $[\text{Mg}_7(\text{Al}_{0.57}\text{Fe}^{3+}_{0.43})_2(\text{OH})_{18}]^{2+}[(\text{Ca}_{0.6}\text{Mg}_{0.4})(\text{SO}_4)_2(\text{H}_2\text{O})_2]^{2-}$ (Rius and Allmann, 1984). For werm-landite, $c' = c\sqrt{2} = 11.28$ Å, a value close to $c = 11.16$ Å determined for the mineral under study. These two minerals differ mainly in their cation composition and

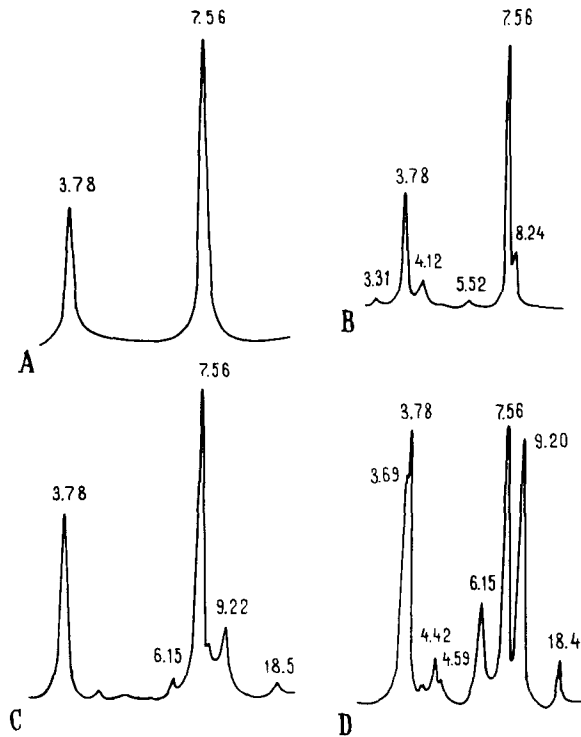


Figure 2. X-ray powder diffraction curves from the oriented fractions of sample 1. Densities = (A) 2.17–2.18 (manasseite only); (B) 2.14–2.15 (manasseite + 16.5-Å phase); (C) 2.11–2.12; and (D) 2.07–2.09 (manasseite + 18.5-Å phase) g/cm³. (Values in Å.)

the R^{2+}/R^{3+} ratio in the brucite-like layers and in the composition and number of interlayer cations calculated per subcell ($a' = a/3$ and $c' = c/2$ for wermlandite and $a' = a/\sqrt{3}$ and $c' = c$ for the 11-Å phase. For model II, the same satisfactory correspondence between calculated and experimental intensities of basal reflections was obtained, as for model I (Table 3).

Na cations and apical oxygens of SO_4 tetrahedra are situated in the center of the interlayer, an arrangement that fixes the z coordinates of the S atoms and basal O atoms of SO_4 tetrahedra. The Na cations are coordinated by water molecules. The amount of these water molecules and their z coordinates were determined on the basis of the structure of wermlandite, taking into account the agreement between the experimental and calculated 001 reflection intensities. The unit-cell composition for model II (Figure 4d) having the best correspondence between calculated and experimental intensity values is $[Mg_4Al_2(OH)_{12}][Na_{0.56}(SO_4)_{1.30} \cdot 6H_2O]$, close to the composition determined from the chemical analyses.

Thus, model II appears to correspond more closely to the structure of the new 11-Å mineral than does model I. The larger interlayer thickness compared with that of the 8.85-Å phase must be due in part to the

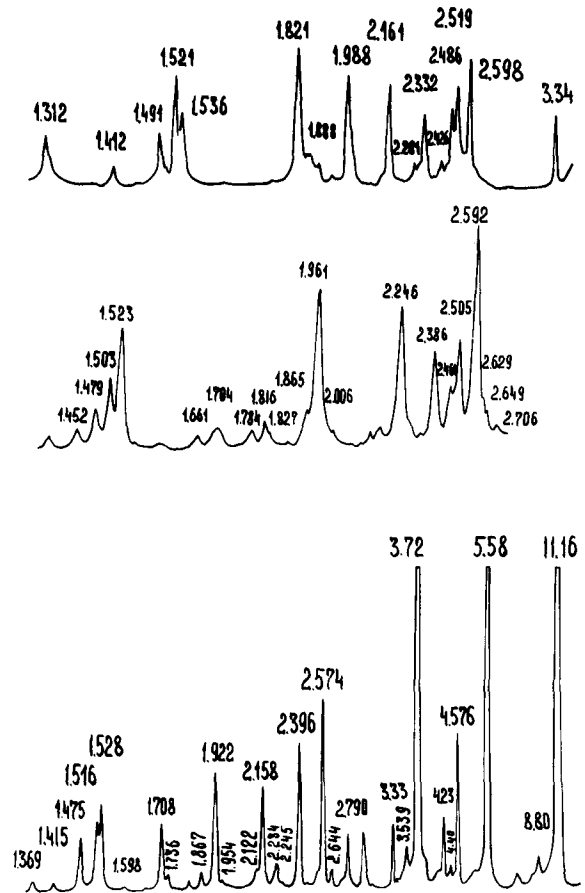


Figure 3. Fragments of X-ray powder diffraction patterns of unoriented powders. Upper, for CO_3 -manasseite; middle, for 18.5-Å ordered mixed-layer phase; lower, for 11-Å phase. Reflections with d equal to 3.34, 2.426, 2.281, 1.888, and 1.816 Å belong to quartz.

existence of interlayers of not only H_2O molecules, but also the presence of interlayer Na cations and additional SO_4 anions. The larger a dimension of the unit cell is probably due to an ordered distribution of SO_4 tetrahedra in the interlayers. Wermlandite also has an ordered distribution of SO_4 anions, leading to an $a = 3a' = 9.303$ Å for the hexagonal unit cell (Rius and Allmann, 1984). Each unit cell of the 11-Å phase contains six OH groups, and $a = 5.292$ Å. Thus, from the crystal chemical formula, SO_4 tetrahedra in the interlayers must be distributed over hexagonal lattice sites, with a probability of .65.

The brucite-like layers of the 8.85-Å phases and the 11-Å phase have similar cation compositions, but different a parameters. The disordered distribution of SO_4 tetrahedra in the interlayers of the 8.85-Å phase is possibly related to a disordered distribution of Mg and Al in octahedral sites of the brucite-like layer (Lisitzina and Drits, 1985). In the 11-Å phase, which has a layer composition of $(Mg_2Al)(OH)_6$, an ordered distribution

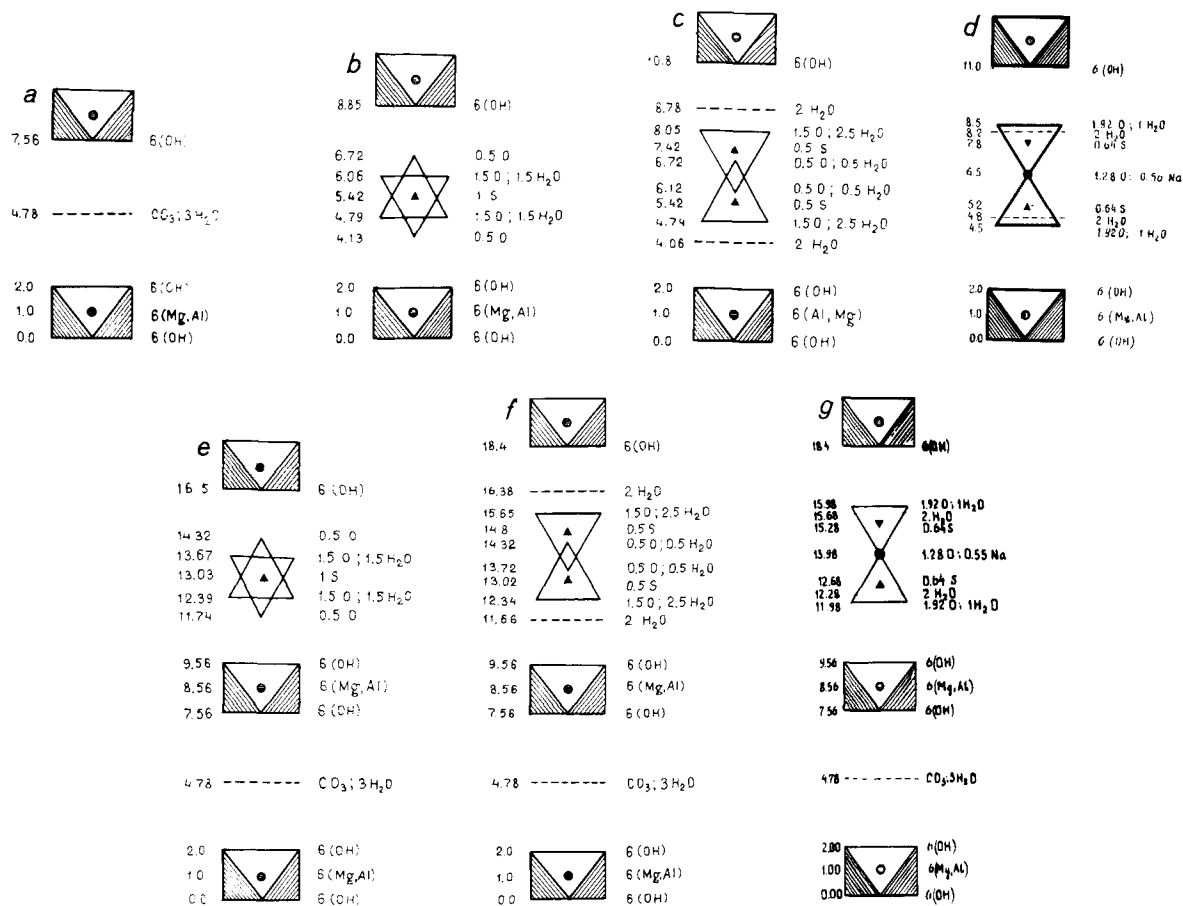


Figure 4. Structural models for the studied mineral varieties (a) CO_3 -manasseite containing 3 H_2O ; (b) 8.85-Å phase containing 3 H_2O ; (c) 11-Å phase containing 10 H_2O (model I); (d) 11-Å phase containing Na in interlayers (model II); (e) 16.5-Å ordered mixed-layer phase containing 6 H_2O ; (f) 18.5-Å ordered mixed-layer phase containing 13 H_2O (model I); and (g) 18.5-Å ordered mixed-layer phase containing Na in interlayers (model II).

of the Al atoms can be achieved easily if each of the Al atoms has six Mg nearest neighbors. The tendency for the charge to become balanced locally leads to the same type of distribution of the negatively charged anions. An ordered distribution of R^{2+} and R^{3+} atoms exists in minerals of the pyroaurite group (Taylor, 1973) and in $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}][(\text{SO}_4) \cdot 6\text{H}_2\text{O}]$ (Allmann, 1977).

For $c = 11.16 \text{ \AA}$, the calculated density is 1.90 g/cm^3 . The observed density is greater because the crystals of the mineral are overgrown by quartz.

16.5-Å ordered, mixed-layer SO_4 - CO_3 -hydrotalcite

XRD patterns of some low-density fractions of samples 1 and 3 ($D = 2.09\text{--}2.13 \text{ g/cm}^3$) gave 001 reflections at 16.5 Å (Figures 6 and 7). This value of $d(001)$ is consistent with an ordered mixed-layer structure consisting of 7.56- and 8.94-Å layers, i.e., layers containing CO_3 and SO_4 anions, respectively. Therefore, the 16.5-Å mineral appears to consist of a sequence of brucite-like layers and an ordered alternation of CO_3 - and SO_4 -

containing layers. The positions and distribution of anions and water molecules in the interlayers of the model shown in Figure 4e are the same as those of CO_3 -hydrotalcite (Allmann and Jepsen, 1969) and 8.85-Å SO_4 -hydrotalcite (Figures 4a and 4b). The experimental and calculated XRD patterns (Figure 6) are highly similar, in particular, the intensities of the basal reflections (Table 3). Thus, the mineral under study has an ordered mixed-layer structure consisting of a regular alternation of SO_4 - and CO_3 -containing interlayers. The compound $6\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot \text{CaCl}_2 \cdot 24\text{H}_2\text{O}$ ($c = 16.7 \text{ \AA}$), described by Kuzel (1966) possibly has a similar ordered, mixed-layer structure.

Chemical analyses were made of fractions in which the 16.5-Å phase was mixed with either the 8.85-Å or the 11-Å mineral (Figure 7) or with 7.56-Å CO_3 -hydrotalcite-2H (i.e., manasseite) (Figure 6). The chemical composition of a mixture of 16.5-, 11.16-, and 8.85-Å phases (chiefly the 16.5-Å phase) is listed in Table 2. The formula calculated on the basis of these

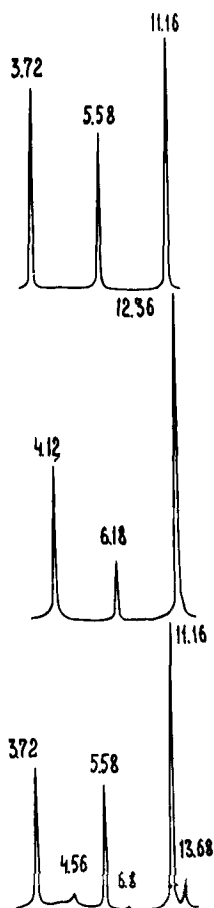


Figure 5. X-ray powder diffraction curves from the 2.10–2.12 g/cm³-density fraction of sample 2 containing 11-Å phase: (upper) air-dry; (middle) ethylene glycol-saturated; (lower) glycerol-saturated. (Values in Å.)

data is $[\text{Mg}_{3.96}\text{Al}_{1.97}\text{Fe}^{3+}_{0.07}(\text{OH})_{12}][(\text{SO}_4)_{0.68}(\text{CO}_3)_{0.34} \cdot 3\text{H}_2\text{O}]$. Chemical formulae of the 16.5-Å phases, mixed with dominant manasseite are listed in Table 2. No XRD patterns of an unoriented mixture containing dominant 16.5-Å material were obtained.

The calculated density of the 16.50-Å ordered mixed-layer phase is 2.06 g/cm³. The observed density [2.09–2.13 g/cm³] is higher because the crystals of this mineral were also overgrown by quartz.

18.5-Å ordered mixed-layer SO_4 - CO_3 -hydrotalcite

XRD patterns of some relatively low-density fractions of sample 1 (1.98–2.11 g/cm³) contained 001 reflections whose d-values were in the ranges 18.5–18.4, 9.25–9.20, 6.17–6.15 Å, etc. (Figures 2 and 6). Here also, the 18.5-Å d-value equals the sum of 7.56 + 10.94 Å, the corresponding thicknesses of CO_3 -hydrotalcite and the 11-Å phase. The 18.5-Å mineral therefore appears to have an ordered, mixed-layer structure.

A complete chemical analysis of the 18.5-Å phase was not made, but density fractions of sample 1, having

different ratios of manasseite and the 18.5-Å phase (Figures 2 and 6), were analyzed for SO_3 and CO_2 . With increasing density, the abundance of the 18.5-Å phase decreased along with the concentration of SO_3 . In particular, for the 2.11–2.13-g/cm³ fraction $\text{CO}_2 = 5.74\%$ and $\text{SO}_3 = 4.63\%$, and for the 2.09–2.11-g/cm³ fraction $\text{CO}_2 = 5.19\%$ and $\text{SO}_3 = 5.70\%$.

If the brucite-like layers have the composition $\text{Mg}_2\text{Al}_1(\text{OH})_6$ and no Na, Ca, or Mg is in the interlayer, the above two fractions will have the following formulae: $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)_{0.7}(\text{SO}_4)_{0.3} \cdot n\text{H}_2\text{O}]$ ($D = 2.11$ – 2.13 g/cm³) and $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)_{0.6}(\text{SO}_4)_{0.4} \cdot n\text{H}_2\text{O}]$ ($D = 2.09$ – 2.11 g/cm³). These assumptions are supported by the fact that the heavier fractions of sample 1, for which complete chemical analyses were made, contained low concentrations of Na_2O and K_2O and no measurable CaO . Na could be present in fractions in which the 18.5-Å phase prevails, and Mg could be present in the SO_4 -containing interlayers of the mixed-layer structure, as, for example, in wermlandite (Rius and Allmann, 1984). We therefore considered two structure models for the 18.5-Å mineral, shown in Figures 4f and 4g. In both models, 7.56- and 10.84-Å layers alternate. The structure of the 7.56-Å component is the same as in CO_3 -hydrotalcite (Figure 4a). Models I and II, considered also in the above discussion of the structure of the 11-Å phase (Figures 4c and 4d), were considered for the 10.94-Å component. Table 3 contains the calculated intensities of the basal reflections for both models compared with observed values. Based on these data, we were unable to select one model over the other, although the calculated and experimental intensities were closer for model II. Figure 6 shows the calculated and experimental XRD patterns for the 18.4-Å ordered mixed-layer phase. The chemical composition of the 18.5-Å phase, corresponding to models I and II, respectively, are as follows: $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)_{0.5}(\text{SO}_4)_{0.5} \cdot 6.5\text{H}_2\text{O}]$ and $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)_{0.5}(\text{SO}_4)_{0.64}\text{Na}_{0.28} \cdot 4.5\text{H}_2\text{O}]$.

The calculated density for the 18.5-Å mixed-layer structure (model II) is 1.99 g/cm³. The observed density (2.09–2.13 g/cm³) is greater because the crystals are overgrown by quartz.

Figure 3 shows part of the XRD pattern of an unoriented sample containing the 18.5-Å phase and smaller amounts of other phases. Distinct hkl reflections are present that can be indexed using the following unit-cell parameters: $a = 3.046$, $c = 55.62$ Å (Table 1). In this material, the brucite-like layers may have a three-layer stacking, as in hydrotalcite, but due to the regular alternation of CO_3 - and SO_4 -containing interlayers, the resulting periodicity has six layers.

It should be noted that for the same phase, the measured relative intensities of the basal XRD reflections were somewhat different in different density fractions. Calculations showed that the intensities of these reflections were highly sensitive to the water content of

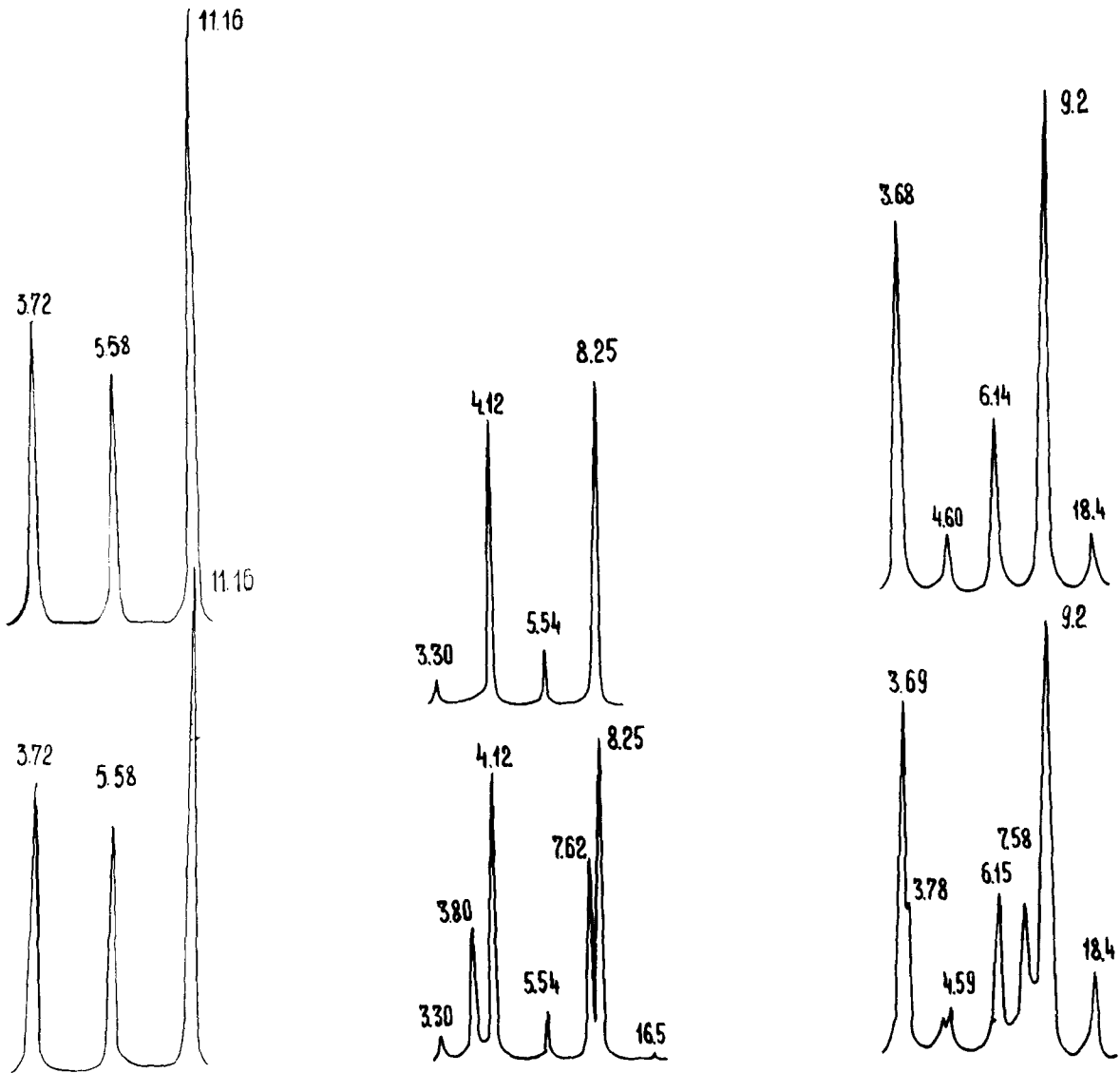


Figure 6. Calculated (upper) and experimental (lower) X-ray powder diffraction patterns for the 11-Å phase and the 16.5- and 18.4-Å ordered mixed-layer phases with manasseite. (Values in Å.)

the interlayers. We have considered here only those experimental XRD patterns whose intensity distributions are most common for the phase under investigation.

Behavior of SO_4 -containing minerals on ethylene glycol or glycerol saturation

Saturating the samples with ethylene glycol or glycerol showed that minerals that contain SO_4 anions in interlayers are capable of intracrystalline swelling, as described earlier by Bish (1980). Typically, the thickness of the SO_4 -containing layers which contain adsorbed ethylene glycol is 12.36 Å, regardless of whether the thickness of the initial layer was 8.9 or 11 Å. Figure 5 shows a series of basal XRD reflections of an oriented

sample of the ethylene-glycol-saturated 11-Å mineral, where $d(001) = 12.36$ Å. Figure 7 shows XRD patterns of the sample containing the 8.85- and 11-Å minerals (all interlayers containing SO_4 anions only) obtained before and after ethylene-glycol saturation, and of the 16.5-Å phase. The XRD pattern of the ethylene-glycol saturated sample contains two different series of basal reflections having periodicities of 12.36 and 19.92 Å. In the mixed-layer structure, interlayers containing CO_3 did not interact with molecules of ethylene glycol, whereas interlayers containing SO_4 expanded, leading to an increased layer thickness of $7.56 + 12.36 = 19.92$ Å, in full accord with the value of $d(001)$ measured on the XRD pattern. The 18.5-Å phase also expanded to 19.92 Å.

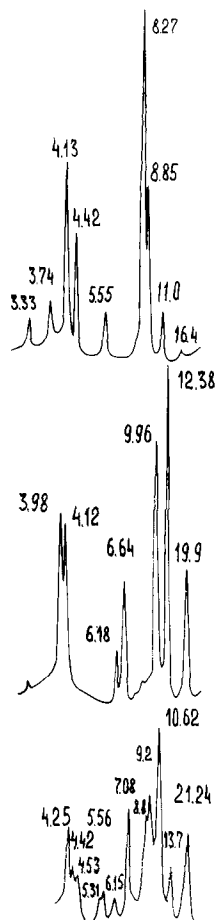


Figure 7. X-ray powder diffraction curves from the 2.08–2.10 g/cm³-density fraction of sample 3 containing 16.5-, 8.85- and 11.-Å phases: (upper) air-dry; (middle) ethylene glycol-saturated; (lower) glycerol-saturated. (Values in Å.)

On glycerol saturation, not all phases expanded; moreover, a given phase in different samples expanded to different degrees. For example, the XRD pattern of the 11-Å phase after glycerol saturation showed additional reflections at 13.7, 6.8, and 4.6 Å, suggesting expansion of only part of the sample (Figure 5). This effect must be connected with structural heterogeneity of the 11-Å microcrystals, possibly different positive charges on the brucite-like layers and/or different concentrations of anions in the interlayers. On the other hand, the data in Figure 7 indicate that on glycerol saturation, the 8.5-Å phase did not expand, whereas the 11-Å phase expanded to 13.7 Å. The 16.5-Å phase, containing some 8.85-Å interlayers of SO₄ anions, yielded an XRD pattern having an 001 reflection at 21.2 = 7.5 + 13.7 Å after glycerol saturation. Part of the 8.85-Å layers in the 16.5-Å phase expanded only to 11 Å, however, as evidenced by the presence of another series of 001 reflections having a periodicity of 18.6 = 7.56 + 11 Å. The varied intracrystalline

swelling of the minerals examined here may also be due to the heterogeneous distribution of CO₃ and SO₄ within individual interlayers.

NOMENCLATURE CONSIDERATIONS

As noted above, an abundant literature exists on this diverse group of natural and synthetic materials whose structures are composed of brucite-like layers intercalated with layers of anions and water molecules. No satisfactory system of nomenclature exists for this group, however, which takes into account cation substitutions in the brucite-like layers, cation and anion substitutions in the interlayers, ordering within either of these two types of layers, and various stacking sequences of the brucite-like layers and the interlayers. The following classification scheme for these materials is therefore offered for consideration.

Structural and crystal chemical characteristics

1. The structures of all members of the hydrotalcite-manasseite group contain positively charged brucite-like layers having the general composition $[R^{2+}_{1-x}R^{3+}_x(OH_2)]^{x+}$, where $R^{2+} = Mg, Ni, Cu,$ and Fe^{2+} ; $R^{3+} = Al, Fe^{3+}, Cr^{3+}, Mn^{3+}$ (or Mn^{4+}); and "x" ranges from 0.20 to 0.35. At present, the following major cation compositions have been recognized for the brucite-like layers of these materials: Mg-Al, Mg-Fe³⁺, Mg-Cr, Mg-Mn, Ni-Al, Ni-Fe³⁺, Cu-Al, and Fe²⁺-Fe³⁺. In addition, cation substitutions, such as Al ↔ Fe³⁺, Ni ↔ Mg, and Ni ↔ Fe²⁺ are known.
2. Interlayers composed of H₂O molecules and anions, such as CO₃, SO₄, Cl, OH, and NO₃, occur between the brucite-like layers. The minimum layer thickness (i.e., brucite-like layer + interlayer) depends chiefly on the nature of the anions in the interlayer, as well as on the net charge of the layers, the number of interlayer water molecules, and temperature and relative humidity. In addition, some minerals in this group contain interlayer cations, such as Ca, Mg, and Na, as well as anions and water molecules.
3. Structurally, these materials may be divided into subgroups having either homogeneous or heterogeneous interlayer compositions. In some minerals, all interlayers contain a single type of anion, whereas others contain two or more different anions (e.g., motukoreaita). Some minerals contain interlayers of anions and water molecules separated by more than one brucite-like layer (e.g., coalingite, coalingite-K).
4. Many minerals of this group possess anion-exchange properties (Bish, 1978, 1980; Miyata, 1983; Brindley, 1979).
5. All of these minerals are characterized by three polytypic modifications, 1H, 2H, and 3R that differ in their stacking sequence of one, two, and three layers, respectively. Some of the minerals appear to

have an ordered distribution of anions in interlayers and of cations (R^{2+} and R^{3+}) in the brucite-like layers. Therefore, the minimum value of a' of the brucite-like layer may increase either to $a = \sqrt{3} \cdot a'$ or $a = 3a'$, depending on the exact distribution of anions and heterovalent cations.

6. Minerals that have identical interlayer compositions usually show similar structural features, regardless of the brucite-like layer composition (Bish, 1978, 1980).

Limitations on new mineral names

On the basis of these considerations, we suggest the following limitations on naming new members of this group: (1) different polytypic modifications, as well as varieties of the same polytype that display different values of a for the hexagonal cell should not be given new mineral names; (2) varieties that have the same sequence of brucite-like layers and interlayers but that differ in the composition of the interlayers should also not be given new mineral names (nor should a new name be given to a material that results from an exchange of anions in the laboratory or to ordered mixed-layer structures whose interlayers incorporate different types of anions); and (3) varieties differing in the amount of charge on the brucite-like layer and in the value of c' , if the latter depends on humidity and/or temperature, should not be given new mineral names.

If these restrictions are adhered to, the only criterion remaining for assigning new mineral names within this group is the chemical composition of the brucite-like layer. Here also, we suggest that it is not necessary to name each member of the compositional series $(Mg_{1-x}Al_x)(OH)_2$. It may be useful to use one name for the entire series, e.g., hydrotalcite. This name would be modified by symbols to indicate the exact composition of the brucite-like layers, the interlayer composition, and the periodicity of the stacking and symmetry of the structure. Thus, manasseite would be described as 7.56-Å CO_3 -hydrotalcite-2H, the 11-Å phase of the present investigation was 11-Å SO_4 -hydrotalcite-1H, Cl-magaluminitite by 7.73-Å Cl-hydrotalcite-2H, the 8.85-Å phase of the present investigation was 8.85-Å SO_4 -hydrotalcite-2H, meixnerite as 7.8-Å OH-hydrotalcite-3R, etc. Minerals having heterogeneous anion compositions in all interlayers may be referred to, e.g., as 11-Å SO_4, CO_3 -hydrotalcite-3R (motukoreaite).

For mixed-layer structures, names such as 16.4-Å mixed-layer SO_4-CO_3 -hydrotalcite or 15.3-Å mixed-layer CO_3-Cl -hydrotalcite might be appropriate. Different anions separated by a comma (e.g., SO_4, CO_3) would mean that all interlayers of the mineral have the same heterogeneous anion composition. Different anions separated by a dash (e.g., Cl- CO_3) would mean that interlayers of different anion composition recur every second layer. If the polytypic modification of the

mineral is not known, polytype symbols would not be used.

For minerals characterized by a different composition of the brucite-like layers, another group name should probably be used, e.g., pyroaurite, which contains $[Mg_{1-x}Fe^{3+x}(OH)_2]$ layers, or takovite, which contains $[Ni_{1-x}Al_x(OH)_2]$ layers. The presence of cation substitutions in the brucite-like layer would be indicated by a cation symbol in the notation; e.g., a nickel-lean pyroaurite might be described as 7.56-Å CO_3Ni -pyroaurite-3R.

Minerals containing interlayers consisting of anions and water molecules separated by more than one layer may be described in the same manner as intercalated graphite (Metz and Hohlwein, 1975). In these structures single intercalate layers alternate regularly with groups consisting of n graphite layers (where $n = 1, 2, 3$, etc.). For example, in stage-2 intercalated graphite every two graphite layers are separated by an intercalate layer. Intercalated graphite structures can be regular, partly ordered, or irregular. The phrase "regular stage- n " signifies periodic structural units consisting of n graphite layers + 1 intercalate layer. Partly ordered stage- n intercalated graphite is therefore a mixed-layer structure in which prevailing n -layer graphite packages are separated by intercalate layers and alternate with packages consisting of other numbers of graphite layers.

Thus, in terms of the above intercalated-graphite nomenclature, regular 17.2-Å CO_3 -pyroaurite-3R (stage 3) consists of CO_3^{2-} interlayers alternating with packages consisting of three brucite-like layers $(Mg_{1-x}Fe^{3+x})(OH)_2$ packed in a 3R sequence. In 13.8-Å SO_4 -hydrotalcite (stage 2), packages consisting of two $(Mg_{1-x}Fe_x)(OH)_2$ layers alternate regularly with SO_4^{2-} interlayers. The d -values of the basal spacings of coalingite suggest an irregular structure in which 12.5-Å packages consisting of brucite-like layer pairs and CO_3^{2-} interlayers alternate with 17.2-Å packages, each of which consists of three brucite-like layers and a CO_3^{2-} interlayer. Because the 12.5-Å packages are 4–5 times more abundant than the 17.2-Å packages, coalingite might be described as a partly ordered, mixed-layer 12.5-Å CO_3 -pyroaurite-3R (stage 2). Alternately, minerals of the coalingite group may be described as partly ordered, mixed-layer pyroaurite/brucite, with the ratio of alternating components being indicated. This description seems less appropriate because the term "brucite" should probably not be applied in a general sense, especially for structures containing no Mg.

A more detailed characterization of such phases should include the structure of alternating components, their thickness, contents, pattern of sequence, and the layer and interlayer compositions. Table 4 lists the offered scheme of nomenclature (system I) for all known members of this group of layered structures. System II in Table 4 is an alternate scheme in which all members

Table 4. Suggested systems of nomenclature.

Name and chemical composition of mineral	Unit-cell parameters (Å)	References	System I	System II
Hydrotalcite [Mg ₆ Al ₂ (OH) ₁₆](CO ₃) ₄ ·4H ₂ O	a = 3.054 c = 7.603 × 3 = 22.81	Allmann and Jepsen (1969)	7.6-Å CO ₃ -hydrotalcite-3R	7.6-Å CO ₃ -Mg,Al-pyroaurite-3R
Manasseite [Mg ₆ Al ₂ (OH) ₁₆](CO ₃) ₄ ·4H ₂ O	a = 3.10 c = 7.8 × 2 = 15.6	Taylor (1973)	7.8-Å CO ₃ -hydrotalcite-2H	7.8-Å CO ₃ -Mg,Al-pyroaurite-2H
Manasseite [Mg ₄ Al ₂ (OH) ₁₂](CO ₃) ₃ ·3H ₂ O	a = 3.042 c = 7.56 × 2 = 15.2	This study	7.56-Å CO ₃ -hydrotalcite-2H	7.56-Å CO ₃ -Mg,Al-pyroaurite-2H
Motukoreaite [Mg ₆ Al ₂ (OH) ₁₆](CO ₃) ₄ ·2.74H ₂ O	a = 3.062 c = 11.17 × 3 = 33.51	Brindley (1979)	11-Å CO ₃ ,SO ₄ -hydrotalcite-3R	11-Å CO ₃ ,SO ₄ -Mg,Al-pyroaurite-3R
SO ₄ -Hydrotalcite [Mg ₄ Al ₂ (OH) ₁₂](SO ₄) ₃ ·3H ₂ O	a = 3.04 c = 8.85 × 3 = 26.55	Lisitzina and Drits (1985)	8.85-Å SO ₄ -hydrotalcite-3R	8.85-Å SO ₄ -pyroaurite-3R
Synthetic phase [Mg ₆ Al ₂ (OH) ₁₆](SO ₄) ₄ ·nH ₂ O	a = 3.05 c = 8.83 × 3 = 26.49	Miyata and Okada (1977)	8.83-Å SO ₄ -hydrotalcite-3R	8.83-Å SO ₄ -Mg,Al-pyroaurite-3R
Synthetic phase [Mg ₆ Al ₂ (OH) ₁₆](SO ₄) ₄ ·nH ₂ O	a = 3.05 c = 8.66 × 2 = 17.32	Miyata and Okada (1977)	8.66-Å SO ₄ -hydrotalcite-2H	8.66-Å SO ₄ -Mg,Al-pyroaurite-2H
11-Å phase [(Mg ₃ , ₃₀ Al ₁ , ₉₈ Fe ³⁺ _{0.06})(OH) ₁₂](Na _{0.56} (SO ₄) _{1.30} ·7.3H ₂ O]	a = 3.04√3 = 5.28 c = 11.16	This study	11-Å SO ₄ -hydrotalcite-1H	11-Å SO ₄ -Mg,Al-pyroaurite-1H
Wernlandite [Mg ₆ (Al ₆ , ₅₇ Fe ³⁺ _{0.43})(OH) ₁₈](Ca _{0.4} Mg _{6.4})(SO ₄) ₂ ·12H ₂ O]	a = 3.101 × 3 = 9.303 c = 11.28 × 2 = 22.57	Rius and Allmann (1984)	11.28-Å SO ₄ -wernlandite-2H	11.28-Å SO ₄ -Mg,Al,Fe ³⁺ -pyroaurite-2H
Chloremagaluminit [(Mg ₅ , ₅₅ Fe ²⁺ _{0.25} Na _{0.05} (Al _{1.03} Fe ³⁺ _{0.07} Ti _{0.01})(OH) ₁₂ ·Cl _{1.48} (0.5CO ₃) _{0.24}) ₂ ·2H ₂ O]	a = 3.045√3 = 5.29 c = 7.73 × 2 = 15.46	Kaschaev <i>et al.</i> (1982)	7.73-Å Cl-hydrotalcite-2H	7.73-Å Cl-Mg,Al-pyroaurite-2H
Meixnerite [Mg ₆ Al ₂ (OH) ₁₆](OH) ₂ ·4H ₂ O]	a = 3.046 c = 7.64 × 3 = 22.92	Kortnig and Süsse (1975)	7.64-Å OH-hydrotalcite-3R	7.64-Å OH-Mg,Al-pyroaurite-3R
16.5-Å phase [Mg ₆ Al ₄ (OH) ₂₄](SO ₄) ₁₀ (CO ₃) ₁₀ ·6H ₂ O]	This study	This study	16.5-Å CO ₃ ,SO ₄ -mixed-layer hydrotalcite	16.5-Å CO ₃ ,SO ₄ -Mg,Al-mixed-layer pyroaurite
18.5-Å phase [Mg ₆ Al ₄ (OH) ₂₄](SO ₄) ₁₀ (CO ₃) ₁₀ ·13H ₂ O]	This study	This study	18.5 Å CO ₃ ,SO ₄ -mixed-layer hydrotalcite-3R	18.5-Å CO ₃ ,SO ₄ -Mg,Al-mixed-layer pyroaurite-3R
Pyroaurite [Mg ₆ Fe ³⁺ ₂ (OH) ₁₆](CO ₃) ₄ ·5H ₂ O]	a = 3.109 c = 7.804 × 3 = 23.41	Allmann (1969)	7.8-Å CO ₃ -pyroaurite-3R	7.8-Å CO ₃ -Mg,Fe ³⁺ -pyroaurite-3R
Sjögrenite [Mg ₆ Fe ³⁺ ₂ (OH) ₁₆](CO ₃) ₄ ·5H ₂ O]	a = 3.113 c = 7.805 × 2 = 15.61	Allmann (1969)	7.8-Å CO ₃ -pyroaurite-2H	7.8-Å CO ₃ -Mg,Fe ³⁺ -pyroaurite-2H
Pyroaurite [Mg ₆ Ni ²⁺ ₂ Fe ³⁺ ₂ (OH) ₁₆](CO ₃) ₄ ·4H ₂ O]	a = 3.10 c = 7.68 × 3 = 23.04	Wilson <i>et al.</i> (1976)	7.68-Å CO ₃ -Ni ²⁺ -pyroaurite-3R	7.68-Å CO ₃ -Mg,Ni ²⁺ ,Fe ³⁺ -pyroaurite-3R
Coalingite [Mg ₁₀ Fe ³⁺ ₂ (OH) ₂₄](CO ₃) ₂ ·2H ₂ O]	a = 3.12 c = 1.25 × 3 = 37.5	Mumpton <i>et al.</i> (1965); Pastor-Rodriguez and Taylor (1971)	1.25-Å partly ordered mixed-layer CO ₃ -pyroaurite-3R (stage 2)	1.25-Å CO ₃ -Mg,Fe ³⁺ -mixed-layer pyroaurite-3R (stage 2)
Coalingite-K [Mg ₁₀ Fe ³⁺ ₂ (OH) ₂₄](CO ₃) ₂ ·2H ₂ O]	a = 3.13 c = 17.2	Pastor-Rodriguez and Taylor (1971)	17.2-Å partly ordered mixed-layer CO ₃ -pyroaurite (stage 3)	17.2-Å CO ₃ -Mg,Fe ³⁺ -mixed-layer pyroaurite (stage 3)

Table 4. Continued.

Name and chemical composition of mineral	Unit-cell parameters (Å)	References	System I	System II
Iowaite $4\text{Mg}(\text{OH})_2 \cdot \text{FeOCl} \cdot x\text{H}_2\text{O}$ or $[(\text{Mg}_{0.63}\text{Fe}^{3+}_{1.32})(\text{OH})_{12}] \cdot [\text{Cl}_{1.22} \cdot 1.95\text{H}_2\text{O}]$	$a = 3.119$ $c = 8.08 \times 3 = 24.25$	Kohls and Rodda (1967)	8.08-Å Cl-pyroaurite-3R	8.08-Å Cl-Mg, Fe ³⁺ -pyroaurite-3R
Mountkeithite $[(\text{Mg}_{0.12}\text{Ni}_{0.85}\text{Cu}_{0.02})(\text{Fe}^{3+}_{1.31}\text{Cr}_{1.02}\text{Al}_{0.65})(\text{OH})_{24}] \cdot [(\text{CO}_3)_{1.1}(\text{SO}_4)_{0.38}(\text{Mg}_{1.76}\text{Ni}_{1.16})(\text{SO}_4)_{0.94}(\text{H}_2\text{O})_{0.39}]$	$a = 10.698$ $c = 11.25 \times 2 = 22.50$	Hudson and Bussell (1981)	11.25-Å CO ₃ SO ₄ -mountkeithite-2H	11.25-Å CO ₃ SO ₄ -Mg, Fe ³⁺ , Cr, Al-pyroaurite-2H
Stichtite $[\text{Mg}_2\text{Cr}_2(\text{OH})_{16}][(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}]$	$a = 3.10$ $c = 7.8 \times 3 = 23.4$	Taylor (1973)	7.8-Å CO ₃ -stichtite-3R	7.8-Å CO ₃ -Mg, Cr-pyroaurite-3R
Stichtite $[\text{Mg}_{0.94}\text{Ca}_{0.03}\text{Sr}_{0.02}\text{Al}_{0.51}\text{Fe}^{3+}_{0.25}\text{Ba}_{0.05}(\text{OH})_{15.1}] \cdot [(\text{CO}_3)_{1.47} \cdot 3.7\text{H}_2\text{O}]$	$a = 6.169$ $c = 7.777 \times 6 = 46.66$	Tatarinov <i>et al.</i> (1985)	7.77-Å CO ₃ -stichtite-6H	7.77-Å CO ₃ -Mg, Cr, Al, Fe ³⁺ -pyroaurite-6H
Barbertonite $[\text{Mg}_2\text{Cr}_2(\text{OH})_{16}][(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}]$	$a = 3.10$ $c = 7.8 \times 3 = 23.4$	Taylor (1973)	7.8-Å CO ₃ -stichtite-2H	7.8-Å CO ₃ -Mg, Cr-pyroaurite-2H
Desautelsite $[\text{Mg}_2\text{Mn}^{3+}_2(\text{OH})_6][(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}]$	$a = 3.114$ $c = 7.79 \times 3 = 23.39$	Dunn <i>et al.</i> (1979)	7.8-Å CO ₃ -desautelsite-3R	7.8-Å CO ₃ -Mg, Mn ³⁺ -pyroaurite-3R
Takovite $[\text{Ni}_6\text{Al}_2(\text{OH})_{16}][(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}]$	$a = 3.025$ $c = 7.53 \times 3 = 22.59$	Bish and Brindley (1977)	7.53-Å CO ₃ -takovite-3R	7.53-Å CO ₃ -Ni, Al-pyroaurite-3R
Takovite $[\text{Ni}_{1.94}\text{Mg}_{0.10}\text{Ca}_{0.02}\text{Fe}^{3+}_{0.13}\text{Al}_{2.81}(\text{OH})_{14.42}] \cdot [(\text{CO}_3)_{2.27} \cdot 5.42\text{H}_2\text{O}]$	$a = 3.018$ $c = 7.53 \times 3 = 22.58$	Nickel <i>et al.</i> (1977)	7.53-Å CO ₃ -takovite-3R	7.53-Å CO ₃ -Ni, Al-pyroaurite-3R
Carboyndite $[(\text{Ni}_1\text{Cu})_6\text{Al}_4\text{OH}]_{21.69}[(\text{SO}_4)_2\text{CO}_3]_{2.78} \cdot 3.67\text{H}_2\text{O}]$	$a = 3.047 \times 3 = 9.14$ $c = 10.34$	Nickel and Clark (1976)	10.34-Å SO ₄ -takovite-2H	10.34-Å SO ₄ -Ni, Al-pyroaurite-1H
SO₄-exchanged takovite $[\text{Ni}_6\text{Al}_2(\text{OH})_{16}][(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}]$	$a = 3.024$ $c = 8.91 \times 3 = 26.74$ $(30\% \text{ RH})$	Bish (1980)	8.91-Å SO ₄ -takovite-3R (at 30% RH)	8.91-Å SO ₄ -Ni, Al-pyroaurite-3R (at 30% RH)
Reevesite $[\text{Ni}_6\text{Fe}^{3+}_2(\text{OH})_{16}][(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}]$	$c = 10.82 \times 3 = 32.47$ $(100\% \text{ RH})$	White <i>et al.</i> (1967)	10.82-Å SO ₄ -takovite-3R (at 100% RH)	10.82-Å SO ₄ -Ni, Al-pyroaurite-3R (at 100% RH)
Honessite $[(\text{Ni}_{1.55}\text{Mg}_{0.10}\text{Fe}^{3+}_{2.33})(\text{OH})_{16}][(\text{SO}_4)_{1.18} \cdot x\text{H}_2\text{O}]$	$a = 3.1$ $c = 7.8 \times 3 = 23.4$ $a = 3.081$ $c = 7.68 \times 3 = 23.05$	Bish and Livingstone (1981)	7.68-Å CO ₃ -reevesite-3R	7.68-Å CO ₃ -reevesite-3R
Hydrohonessite $[\text{Ni}^{2+}_{3.43}\text{Fe}^{3+}_{2.57}(\text{OH})_{16}][6.95\text{H}_2\text{O}(\text{SO}_4)_{1.28} \cdot 0.98\text{NiSO}_4]$	$a = 3.083$ $c = 8.90 \times 3 = 26.71$ $a = 3.09$ $c = 10.80$ $a = 3.087$ $c = 11.12 \times 3 = 33.4$ $a' = 3.07$ $c' = 10.9$	Bish and Livingstone (1981) Nickel and Wildman (1981) Bish and Livingstone (1981) Nickel (1976); Bish (1980)	8.9-Å SO ₄ -reevesite-3R 10.8-Å SO ₄ -reevesite-1H 11.12-Å SO ₄ -reevesite-3R 10.9-Å SO ₄ -woodwardite	8.9-Å SO ₄ -Ni, Fe ³⁺ -pyroaurite-3R 10.8-Å SO ₄ -Ni, Fe ³⁺ -pyroaurite-1H 11.12-Å SO ₄ -Ni, Fe ³⁺ -pyroaurite-3R 10.9-Å SO ₄ -Cu, Al-pyroaurite

are referred to by a single common name, the cation content of the brucite-like layers being indicated by additional symbols.

If this nomenclature system is adopted, additional names will not be required for every compositional and stacking variant that now exists or that will be discovered, which eventually will number into the hundreds. The system offered here is more descriptive than the present system of individual names. The chemical and structural characteristics of individual species are readily apparent from the symbols used in their names.

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