

POLYTYPE DIVERSITY OF THE HYDROTALCITE-LIKE MINERALS II. DETERMINATION OF THE POLYTYPES OF EXPERIMENTALLY STUDIED VARIETIES

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Abstract.—Polytype diversity of hydrotalcite-like minerals is mainly a function of the nature of the interlayer anion. Among the varieties with CO_3^{2-} anions, only two- and three-layer polytypes having the same structure as manasseite and hydrotalcite have been confirmed. Stichtite and reevesite, which have been previously identified as six-layer polytypes, are in fact three-layer polytypes.

Among SO_4^{2-} varieties, one-layer and three-layer polytypes have been identified, but the one-layer types are only present in more hydrated minerals with larger interlayer spacings. The three-layer varieties are of three different polytypes, with both P- and O-types of interlayers. Both rhombohedral and hexagonal varieties exist. Interlayer type may change during hydration-dehydration or anion exchange. Thus, in contrast with the CO_3^{2-} -bearing minerals, a complete description of the polytype of the SO_4^{2-} -bearing minerals cannot be made by simply indicating the number of the brucite-like layers in the unit cell.

The two-layer unit cell seen in refined crystal structures of some minerals with SO_4^{2-} interlayers is not due to a doubled periodicity of alternation of brucite-like layers but to periodicity of interlayer anions, or layer cations.

Key Words—Hydrotalcite-like group, Polytype, X-ray diffraction criteria.

INTRODUCTION

Many investigations devoted to finely dispersed hydrotalcite-like minerals determine the polytypes of minerals without any analysis of the intensities of reflections. Descriptions of structures have been limited to the number of layers per unit cell and by the assumption that three-layer varieties always have rhombohedral symmetry. The spectrum of polytypes possible in hydrotalcite-like minerals is more diverse than usually believed; and in our introductory paper (Bookin and Drits, 1993, hereinafter referred to as Part I) we derived the possible polytypes with a periodicity along the *c* axis of one, two, and three layers, as well as the simplest six-layer polytypes, and proposed criteria to help distinguish polytypes.

The intent of this paper is to determine the polytypes of those natural and synthetic hydrotalcite-like minerals for which X-ray diffraction data are available. The analysis of polytype diversity in this group of minerals and of the factors that control different structural modifications is important to the study of the relationships between structure, composition and properties, their rational classification, and nomenclature.

POLYTYPES WITH CO_3^{2-} INTERLAYER ANIONS

Minerals with interlayer CO_3^{2-} anions are the most common in the hydrotalcite-like family and have been studied in more detail than other anion varieties. Out of the large number of refined structures not one single mineral has the one-layer polytype. Irrespective of the

cation composition of the brucite-like layers, 2H and 3R polytypes predominate. However, in the light of the results reported in Part I, it is of interest whether they all belong to one polytype of all the possible two- and three-layer polytypes or whether there are polytypes with different alternating layer schemes. In the latter case, the commonly used description of the polytype affinity is incomplete and requires the additional symbols proposed in Part I.

Refinements of hydrotalcite and pyroaurite have shown that their structures are, in our notation, the 3R₁ polytype and that manasseite and sjogrenite (Allmann, 1969; Allmann and Jepsen, 1969; Taylor, 1973) are the 2H₁ polytype. Comparison of intensities from XRD powder patterns of takovite (Bish and Brindley, 1977) and eardleyite (Nickel *et al.*, 1977) with that of hydrotalcite or with calculated intensities (Part I, Table 4) suggests that they are also the 3R₁ polytype.

First described with a three-layer cell, stichtite (Taylor, 1973) and reevesite (White *et al.*, 1967) were later found to contain additional reflections that led to doubling of the number of layers in the cell (De Waal and Viljoen, 1971). Our study of a stichtite specimen (Bookin *et al.*, 1993) has shown that its XRD pattern shows stichtite peaks with three-dimensional order and peaks from a disordered product of its transformation, which takes place under exposure to light or X-rays. Positions of all experimental reflections of stichtite proper can be indexed in a three-layer cell instead of a six-layer one, and peak intensities of stichtite resemble those of hydrotalcite, suggesting that these two minerals are isostructural. The same interpretation of the

reevesite XRD pattern allows us to identify it as the $3R_1$ polytype.

SO₄²⁻-BEARING POLYTYPES WITH A MINIMUM PERIODICITY OF 8.8 Å

Among natural and synthetic SO₄²⁻ varieties having $c_0 = 8.8$ Å, only three-layer polytypes have been found. The crystalline phase with a composition of [Mg₃Al](OH)₈ ½SO₄ nH₂O, synthesized by Miyata and Okada (1977), has unit cell parameters of $a = 3.05$ Å and $c = 25.79$ Å = 3·8.6 Å. Since extinctions typical of rhombohedral structures are observed in the XRD pattern, the choice of polytypes is limited to $3R_1$ or $3R_2$. The reflections 012 , 015 , and 018 are present on the XRD diagram while reflections 101 , 104 , and 107 are missing, indicating that the phase is the $3R_1$ polytype according to the diffraction criteria outlined in Part I.

Bish (1980) described two samples of natural takovites in which the carbonate ion was replaced by sulfate. An idealized crystal-chemical formula for these products can be represented as [Ni₃Al](OH)₈ ½SO₄·nH₂O. The XRD patterns of both samples can be indexed in a three-layer rhombohedral cell with $a = 3.024$ Å and $c = 26.74$ Å = 3·8.91 Å. In the first sample, the diffraction criterion for $3R_2$ polytype is valid for the pairs of reflections $101/012$ and $104/015$, but violated for the $107/018$ pair. The calculated pattern predicts a very intense 107 peak (Part I, Table 4), but the experimental one shows no such reflection. This discrepancy may be attributed to the assumption that inaccuracies in atom coordinates and cation occupancies in the model can lead to errors in calculated intensities that are most significant for large l values. The same reason accounts for the absence of all reflections with $l > 8$ on the XRD pattern of the second sample, whereas hkl reflections with $l < 8$ are present. With these conditions in mind, the SO₄ varieties of exchanged takovite can be identified as the $3R_2$ polytype.

Honessite found near a chrome deposit (Unst, Shetland) and described by Bish and Livingstone (1981) was mixed with hydrohonessite and reevesite. The three varieties have the same composition brucite-like layers, [Ni_{2.8}Fe_{1.2}³⁺](OH)₈, but differ in the composition of interlayers, thereby suggesting to the authors a genetic affinity. Reflections in the honessite XRD pattern were indexed in a cell with $a = 3.08$ Å and $c = 26.71$ Å = 3·8.90 Å. Relative intensities of $h0l$ and $0kl$ reflections identify this sample as the $3R_1$ polytype.

A three-layer Mg₃Al-mineral with interlayer SO₄²⁻ anions was found mixed with barite amid products of low-temperature alteration of volcano-sedimentary rocks on a North Atlantic seamount (Lisitsina *et al.*, 1985). Reflections in the XRD pattern of a randomly oriented specimen were indexed in a hexagonal cell with $a = 3.05$ Å and $c = 26.50$ Å = 3·8.83 Å. The presence of peaks violating the rhombohedral lattice

Table 1. Experimental (exp) and calculated (cal) peak positions and intensities of the $6R_4$ -hydrotalcite XRD diagram.

<i>hkl</i>	d_{exp} (Å)	d_{cal}^1 (Å)	I_{exp}^2	I_{cal}
003	18.54	18.54	15	33
006	9.27	9.270	100	100
009	6.18	6.180	33	23
00.12	4.64	4.635	8	3
00.15	3.706	3.708	46	34
00.18	—	3.090	—	0
00.21	2.649	2.649	1	1
101	—	2.635	—	0
012	2.629	2.626	2	2
104	2.592	2.592	11	9
015	—	2.567	—	0
107	2.505	2.504	5	5
018	2.461	2.466	2	0
10.10	2.386	2.383	4	3
01.11	—	2.339	—	1
10.13	2.246	2.245	7	4
01.14	—	2.198	—	0
10.16	—	2.101	—	0
01.17	2.006	2.054	<1	1
10.19	1.961	1.960	8	14
01.20	—	1.914	—	0
10.22	1.827	1.825	1	3
01.23	1.784	1.783	1	1
10.25	1.704	1.701	1	2
01.26	1.661	1.662	1	4
10.28	—	1.587	—	1
01.29	—	1.551	—	1
110	1.523	1.523	4	7
113	—	1.518	—	0
116	1.503	1.503	3	1
119	1.479	1.478	1	1
11.12	1.452	1.447	<1	0

¹ $a = 3.064$ Å; $c = 55.62$ Å.

² Intensities of basal reflections were measured on the diagram of oriented film and normalized to 100%. Intensities of other reflections were measured on the diagram of randomly oriented sample and normalized to fit calculated pattern.

extinctions (reflections with d equal to 2.53 Å and 2.276 Å can be indexed as 103 and 106) suggests that the sample may be one of the hexagonal $3H$ polytypes or may be a mixture of $1H$ and $3R$ polytypes. In the latter case, the questionable reflections have indices 101 and 102 for a one-layer cell.

Intensities calculated for the $3R_1$ polytype (Part I, Table 4) do not agree with experimental data from this sample. The 015 and 018 reflections are the most intense among the calculated peaks, yet they are very weak experimentally, and the 107 reflection is the strongest among the experimental ones although it has a calculated intensity of zero. Disagreements are also present between experimental data and the pattern for the $3R_2$ polytype. If we assume that the one-layer polytype is present in the sample, then, along with reflections at 2.53 Å and 2.27 Å, the diffraction pattern should contain equally intense reflections at 2.64 Å, 1.96 Å, and 1.69 Å (Part I, Table 1, Column D). There-

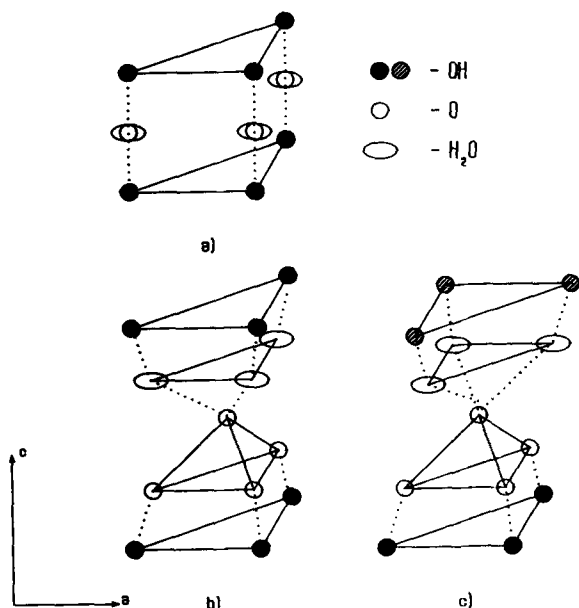


Figure 1. Arrangement of water molecules and carbonate (a) or sulphate (b and c) anions in the interlayers of P- (a and b) and O-types (c). OH are hydroxyl groups of brucite-like layers; O are oxygens of interlayer anions. In carbonate varieties, water molecules occupy the same crystallographic sites as oxygens of the anion. In sulphate varieties, triangles of water molecules together with a SO_4 -pyramid construct dumbbells. Dotted lines represent H-bonding net in the interlayers.

fore, it appears that the sample is not a mixture of 1H and 3R polytypes but is probably one of the hexagonal polytypes. Because of the significant amount of barite in the sample and difficulties in discriminating between the 3H₁ and 3H₂ polytypes (see Part I), it is difficult to choose unambiguously between them. However, the fact that only two of four reflections with $(-h+k+l) \neq 3n$ are seen on the diffraction pattern (Lisitsina *et al.*, 1985, Fig. 4a) favors the 3H₂ polytype. In any case the structure is extraordinary because it lacks homogeneity, i.e., the symmetry operation connecting the first and second layers differs from that connecting the second and third layers.

SO_4^{2-} -BEARING POLYTYPES WITH A MINIMUM PERIODICITY OF 11 Å

In contrast to carbonate varieties and sulfate varieties with $c_0 = 8.8$ Å, the SO_4^{2-} -bearing phases with $c_0 = 11$ Å included two examples of the one-layer polytype. One of them is an unnamed mineral from Jurassic salt-bearing deposits (Gaurdak, Central Asia) with brucite-like layers of $[\text{Mg}_2\text{Al}](\text{OH})_6$ (Drits *et al.*, 1987). The other is hydrohonessite from ore wastes (Otter Shoot, West Australia) with a cation composition of $[\text{Ni}_{2.7}\text{Fe}_{1.3}^{3+}](\text{OH})_6$ (Nickel and Wildman, 1981). Both one-layer minerals are characterized by similar c values (11.16 Å and 10.80 Å, respectively), although their a dimensions are different. In the Mg, Al-mineral, $a =$

5.29 Å, indicating an ordered distribution of SO_4 tetrahedra in the interlayer, since Al and Mg have similar scattering powers. In hydrohonessite, heterovalent cations and interlayer anions are distributed at random and $a = a_0 \approx 3.09$ Å.

Motukoreaite was described by Rodgers *et al.* (1977) as a four-layer polytype. Brindley (1979) considered it to be a three-layer non-rhombohedral polytype, but remarked that most reflections in the XRD pattern fit a one-layer unit cell with the a value increased to 5.3 Å. The idealized chemical composition, $[\text{Mg}_2\text{Al}](\text{OH})_6 \cdot \frac{1}{2}\text{SO}_4 \cdot n\text{H}_2\text{O}$, and the XRD pattern of motukoreaite are very close to those of the material from Guardak mentioned above, suggesting that both specimens may be the same mineral with 1H polytype and ordered SO_4^{2-} groups in the interlayers.

No structural studies have been carried out on one-layer minerals, although Drits *et al.* (1987) proposed a scheme of anions and water molecules distributed along c for the (Mg, Al) variety, based on the refined structure of wermlandite (Rius and Allmann, 1984). In the interlayers, an SO_4^{2-} tetrahedron and three water molecules form a dumbbell extending parallel to c . The dumbbell is formed by the joining of two tetrahedra whose bases are composed of oxygens of the sulfate anion on the one hand and water molecules on the other, while the shared apex is formed by the apical oxygen of the SO_4^{2-} tetrahedron (Figure 1). Two possible orientations of SO_4^{2-} and water-tetrahedra in the dumbbell along c are equally probable in each crystallographic site.

There are two multilayer SO_4^{2-} -bearing varieties whose structures have been refined from single-crystal diffraction data. Wermlandite (Rius and Allmann, 1984) has a two-layer cell, whereas (Ca, Al) hydroxide (Allmann, 1977) has a three-layer cell. In both species, $c_0 \approx 11$ Å. In (Ca, Al) hydroxide, a unit cell with $a = a_0\sqrt{3} \approx 5.2$ Å agreed well with a ratio of Ca:Al = 2:1 (Taylor, 1969). For wermlandite, a equals $3a_0 \approx 9.3$ Å, which also agrees well with $\text{R}^{2+}:\text{R}^{3+} = 7:2$. However, if we consider these structures from the point of view of layer stacking, brucite-like layers in both wermlandite and (Ca, Al) hydroxide are stacked according to the one-layer polytype rule, and, in wermlandite, deviations of the OH groups from close-packed stacking sites never exceed 0.06 Å. In addition, the R^{3+} cations and the SO_4^{2-} anions in wermlandite are positioned one above the other along a line normal to the layers. The two-layer periodicity in the mineral is derived from the azimuthal orientation of the dumbbell bases in consecutive interlayers. Due to significant distortion of the Ca-octahedra in (Ca, Al) hydroxide, deviations in the OH positions from the ideal sites in close-packed stacking may be up to 0.4 Å. The three-layer periodicity in (Ca, Al) hydroxide is due to the exchange of the positions of the Ca- and Al-octahedra and sulfates.

Three-layer minerals with $c_0 \approx 11$ Å have also been

reported in the literature. Bish (1980) described two samples of sulfate-treated takovite with $c = 32.47 \text{ \AA} = 3 \cdot 10.82 \text{ \AA}$ and $32.50 \text{ \AA} = 3 \cdot 10.83 \text{ \AA}$, respectively. In the XRD patterns of the two samples, the 012 , 015 , 018 , and 01.11 reflections are more intense than the 101 , 104 , 107 , and 10.10 reflections, suggesting a $3R_1$ polytype.

Carboydite, $\text{Ni}_7\text{Al}_{4.5}(\text{OH})_{22}(\text{SO}_4, \text{CO}_3)_{2.8} \cdot 3.7\text{H}_2\text{O}$, was discovered in a nickel mine near Calgary, West Australia (Nickel and Clark, 1976), along with a carboydite-like phase that authors called simply the "11 \AA phase." Judging from the chemical analysis, carboydite contains primarily Ni^{2+} and Al^{3+} cations in a ratio of about 3:2. The authors described the carboydite structure in terms of a one-layer cell with $c = 10.34 \text{ \AA}$ and $a = 3a_0 = 9.14 \text{ \AA}$. The proposed model for carboydite has double brucite-like layers sharing the same hydroxyl sheet. Bish (1980) noted that the diffraction pattern of exchanged-takovite looked like that of carboydite and the "11 \AA phase." Since the cation composition of takovite is similar to that of carboydite only having a smaller proportion of Al, Bish suggested that neither carboydite nor the "11 \AA phase" was based on a double brucite-like layer model. Similarities in peak intensities between the carboydite XRD patterns and the model calculations (Part I) suggest that carboydite and the "11 \AA " phase are composed of single brucite-like layers stacked according to the $3R_1$ polytype. Therefore, SO_4 -exchanged takovite appears to be a synthetic form of natural carboydite.

In contrast with hydrohonesite from West Australia (Nickel and Wildman, 1981), which has a one-layer unit cell, a Shetland sample of hydrohonesite was found to have a three-layer cell with $c = 33.4 \text{ \AA} = 3 \cdot 11.1 \text{ \AA}$ (Bish and Livingstone, 1981). The presence of the 101 reflection and the absence of the 012 reflection distinguish the XRD patterns of the Shetland hydrohonesite from that of carboydite and SO_4 -exchanged takovite of the same periodicity and suggest that it is the $3R_2$ polytype.

In addition to 3H_2 hydrotalcite with $c_0 = 8.8 \text{ \AA}$, products of low-temperature alteration of volcano-sedimentary rocks at North Atlantic seamounts were found to contain a three-layer mineral with $c_0 = 32.4 \text{ \AA} = 3 \cdot 10.8 \text{ \AA}$ (Lisitsina *et al.*, 1985). Although admixtures interfere with peak intensity estimates, qualitative analysis of the diffraction pattern (Lisitsina *et al.*, 1985, Fig. 4b) gives evidence of rhombohedral symmetry and the presence of a reflection with $d = 2.605 \text{ \AA}$ (012) as well as intense reflections with $d = 2.215 \text{ \AA}$ (018) and 1.973 \AA (01.11). All suggest that this mineral is the $3R_1$ polytype.

One component of the above sample is a phase with a two-layer unit cell. Since it was not possible to isolate this phase, we could not analyze the distribution of intensities in the diffraction pattern to find out if it was really a two-layer polytype (and then to determine to

which of the three possible polytypes it corresponds) or if the two-layer cell has the same origin as in wormlandite.

POLYTYPISM OF MINERALS CONTAINING OH^- , Cl^- , AND CrO_4^{2-} ANIONS

The charge compensation of natural and synthetic hydrotalcite-like minerals may be provided by anions other than SO_4^{2-} or CO_3^{2-} . Mascolo and Marino (1980) described a synthetic mineral with the composition $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_{2+2x} \cdot n\text{H}_2\text{O}$, similar to that of natural meixnerite (Korting, 1976). In this mineral, hydroxyl groups seem to be the interlayer anions. The unit cell is rhombohedral with $c = 23.4 \text{ \AA}$, indicating that the structure in question may be similar to three-layer hydrotalcite. Analysis of the XRD pattern of a synthetic mineral given by Mascolo and Marino (1980) showed that both the reflections present and their relative intensities are identical to those of the $3R_1$ polytype with CO_3^{2-} anions in interlayers, implying the same layer stacking in meixnerite.

Under natural conditions, the interlayer Cl^- anions in iowaite, $[\text{Mg}_4\text{Fe}(\text{OH})_{10}] \text{Cl} \cdot n\text{H}_2\text{O}$, can be replaced by CO_3^{2-} anions (Kohls and Rodda, 1967). Based on this observation and the fact that unit cells of the two anionic forms are similar, Allman and Donnay (1969) suggested that iowaite is isostructural with CO_3^{2-} -bearing pyroaurite. Among seven possible hexagonal structures, only the 3H_7 polytype with layer sequence $\dots \text{AC}-\text{AC}-\text{BA}=\text{AC} \dots$ can be transformed into a rhombohedral pyroaurite-like phase through planar displacements of layers during anion exchange.

Diffraction results from a synthetic Al-Mg-phase containing interlayer CrO_4^{2-} anions (Miyata and Okada, 1977) are practically identical to those of the SO_4^{2-} -containing phase prepared in the same work and discussed above. Hence, it probably is the $3R_1$ polytype.

POLYTYPES WITH HETERO-ANIONIC INTERLAYERS

Natural formations often contain minerals whose chemical and IR analyses indicate the presence of both SO_4^{2-} and CO_3^{2-} anions. In a later section we will briefly discuss whether coexistence of these two types of anions in the same interlayer is possible, but first we shall analyze the minerals with regularly alternating SO_4^{2-} and CO_3^{2-} -bearing interlayers.

In the Caspian depression salt-bearing deposits (Inder dome), a mineral was discovered with rhombohedral cell parameters $a = 3.05 \text{ \AA}$ and $c = 55.62 \text{ \AA}$ (Drits *et al.*, 1987). The crystal-chemical formula was $[\text{Mg}_4\text{Al}_2](\text{OH})_{12}(\text{CO}_3)_{0.5}(\text{SO}_4)_{0.5} \cdot n\text{H}_2\text{O}$. This phase can be regarded as a mixed-layer mineral with regularly alternating CO_3^{2-} and SO_4^{2-} -bearing interlayers whose heights are 6.56 \AA and 9.98 \AA , respectively, resulting in a total layer thickness c_0 of 18.54 \AA . These layer

Table 2. Polytype description of SO_4^{2-} -bearing minerals.

Mineral	Chemical composition of brucite-like layers	Principal basal spacing	Layer sequence	Polytype	Inter-layer type
Synthetic hydrotalcite	$\text{Mg}_3\text{Al}(\text{OH})_8$	8.6	...AC=CB=BA=AC...	3R_1	P
SO_4 -takovite	$\text{Ni}_3\text{Al}(\text{OH})_8$	8.9	...AC-BA-CB-AC...	3R_2	O
Honessite	$\text{Ni}_{2.8}\text{Fe}_{1.2}(\text{OH})_8$	8.9	...AC=CB=BA=AC...	3R_1	P
SO_4 -hydrotalcite (N. Atlantic)	$\text{Mg}_3\text{Al}(\text{OH})_8$	8.8	...AC-AB-CB-AC...	3H_2	O
Ca,Al-hydroxide	$\text{Ca}_2\text{Al}(\text{OH})_6$	8.9	...AC-AC...	1H^1	O
SO_4 -hydrotalcite (M. Asia)	$\text{Mg}_2\text{Al}(\text{OH})_6$	11.2	...AC-AC...	1H	O
Hydrohonessite (W. Australia)	$\text{Ni}_{2.7}\text{Fe}_{1.3}(\text{OH})_8$	10.8	...AC-AC...	1H	O
Wernlandite	$\text{Mg}_7(\text{Al,Fe})_2(\text{OH})_{18}$	11.3	...AC-AC...	1H^2	O
SO_4 -takovite	$\text{Ni}_3\text{Al}(\text{OH})_8$	10.8	...AC=CB=BA=AC...	3R_1	P
Carboidite	$\text{Ni}_3\text{Al}_2(\text{OH})_{10}$	10.3	...AC=CB=BA=AC...	3R_1	P
Hydrohonessite (Shetlands)	$\text{Ni}_{2.7}\text{Fe}_{1.3}(\text{OH})_8$	11.1	...AC-BA-CB-AC...	3R_2	O
SO_4 -hydrotalcite (N. Atlantic)	$\text{Mg}_3\text{Al}(\text{OH})_8$	10.8	...AC=CB=BA=AC...	3R_1	P

¹ Real polytype has three-layer periodicity.

² Real polytype has two-layer periodicity.

pairs stacked according to the rhombohedral law produce a six-layer cell with $c = 3c_0 = 55.62 \text{ \AA}$. Since the possible polytype of this phase is limited only to rhombohedral structures, it can be described by one of the sequences 6R_1 to 6R_5 (Part I). In fact nine different structural models should be considered since polytypes with alternating types of interlayers (6R_2 , 6R_3 , and 6R_4) should give two different XRD patterns, each depending on the spacings of P- and O-type interlayers. Table 1 lists the experimental d -values and peak intensities taken from Drits *et al.* (1987) and the results of a calculation carried out for the 6R_4 polytype in which O-type interlayers are occupied by sulphate groups and P-type interlayers are occupied by carbonate groups.

DISCUSSION

The range of diversity in hydrotalcite-like mineral polytypes depends on the nature of the interlayer cation. Structural studies show that CO_3^{2-} anions are positioned in the interlayer so as to have their oxygens form hydrogen bonds with OH-groups of the adjacent brucite-like layers (Taylor, 1978). This can be easily achieved only in structures with P-interlayers where oxygen atoms of the CO_3^{2-} anion are positioned at equal distances from the OH-sheets near the straight lines that join hydroxyls of the adjacent layers (Figure 1a). This explains why the one-layer polytype with O-type interlayers has not been found among CO_3^{2-} -bearing minerals, and why, out of all the two- and three-layer varieties, only two structures are possible, 3H_1 and 3R_1 (those which have only P-type interlayers). Hence, an indication of the number of layers in the unit cell completely describes the structure of the carbonate-bearing varieties. Theoretically, nine hex-

agonal six-layer varieties with P-interlayers are possible as well, but six-layer polytypes have not been found among CO_3 -varieties.

The above holds true for other anions arranged in a 2D triangle (e.g., NO_3^-). A similar conclusion, supported by a smaller number of experimentally verified examples, follows for minerals with halogen anions and hydroxyls. It is not clear in terms of crystal chemistry, however, why such anions would be positioned over OH-groups of the brucite-like sheet instead of over interlayer cations.

In the case where the interlayer contains tetrahedral SO_4^{2-} and CrO_4^{2-} anions, the polytype diversity increases dramatically. The reason for this is that basal oxygens of SO_4^{2-} or CrO_4^{2-} tetrahedra form hydrogen bonds with hydroxyls of either the upper or the lower interlayer surface only (Figures 1b and 1c). If the position of the tetrahedral base in relation to the brucite-like layer's hydroxyl sheet is rigid enough, the apical oxygens bond with the hydroxyls of the upper sheet of this interlayer through water molecules. This allows the next brucite-like layer to have different positions relative to the apical oxygens of the tetrahedra and relative to the first layer. As a result, the minerals containing these anions may form structures with both P- and O-types of interlayers.

The nomenclature of the SO_4^{2-} varieties is further complicated since different interlayer types have been found in less hydrated varieties with $c_0 < 9 \text{ \AA}$ and in more hydrated varieties with $c_0 > 10 \text{ \AA}$. Table 2 lists polytype data for all the SO_4^{2-} varieties discussed in this paper. The data suggest that neither the chemical composition of brucite-like layers nor the degree of hydration affect the type of interlayer or the polytype. (Mg, Al) varieties were assigned to four structural states,

each hydrated form having one O- and one P-interlayer variety. Where the $3R_1$ polytype with $c_0 = 8.6 \text{ \AA}$ can be regarded as a dehydration product of $1H$ or $3R_1$ varieties with $c_0 = 11 \text{ \AA}$, the $2H_2$ polytype cannot be derived from these polytypes solely by layer displacement due to dehydration. The two hydrohonesites in Table 2 have similar cation compositions in the brucite-like layers and O-type interlayers, although they differ in the number of layers in the unit cell. Two different hydrated varieties of SO_4^{2-} -exchanged takovite retain the three-layer periodicity of the original takovite but have different interlayer types. One must assume, therefore, that polytype modification, even under the most common conditions of hydration-dehydration, is conditioned by the thermodynamic parameters of the medium rather than those of the mineral phase.

The above data support the need to establish a standardized nomenclature (Taylor, 1973; Drits *et al.*, 1987). Moreover, when using the nomenclature proposed by Drits *et al.* (1987), the symbolic notation for each of the polytypes will have to be specified for 3D anions using symbols similar to those proposed in Part I and illustrated by data in Table 2.

We still have to explain why varieties that have different cation composition and types of interlayers are dominated by three-layer polytypes, while one-layer varieties are much rarer, and genuine two-layer polytypes, in which the two-layer periodicity results from the mutual arrangement of OH-layers instead of different structures of alternating interlayers, have not been reported. The nomenclature of minerals with regularly alternating interlayers of different anion compositions also needs refinement. For these minerals, it should be clearly stated which anions are present, and in which type of interlayer. The nomenclature proposed by Drits *et al.* (1987) can satisfy this requirement by assigning a P or O subscript depending on the type of interlayer containing the anion. For example, a symbolic notation for the six-layer, mixed-layer mineral discussed above can be given as $18.4 \text{ \AA} (\text{CO}_3)_P(\text{SO}_4)_O$ -hydrotalcite $6R_4$.

Further investigations are needed to specify structural properties and to classify those varieties described in the literature that are assumed to have a hetero-anion composition within individual interlayers. The mole ratio of the different anions (often CO_3^{2-} and SO_4^{2-}) is usually other than 1:1. From crystal-chemical arguments, it is difficult to imagine that an individual interlayer in these minerals would contain both types of anions because each requires a different interlayer spacing and permits different stacking modes of adjacent layers. If deviations from mole ratios of one cannot be explained by a mixture of mineral varieties with different anion compositions or an admixture of a non-hydrotalcite-like phase, then we have to assume that a disordered mixed-layer mineral may exist.

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