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POLYTYPE DIVERSITY OF THE HYDROTALCITE-LIKE MINERALS I. POSSIBLE POLYTYPES AND THEIR DIFFRACTION FEATURES

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Abstract—All possible polytypes of hydrotalcite-like minerals with a periodicity along the *c* axis of one-, two- and three-layers, as well as the simplest six-layer polytypes, were derived on the basis of the concept of closely packed brucite-like layers. Multilayer structures were found to be possible in several polytype modifications—three two-layer, nine three-layer, and a set of six-layer polytypes. The neighboring layers may be stacked in two different ways, building two kinds of interlayers: P-type where OH sheets lie one above another forming prisms and O-type where OH groups forms octahedra. Based on the kind of interlayer space, all polytypes may be separated into three groups: homogeneous interlayers of O-, or P-type, and alternating interlayers of both types. For the members of the first two groups, powder XRD patterns were calculated and criteria for distinguishing polytypes with the same number of layers per unit cell are suggested.

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

INTRODUCTION

Already composed of an impressive number of members, the literature on the hydrotalcite-like group of minerals is being continuously replenished with new data on natural and synthetic varieties (Croviesier *et al.,* 1983; Dunn *et al.,* 1979; Drits *et al.,* 1978; Koritning and Susse, 1975; Miyata, 1975; Stoffyn *et al.,* 1977). These minerals are based on positively charged brucite-like layers $(R_{1-x}^{2+}R_x^{3+})(OH)_2$ where the R^{2+} cations are most often Mg, but may be Ni, Cu, Ca, and Fe^{2+} as well, and the R^{3+} cations are Al, Cr^{3+}, and Fe^{3+}. The *a* dimension of the hexagonal cell varies with the number and arrangement of trivalent cations. With a disordered distribution of cations, the unit cell equals the basic cell of the brucite-like layer with $a_0 \approx 3$ Å; whereas, with an ordered arrangement of cations and $R^{2+}:R^{3+} = 1:2$, $a = a_0\sqrt{3} \approx 5.2$ Å. With other compositions and other modes for the distribution of heterovalent cations, values of *a* will be different (Taylor, 1969).

The interlayer of these minerals may contain CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-, and other anions that compensate for the positive charge of brucite-like layers, as well as water molecules and sometimes cations. Anions can easily exchange with solutions, leading to variations in interlayer spacings (Miyata, 1983; Bish, 1980; Hudson and Bussell, 1981). If the interlayers contain the carbonate anion, CO_3^{2-}, the minimum repeat distance normal to the layers, c_0, is 7.6 Å, and the height of the interlayer space proper is 5.6 Å. If the anion is a sulfate group, SO_4^{2-}, c_0 is 8.8 Å, and the interlayer spacing is 6.8 Å. Some SO_4-bearing varieties may have larger values of c_0 ranging up to around 11 Å. Occasionally, as a result of drying, varieties with $c_0 = 11$ Å lose some of their interlayer water and pass reversibly to a state with $c_0 = 8.8$ Å (Bish and Livingstone, 1981; Nickel and Wildman, 1981). There are also hetero-anion varieties, the most impressive being a mineral with an ordered alternation of CO_3- and SO_4-interlayers (Drits *et al.,* 1987), as well as koenenite, with an ordered alternation of layers with different cation-anion compositions (Allmann *et al.,* 1968).

The unit cell of hydrotalcite-like minerals may consist of several brucite-like layers producing crystals of different polytypes. For example, an Al-Mg mineral with CO_3^{2-} in the interlayers may be two-layer manasseite (polytype 2H) or three-layer hydrotalcite (polytype 3R). One-layer and six-layer polytypes of different chemical compositions have also been described (Drits *et al.,* 1987; Nickel and Wildman, 1981). The combination of these many variable properties probably accounts for the abundance of varieties within the group of minerals. Possibilities for the discovery of new members are far from being exhausted.

A recent review of hydrotalcite-like minerals revealed an excess of mineral names (often formally unacceptable) and a simple and rational nomenclature was proposed (Drits *et al.,* 1987). It reduces the diversity of names to several fundamental types, each having distinctive features, particularly with respect to polytypes. To date, however, polytype classifications have been limited to information on the number of brucite-like layers in the unit cell, because the interpretation of experimental X-ray diffraction (XRD) data obtained for finely dispersed powders of hydrotalcite-like minerals was often limited to an analysis of the positions, and not the intensities, of reflections (although the latter were frequently cited). Such an ap-

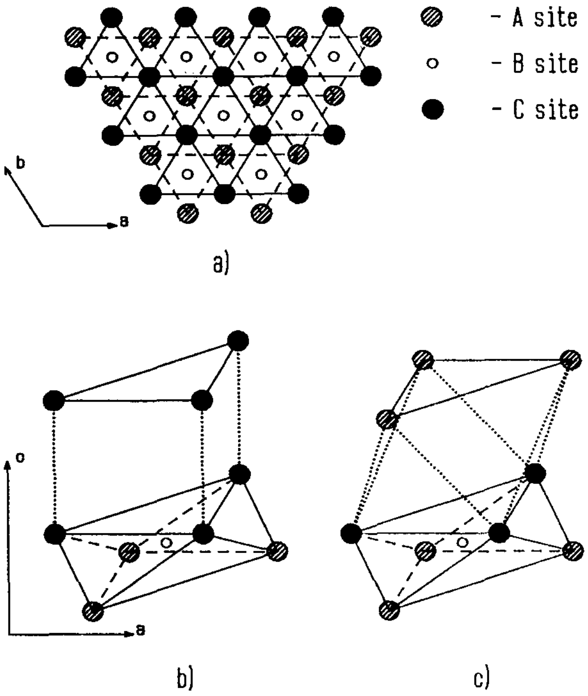

Figure 1. Essential segments of the structure of hydrotalcite-like minerals: a) hexagonally packed atoms in brucite-like layer. Stacking of layers with P-type (b) and O-type (c) interlayers. Only lower OH sheet of the upper layer is shown. If the upper layer starts with hydroxyls in **B** sites, the interlayer space is of O-type similar to that in Figure 1c, but the octahedron is built above a vacant cavity of the brucite-like layer. Dotted lines connect nearest hydroxyls of adjacent layers to display the polygons in the interlayer space. In b and c, large circles = OHs; small circles = cations.

proach misses certain rather important structural regularities associated with the stacking of consecutive brucite-like layers.

The aim of this two-part study is to apply the polytype approximation to the hydrotalcite group of minerals. In Part I, we deduce systematically theoretically possible polytypes in the group, calculate the XRD powder patterns for most polytypes, and identify diffraction criteria that help to discriminate polytypes with the same unit cells. In Part II, we shall present an analysis of literature data, showing which of the simulated polytypes occur among natural and synthetic varieties (Bookin *et al.*, 1993, hereinafter referred to as Part II). The crystal chemical factors that may control the occurrence of different polytypes and their mutual transformations will be also considered there.

MUTUAL ARRANGEMENT OF LAYERS

We start our discussion on polytypes with hexagonal cells having $a = a_0 \approx 3$ Å, and periodicity along the c axis of 1, 2, 3, and 6 layers. As usual for close-packed crystals, we shall denote unequivalent crystallographic sites of OH groups within the brucite-like layers with the capital letters **A**, **B**, and **C**, and the positions of cations in those layers with corresponding lowercase letters (Figure 1a). Let us assume that the lower surface of the first brucite-like layer is a hydroxyl sheet in which OH groups occupy **A** sites, that cations fill in octahedral positions **b**, and that the upper surface is formed by OH groups in **C** sites. Such a layer can be symbolically represented as **AbC**. To shorten the notation, we shall omit symbols of cation positions since they depend entirely on the arrangement of hydroxyls.

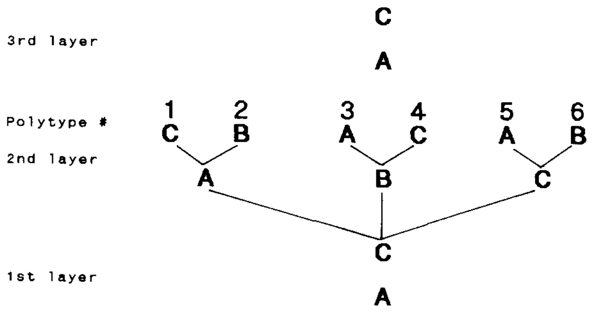

Figure 2. Scheme for derivation of all two-layer polytypes.

In the theoretical simulation of idealized polytypes, we assume that the OHs in the lower sheet of the next brucite-like layer in a stack can occupy any of the **A**, **B**, or **C** positions. If they reside in **C** sites, triangular roofs of the occupied octahedra form prisms in the interlayer (Figure 1b). This type of interlayer will be referred to henceforth as a P-type interlayer and denoted with an equal sign (=). If the hydroxyls in the lower sheet reside in either **A** or **B** sites, the roofs form octahedra (Figure 1c). Such interlayers will be referred to as O-type and denoted with a dash (–) to distinguish them from the P-type interlayers.

In the above notation we can describe a one-layer polytype with a P-type interlayer as:

. . .**AC–AC**. . . (1H)

Note that in the one-layer polytype all the cations reside in the **b** position on a line normal to the layers.

Two-layer polytypes

All two-layer polytypes can be derived from the scheme presented in Figure 2. Of the six illustrated structures, 1 describes the one-layer polytype, while the pairs 2 and 4, and 3 and 6 are symmetrically equivalent. Thus there are three different hexagonal two-layer polytypes:

...**AC=CA=AC**... ($2H_1$)

...**AC–AB–AC**... ($2H_2$)

...**AC–BA=AC**... ($2H_3$)

We use in the notation a digit indicating number of layers, a letter referencing symmetry, and a numerical subscript differentiating the particular polytype.

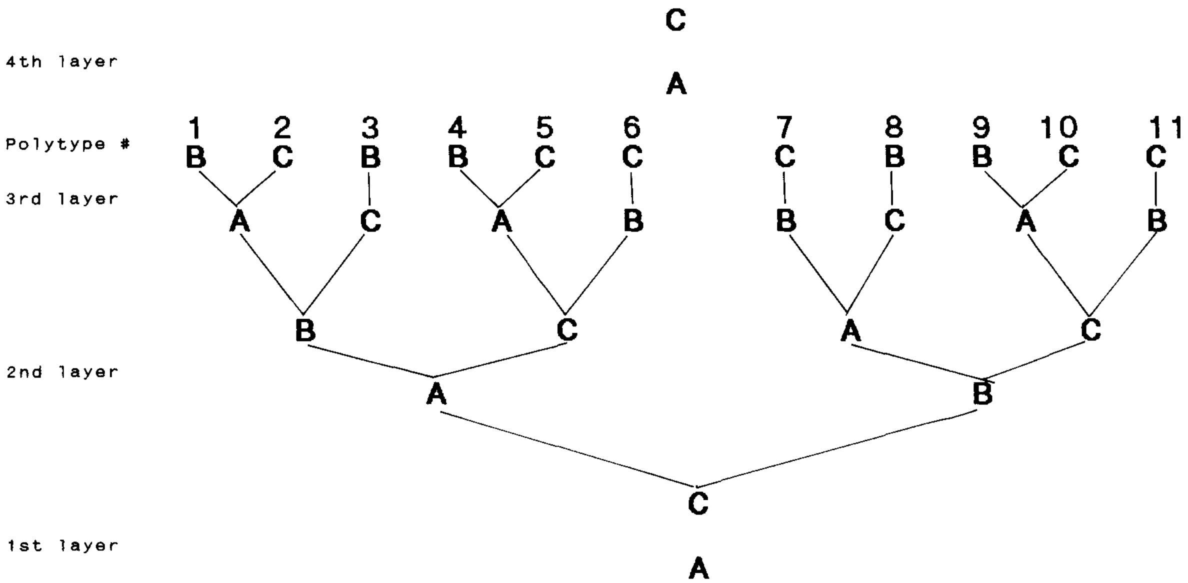

Figure 3. Scheme for derivation of three-layer polytypes with O-type interlayers only.

In polytype . . .**AC=CA=AC**. . ., all interlayers are of O-type and cations occupy only **b** sites as in polytype 1H. Polytype . . .**AC–AB–AC**. . . has all interlayers of the O-type and cations of the brucite-like layers alternate in **b** and **c** sites. The last polytype . . .**AC–BA=AC**. . . has alternating interlayers of both types.

Three-layer polytypes

A scheme for the derivation of all three-layer polytypes can be constructed on the same principle as presented in Figure 2. Let us simulate the possible three-layer polytypes separately depending on the type of the interlayers.

A three-layer crystal with P-type interlayers is represented by the unique sequence:

. . .**AC=CB=BA=AC**. . . $(3R_1)$

This polytype has rhombohedral symmetry (3R) and the distribution of cations over possible sites is the most homogeneous.

All three-layer polytypes with O-type interlayers can be derived from the schematic diagram presented in Figure 3. Polytype 5 is the one-layer crystal, and the others represent three symmetrically independent three-layer polytypes.

...**AC–BA–CB–AC**...	8	$(3R_2)$
...**AC–AB–AB–AC**...	1, 2, 4, 6, 10, 11	$(3H_1)$
...**AC–AB–CB–AC**...	3, 7, 9	$(3H_2)$

The first structure in this group has rhombohedral symmetry while the other two have hexagonal symmetry. In the $3R_2$ and $3H_2$ polytypes, cations are homogeneously distributed over the possible sites as in the $3R_1$ polytype.

The group of symmetrically independent polytypes with interlayers of both types is represented by five possible structures, all hexagonal:

...**AC–AB=BA=AC**...	$(3H_3)$
...**AC–AC=CA=AC**...	$(3H_4)$
...**AC–AB=BC–AC**...	$(3H_5)$
...**AC–AB–CA=AC**...	$(3H_6)$
...**AC–AC–BA=AC**...	$(3H_7)$

Six-layer polytypes

Of the great number of possible six-layer polytypes, we are only interested in those which have rhombohedral symmetry because they are the only ones described in the literature. To construct a six-layer polytype of this symmetry it is necessary to take a pair of layers and stack the pairs by shifting them along the $[\bar{1}10]$ direction, one third of the unit cell. To simulate all possible polytypes it is sufficient to apply the described procedure to all different pairs, which are the three two-layer polytypes listed above and a pair of identical layers. This gives five symmetrically independent polytypes:

...**AC–AC–BA–BA–CB–CB–AC**...	$(6R_1)$
...**AC–AC=CB–CB=BA–BA=AC**...	$(6R_2)$
...**AC=CA–BA=AB–CB=BC–AC**...	$(6R_3)$
...**AC=CA–CB=BC–BA=AB–AC**...	$(6R_4)$
...**AC–AB–CB–CA–BA–BC–AC**...	$(6R_5)$

Table 1. Intensities of XRD reflections in the 1H polytype with different chemical compositions of brucite-like layers and interlayers, and with disordered cation and anion distribution in *ab* plane ($a = 3.050$ Å).

Anion:	CO_3^{2}						SO_4^{2}						
c (Å):	7.560				8.830			10.830					
hkl	d (Å)	A	B	C	*hkl*	d (Å)	D	*hkl*	d (Å)	E	F	G	H
100	2.641	52	31	8	*100*	2.641	34	*100*	2.641	6	11	35	37
101	2.494	100	85	58	*101*	2.531	86	*101*	2.566	39	48	85	62
102	2.165	90	100	100	*102*	2.267	100	*102*	2.374	86	100	100	100
103	1.823	63	76	70	*103*	1.966	85	*103*	2.132	100	81	100	74
104	1.537	40	48	44	*104*	1.694	62	*104*	1.891	79	81	84	67
110	1.525	24	34	43	*110*	1.525	32	*105*	1.675	54	70	61	58
111	1.495	39	50	44	*111*	1.503	52	*110*	1.525	36	56	33	36
112	1.414	25	23	15	*105*	1.468	39	*111*	1.510	61	44	55	39
105	1.312	24	28	24	*112*	1.441	30	*106*	1.490	36	33	42	33
113	1.305	14	7	1	*113*	1.354	12	*112*	1.468	32	33	38	32
								113	1.405	11	15	21	19
								107	1.335	25	30	23	26

A) Ni_3Fe without scattering by interlayer.
B) Mg_2Al without scattering by interlayer.
C) Mg_2Al ½CO_3 + $2.2H_2O$ interlayer.
D) Ni_3Al without scattering by interlayer.
E) Mg_2Al without scattering by interlayer.
F) Mg_2Al ½SO_4 + 1½H_2O interlayer.
G) Ni_3Fe without scattering by interlayer.
H) Ni_3Fe ½SO_4 + 1½H_2O interlayer.

Among them there is not a single structure with all interlayers of the P-type. Two structures contain only interlayers of the O-type, and three structures contain alternating P- and O-interlayers.

Out of numerous six-layer polytypes with a hexagonal symmetry (6H), the group with all interlayers of P-type is of a particular interest because the interlayers of this type correlate with carbonate anions (Part II). The derivation is straightforward and gives nine polytypes.

XRD FEATURES OF THE HYDROTALCITE-LIKE POLYTYPES

Approximations

Since different polytypes with the same number of layers per unit cell and the same symmetry show similar reflections, the only way to identify a polytype through the powder XRD pattern is to analyze peak intensities. For each of the structural models proposed above, peak intensities I(*hkl*) were calculated as:

$$I(hkl) = |F(hkl)|^2/\sin^2\theta \cos\theta,$$

where F(*hkl*) is the structure factor for *hkl* reflection, and θ is the Bragg diffraction angle. Exact values of F(*hkl*) were replaced by estimates calculated for idealized structures of the polytypes. Refinements of the structures of numerous layer silicates have shown that approximations of ideal models provide an acceptable result because the relative intensities of strong, moderate, and weak reflections change very little between ideal and real structures. In our case, the calculated patterns neglect X-ray scattering of anions and water molecules in interlayers, changes in the cation composition of brucite-like layers, and distortions in the hydroxide framework. In the structure models, OHs and cations of brucite-like layers occupy special sites in the basic unit cell ($a = a_0$): (0, 0, z); (⅔, ⅓, z) and (⅓, ⅔, z) respectively, where z-coordinates were taken from one-dimensional models (Drits *et al.*, 1987). When required, the interlayer atom positions were taken from single crystal refinements of the hydrotalcite (Allmann and Jepsen, 1969) and wermlandite (Rius and Allmann, 1984) structures. In all polytypes, calculations were made for varieties with minimum periodicities c_0 of 7.56 Å, 8.83 Å and 10.83 Å, which correspond to the CO_3^{2-} and SO_4^{2-} varieties described in the introduction.

Results of calculations

Tables 1–4 list d-values, *hkl* indices, and intensities of reflections calculated for one-, two- and three-layer polytypes. The intensity of each peak on the XRD pattern is the sum of intensities of six separate reflections with equal d-values, but indices of only one of them are shown in the tables. For example reflections of the *10l* series incorporate intensities of *10l*, *01l*, $\bar{1}1l$, $\bar{1}0l$, $0\bar{1}l$ and $1\bar{1}l$ peaks. In the case of $l = 0$, the number of contributing reflections decreases to three. Calculations have been made for models differing in cation composition and cation distribution pattern in brucite-like layers and for models with and without scattering matter in interlayers. XRD patterns start at the position of the reflection with the highest d-value and end at $d = 1.3$ Å, after which no intense reflections appear.

Analysis of the data shows that relative intensities

Table 2. Intensities of XRD reflections in 1-layer polytype with ordered cation distribution in *ab* plane (a = 5.283 Å).

Anion:	SO_4^{2-}			
c (Å):	10.830			
hkl	d (Å)	A	B	C
100	4.575	17	28	100
101	4.215	28	16	1
102	3.495	18	26	0
103	2.834	10	10	0
110	2.642	17	16	2
111	2.566	58	69	27
112	2.374	92	100	40
104	2.330	7	6	0
113	2.132	100	89	36
105	1.958	4	5	0
114	1.891	84	89	37
106	1.679	3	2	0
115	1.675	58	69	28
300	1.525	36	46	21
301	1.510	60	55	23
116	1.490	41	42	16
302	1.468	36	33	12
107	1.466	2	2	0
117	1.335	28	29	12

A) Mg_2Fe without scattering by interlayer.
B) Mg_2Fe ½SO_4 + 1½H_2O interlayer.
C) Mg_2Al ½SO_4 + 1½H_2O interlayer.

of reflections of the basic unit cell ($a_0 \approx 3$ Å) vary within a rather small range when Mg is replaced by Ni, or when Al is replaced by Fe^{3+} (columns A and B, F and H in Table 1). Due to the small difference in scattering power, the substitutions of Fe^{2+} or Cu for Mg and of Cr^{3+} for Al do not strongly modify the XRD pattern either. Similarly, a small change is found in these intensities due to the presence or absence of interlayer anions (columns B and C, E and F, G and H in Table 1; A and B in Table 2). In all cases strong reflections remained strong, and weak reflections remained weak.

For structures with cations and anions ordering in the *ab* plane where $a \approx 5.3$ Å (Table 2), superlattice reflections appear that do not obey the rule described above. Their intensities depend heavily on the scattering power of the R^{3+} and R^{2+} cations and on the type of anions in interlayers. For example, the Fe-variety shows a set of superlattice reflections, the strongest being *100, 101,* and *102.* In the Al,Mg-variety a single but very strong *100* reflection is observed.

The data just presented have shown that the intensities of reflections of the basic unit cell are determined largely by the mutual arrangement of brucite-like layers and depend weakly on variations in cation composition of brucite-like layers and scattering by interlayer anions (but not the anions themselves, because they determine c_0 distance). These observations allow us to apply the polytype approximation to the hydrotalcite-like family of minerals, i.e., to use an XRD pattern estimated for a model structure with a particular chemical composition and water content as an "abstract" picture of a polytype and to search for common rules for differentiating polytypes.

Table 3. Intensities of XRD reflections in different two-layer polytypes with disordered cation[1] distributions in *ab* plane (a = 3.050 Å).

Anion:	CO_3^{2-}				SO_4^{2-}										
c_0 (Å):	7.560				8.830					10.830					
c (Å):	15.120				17.660					21.660					
hkl	d (Å)	$2H_1$	$2H_2$	$2H_3$	*hkl*	d (Å)	$2H_1$	$2H_2$	$2H_3$	*hkl*	d (Å)	$2H_1$	$2H_2$	$2H_3$
100	2.641	3	10	2	*100*	2.641	42	12	12	*100*	2.641	40	12	11
101	2.602	27	21	30	*101*	2.612	0	80	75	*101*	2.622	0	80	72
102	2.494	60	41	22	*102*	2.531	92	40	25	*102*	2.566	86	36	27
103	2.340	77	82	96	*103*	2.410	21	90	100	*103*	2.481	16	90	88
104	2.165	90	82	35	*104*	2.267	100	50	30	*104*	2.374	93	50	32
105	1.989	100	50	100	*105*	2.115	18	100	96	*105*	2.255	20	100	100
106	1.823	43	100	26	*106*	1.966	100	40	30	*106*	2.132	100	47	32
107	1.672	73	2	59	*107*	1.824	0	80	75	*107*	2.009	12	90	88
108	1.537	20	68	15	*108*	1.694	75	22	20	*108*	1.891	86	35	26
110	1.525	67	59	52	*109*	1.575	0	54	50	*109*	1.779	0	76	68
111	1.517	0	0	0	*110*	1.525	36	45	42	*10.10*	1.675	68	22	19
112	1.495	90	79	71	*111*	1.519	0	0	0	*10.11*	1.579	0	55	48
113	1.460	0	0	0	*112*	1.503	65	76	70	*110*	1.525	36	45	40
109	1.418	43	40	36	*113*	1.476	0	0	0	*111*	1.521	0	0	0
114	1.414	24	21	19	*10.10*	1.468	48	15	13	*112*	1.510	64	80	72
115	1.362	0	0	0	*114*	1.441	36	42	40	*113*	1.491	0	0	0
					115	1.400	0	0	0	*114*	1.468	43	54	48
					10.11	1.372	0	33	32	*115*	1.438	0	0	0
					116	1.354	15	18	17	*116*	1.405	23	30	26
					117	1.305	0	0	0	*117*	1.368	0	0	0

[1] Cations are Mg,Al for CO_3-bearing varieties and Ni,Al for SO_4 ones.

Table 4. Intensities of XRD reflections in different 3-layer polytypes with disordered cation[1] distribution in *ab* plane (a = 3.050 Å).

Anion:	CO_3^{2}					SO_4^{2}											
c_0 (Å):	7.560					8.830						10.830					
c (Å):	22.680					26.490						32.490					
hkl	d (Å)	$3R_1$	$3R_2$	$3H_1$	$3H_2$	*hkl*	d (Å)	$3R_1$	$3R_2$	$3H_1$	$3H_2$	*hkl*	d (Å)	$3R_1$	$3R_2$	$3H_1$	$3H_2$
100	2.641	0	0	4	0	*100*	2.641	0	0	54	0	*100*	2.641	0	0	57	0
101	2.624	1	20	10	22	*101*	2.628	28	54	55	66	*101*	2.633	29	49	58	66
102	2.573	41	0	14	14	*102*	2.590	69	22	58	54	*102*	2.607	62	23	60	53
103	2.494	0	0	66	28	*103*	2.531	0	0	79	8	*103*	2.566	0	0	75	6
104	2.394	1	83	28	81	*104*	2.454	14	94	65	95	*104*	2.512	15	85	67	88
105	2.283	100	1	36	37	*105*	2.364	100	13	68	56	*105*	2.447	92	14	67	55
106	2.165	0	0	100	40	*106*	2.267	0	0	100	14	*106*	2.374	0	0	100	13
107	2.047	1	100	36	100	*107*	2.166	15	100	71	100	*107*	2.296	13	100	74	100
108	1.933	91	4	47	50	*108*	2.065	91	17	65	58	*108*	2.214	100	14	74	58
109	1.823	0	0	58	12	*109*	1.966	0	0	80	7	*109*	2.132	0	0	97	11
10.10	1.721	15	52	28	59	*10.10*	1.871	23	68	60	77	*10.10*	2.050	18	89	74	93
10.11	1.625	36	19	36	49	*10.11*	1.780	53	27	54	52	*10.11*	1.969	80	20	67	57
10.12	1.537	0	0	27	0	*10.12*	1.694	0	0	48	0	*10.12*	1.891	0	0	74	4
110	1.525	41	40	69	71	*10.13*	1.614	30	32	42	47	*10.13*	1.816	26	57	59	71
111	1.522	0	0	0	0	*10.14*	1.539	23	30	36	40	*10.14*	1.744	46	28	54	52
112	1.511	0	0	0	0	*110*	1.525	36	37	94	54	*10.15*	1.675	0	0	48	0
113	1.495	56	54	94	96	*01.15*	1.468	0	0	32	1	*110*	1.525	35	35	77	53
114	1.473	0	0	0	0												
10.13	1.456	25	14	17	24												

[1] Cations are Mg,Al for CO_3-bearing varieties and Ni,Al for SO_4 ones.

DISCUSSION

As is the case with many other minerals consisting of layers having pseudohexagonal symmetry, polytypes having equal numbers of layers per unit cell, but differing substantially in layer arrangements, are theoretically possible for the hydrotalcite-like minerals. Three two-layer polytypes differing in interlayer type are possible. One of them has all interlayers of P-type, another has all interlayers of O-type, and the last has alternating interlayers of both types. Among the nine three-layer polytypes, there is one structure with all interlayers of P-type, three structures with all interlayers of O-type, and five structures having heterogeneous interlayers. Numerous six-layer polytypes are possible. Nine six-layer structures having P-type interlayers have been derived, all with hexagonal symmetry.

Not all polytypes can be easily identified from powder XRD data. Intensities of the basic unit cell reflections in the $2H_1$ polytype with SO_4^{2} anions in both hydrated states (Table 2) are similar to those of the one-layer polytype (Table 1). This may be due to the similarity in the distribution of cations in the brucite-like layers. Weak reflections of the two-layer cell at d = 2.115 Å and d = 2.410 Å for the 8.8 Å variety, and at d = 2.481 Å and d = 2.255 Å for the 11 Å variety seem to be the unique features allowing recognition of the two-layer polytype. It may be practically impossible to distinguish the $2H_2$ and $2H_3$ polytypes for SO_4 varieties, although they are dramatically different in their structures because of their identical distribution of cations.

On the contrary, some polytypes can be easily distinguished. On the XRD pattern of a two-layer crystal with SO_4^{2-} anions, reflections in the *10l* series with $l = 2n$ are more intense for the $2H_1$ polytype, whereas reflections with $l = 2n + 1$ are more intense for the other two polytypes. Several empirical rules may be developed for three-layer polytypes. Hexagonal polytypes differ from the rhombohedral polytypes by the presence of intense reflections with $(-h + k + l) \neq 3n$. The following diffraction criteria may be suggested to differentiate between the $3R_1$ and $3R_2$ modifications. For each pair of reflections $h0l$ and $h0(l + 1)$ $(l = 3n + 1 < 13)$, the intensity of the first reflection is higher than that of the second for polytype $3R_2$ and vice versa in polytype $3R_1$. The rule is equally good for the varieties with light (Al, Mg) and heavy (Ni^{2+}, Fe^{2+}) cations. The criteria for the discrimination of hexagonal polytypes depend on the nature of the interlayer anion. In SO_4-varieties, in polytype $3H_1$, all reflections with $d > 1.5$ Å, including reflection *100*, show intensities of the same order, while in polytype $3H_2$, reflections with $(-h + k + l) \neq 3n$ are much weaker than the rest. In the case of CO_3-varieties, in each triplet of reflections $10(3n + m)$ (n = 1, 2, 3; m = 0, 1, 2), in polytype $3H_1$ the strongest is the reflection with m = 0, while in polytype $3H_2$ it is the reflection with m = 1.

Among the possible processes of mutual transformation of the polytypes, the simplest is by displacement of the layers. Displacement may occur at low temperatures during hydration-dehydration processes or it may follow anion exchange. Among the whole family of hydrotalcite-like minerals there is a subset of polytypes that can be constructed from the one-layer structure by shifting the layers. This subset includes $2H_3$, all rhombohedral, and one hexagonal ($3H_7$) three-layer polytypes. All members of this group can be transformed to each other by displacement. For example, when the symbolic notation of the $2H_2$ polytype . . .**AC–AB–CB–AC**. . . is compared with that of a rhombohedral $3R_2$ polytype . . .**AC–BA–CB–AC**. . . , it can be seen that the difference is in the "inverted" sequence of hydroxyl sheets in the second layer of the $2H_2$ polytype.

CONCLUSION

The results of the current work have shown that the main contributor to the diffraction patterns of the polytypes are brucite-like layers. Peak intensities strongly depend on the mutual position of the layers and on the arrangement of cations. The contributions of interlayer anions and water molecules are marginal. This allows the identification of the polytypes from powder XRD data independent of the specific cation composition, anion type, and the degree of hydration of the interlayers.

The role of interlayer anions is not negligible from the diffraction point of view nor from the crystal-chemical point of view, because it contributes to the unit cell parameters. The interlayer type, as will be shown in Part II, is closely connected with the type of anion present in the interlayer.

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