

## CRYSTAL CHEMISTRY, CLASSIFICATION POSITION AND NOMENCLATURE OF LAYERED DOUBLE HYDROXYDES

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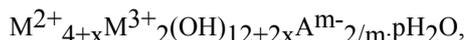
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The layered double hydroxides (LDH), also known as hydrotalcite-like minerals, have very versatile properties and find a very wide application in practice [1]. They are known as minerals since 1842, when *Hohsteter* has discovered hydrotalcite but even nowadays new minerals of this group are still discovered (see table 1). The crystal structures of these minerals and some of their useful properties have been studied using natural varieties. [2,3].

### Crystal chemical characteristics

The layered double hydroxides have the following common chemical formula:



where:

$M^{2+}$  is Mg, Ni, Zn, Ca, Cu, Co, Fe, Mn etc.

$M^{3+}$  is Al, Fe, Cr, Mn, Co, V etc.

$A^{m-}$  is  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$  etc.

Most of the minerals have Mg and Al as cations and the supplementary anion is most often carbonate. The crystal structure of LDH consists of brucite-like layers of octahedra  $[M^{2+}_{4+x}M^{3+}_2(OH)_{12+2x}]^{2+}$ , separated with an interlayer of anions and water molecules  $[A^{m-}_{2/m} \cdot pH_2O]^{2-}$  (Fig.1).

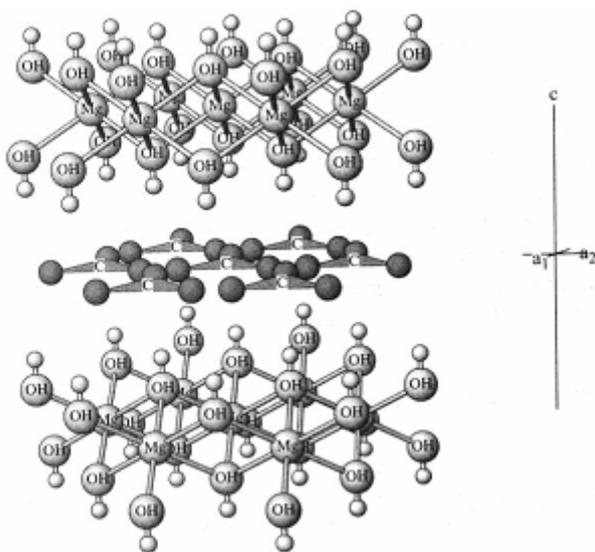


Fig. 1. Crystal structure of hydrotalcite (Gaines et al. [10]).

The interlayer anions compensate the charge emerging from the substitution of  $M^{2+}$  with  $M^{3+}$  in the hydroxide layer. There has been established a strict relationship between the charge of the layer (the proportion  $M^{2+}/M^{3+}$ ) and the thickness of the interlayer. In the natural varieties there have been described the polytypes 1H, 2H<sub>1</sub>, 3H<sub>2</sub>, 3R<sub>1</sub>, 3R<sub>2</sub> and 6R, often occurring as mixtures [4,5,6]. Among the synthetic varieties mostly the 3R<sub>1</sub> polytype has been obtained. The interlayer water molecules can be reversibly extracted from the structure by means of heating or vacuumation and the anions can be exchanged with other anions in solutions. The LDH are the only minerals known which have anion exchange ability.

### LDH in the mineralogical classifications

Table 1 contains information about some of the members of the group and their position in the classifications given in the most popular mineralogical handbooks in Bulgaria and abroad. All these classifications are based on chemical and crystal chemical criteria. This means that the rough classification is based on the structure defining anion. In this table it is visible that the meixnerite, which has a hydroxide as charge balancing anion indisputably belongs to the subclass of the hydroxides. In this same subclass we also find most of the minerals containing Cl in the interlayer. The only exception to this rule is the chlormagaluminite, in which Cl and  $CO_3$  do the charge compensation. The latter is the explanation why this mineral is found in the carbonate class in the classifications of Kostov [7] and Strunz [9] and in the halogenide class in the classification of Dana [10]. Because of its distinct similarity with hydrocalumite, kuzelite, which has a sulfate interlayer, is also treated as hydroxide. All the rest minerals with a sulfate charge compensating anion are placed in the sulfate class. In most of the LDH minerals the compensating anion is carbonate, which is the reason used by most of the authors to classify these minerals as carbonates. The only exception is the handbook Minerals [11], where these minerals are treated as hydroxides. The classification of pyroaurite, sjxgrenite and takovite in subclass hydroxides in some of the reference materials is due to the inaccurate formulas used by the authors.

### Hydroxide or carbonate is hydrotalcite?

Till the end of 19<sup>th</sup> century the known LHD minerals are described as pure hydroxides and the carbonate anions found out by the chemical analyses, are treated as impurities [12]. It is in 1915 when Manasse proved (after Frondel [4]) that the additional anions are peculiar for the hydrotalcite-like minerals. This remarkable discovery led to the fact that those minerals have started to be classified differently depending on the compensating anion inside.

As seen in Table 2, from 86 to 91 % of the negative charges in the LDH structure are due to the hydroxide groups and only 10 to 14 percent - to the compensating

anions in the interlayer. The hydroxyl anions are the basic, and stable component in the hydrotalcite structure - the octahedral brucite-like layers. Moreover, the specific hydroxyl anion characteristic - a clearly marked dipole structure and tendency to make hydrogen bonds - leads to the layered nature of the structures in which it dominates [13]. The interlayer anions in such minerals under certain circumstances have the possibility to exchange with other charge balancing anions.

Table 1. Selected Spaces of the Layered Double Hydroxides in Mineralogical Classifications. H - hydroxides; C - carbonates; Cl - halogenides; S - sulfates; n.i. - no information.

Year of Discovery	Mineral name	Polytype	Chemical formula	Crystal class according to:				
				Kostov, 1993	Strunz, 1941	Strunz, 2004	Dana's New Mineralogy Gaines, 1997	Minerals, vol. II, 1967
1975	meixnerite	3R	Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> (OH) <sub>2</sub> .4H <sub>2</sub> O	H	-	H	H	-
1842	hydrotalcite	3R	Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	C	C	C	H
1940	manasseite	2H	Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	-	C	C	H
1997	quintinite-2H	2H	Mg <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> CO <sub>3</sub> .4H <sub>2</sub> O	-	-	C	C	-
1997	quintinite -3T	3R	Mg <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> CO <sub>3</sub> .4H <sub>2</sub> O	-	-	C	C	-
1865	pyroaurite	3R	Mg <sub>6</sub> Fe <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	H	C	C	H
1900	sjögrenite	2H	Mg <sub>6</sub> Fe <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	H	C	C	H
1910	stichtite	3R	Mg <sub>6</sub> Cr <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	C	C	C	H
1941	barbertonite	2H	Mg <sub>6</sub> Cr <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	-	C	C	H
1979	desautelsite	3R	Mg <sub>6</sub> Mn <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	-	C	C	-
1957	takovite	3R	Ni <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	H	-	C	C	H
1967	reevesite	3R	Ni <sub>6</sub> Fe <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	C	-	C	C	-
1980	comblainite	6R	Ni <sub>6</sub> Co <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> .4H <sub>2</sub> O	-	-	C	C	-
1992	caresite	3R	Fe <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> CO <sub>3</sub> .4H <sub>2</sub> O	-	-	C	C	-
1997	zaccagnaite	2H	Zn <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> CO <sub>3</sub> .3H <sub>2</sub> O	-	-	C	C	-
1998	charmarite (2H, 3T)	2H3R	Mn <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> CO <sub>3</sub> .4H <sub>2</sub> O	-	-	C	C	-
1982	chlormagaluminite	2H	Mg <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> (Cl,CO <sub>3</sub> ).4H <sub>2</sub> O	C	-	C	Cl	-
1967	iowaite	3R	Mg <sub>5</sub> Fe(OH) <sub>12</sub> Cl.2H <sub>2</sub> O	H	-	H	H	-
2000	woodallite	3R	Mg <sub>6</sub> Cr <sub>2</sub> (OH) <sub>16</sub> Cl <sub>2</sub> .4H <sub>2</sub> O	-	-	H	H	-
1934	hydrocalumite	2M	Ca <sub>8</sub> Al <sub>4</sub> (OH) <sub>24</sub> (CO <sub>3</sub> ,Cl,OH) <sub>3</sub> .11H <sub>2</sub> O	H	H	H	H	H
1996	kuzelite	6R	Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> SO <sub>4</sub> .6H <sub>2</sub> O	-	-	H	H	-
1956	honessite	3R	Ni <sub>6</sub> Fe <sub>2</sub> (OH) <sub>16</sub> SO <sub>4</sub> .nH <sub>2</sub> O	S	-	S	S	n.i..
1866	woodwardite	3R	Cu <sub>5</sub> Al <sub>2</sub> (OH) <sub>12</sub> SO <sub>4</sub> .2-4H <sub>2</sub> O	-	S	S	S	n.i.
1995	zincowoodwardite	3R	Zn <sub>5</sub> Al <sub>2</sub> (OH) <sub>12</sub> SO <sub>4</sub> .2-4H <sub>2</sub> O	-	-	S	S	-

Table 2. Distribution of the valence strains in LDH with different M<sup>2+</sup>/M<sup>3+</sup> ratio.

M <sup>2+</sup> : M <sup>3+</sup>	Valence strains, percent			
	M <sup>2+</sup>	M <sup>3+</sup>	OH <sup>-</sup>	A <sup>2-</sup>
2:1	57.1	42.9	85.7	14.3
3:1	66.7	33.3	88.9	11.1
4:1	72.7	27.3	90.9	10.1

Consequently, the natural position of the LHD-group in the chemical and crystal chemical classifications of minerals is in the subclass of the hydroxides. A finer subdivision of this group can be done on the basis of the type of cations compensating anions.

By the way, the discussed example is a part of another more general problem. If we take a look at the classes of halogenides and oxysalts in most of the contemporary handbooks it is evident that those classes

contain a big number of minerals in which the hydroxyl anions are the basic, and structure defining anion and the halogen and oxysalt anions have a minor significance. Such examples are: claringbullite ( $\text{Cu}_4(\text{OH})_7\text{Cl}_n\text{H}_2\text{O}$ ) and simonkolleite ( $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ ) in the class of halogenides, basaluminite ( $\text{Al}_4\text{SO}_4(\text{OH})_{10}\cdot 5\text{H}_2\text{O}$ ) and connellite ( $\text{Cu}_{19}\text{SO}_4(\text{OH})_{32}\text{Cl}_4$ ) in the class of sulfates, and others. Apparently, from the crystal chemical point of view there exist hydroxides with additional anion, just like sulfates, for example. Possibly, because the hydroxyl anions in the minerals are widely spread this anion has been differently treated than the other anions, although it often displays a structure defining role.

### Nomenclature

If we now look at the present state of the LDH-group of the, part of which is given in Table 1, we find that the names have been given on the basis of: 1) differences in the cation anions in the interlayer; 3) differences in the polytype modification; and even 4) differences in the cation ratio –  $\text{M}^{2+}/\text{M}^{3+}$ . In the last years, however, the Commission on New Minerals and Mineral Names of IMA recommends to differentiate between the polytype varieties by denoting the polytype modification together with the name of the mineral and

not giving a new mineral name. For the zeolites it is recommended [14] to show also the exchange cations together with the name of already known ion form of this mineral.

Following such recommendations would lead to significant reduction in the number of used names. Such a limitation attempt was driven by Drits et al. [15]. They propose the following two possibilities:

1) Keep one name for each pair of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  cations in the octahedral layer and give details about the thickness of the single packet (layer + interlayer), the anion in the interlayer, and the polytype; or

2) Keep only one name for the whole group (for example pyroaurite) and give details about the cation and anion composition, the thickness of the single packet, and the polytype.

In this way the manasseite, which is a hexagonal polytype of hydrotalcite, will be denoted as 7.8-E  $\text{CO}_3$ -hydrotalcite-2H or 7.8- E  $\text{CO}_3$ -Mg, Al-pyroaurite-2H. According to us, for proper determining of the type it is enough to indicate the anion and the polytype variety. Clarification on the thickness of the single packet and the ratio,  $\text{M}^{2+}/\text{M}^{3+}$ , is only needed in very specific texts and should not be used for creating a new mineral type.

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