SYNTHESES OF DISORDERED AND Al-RICH
HYDROTALCITE-LIKE COMPOUNDS

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Abstract—Hydrotalcite-like compounds, $[Mg_{1-x}Al_x(OH)_2]^{x+}$ $[xX^- \cdot n\,H_2O]$, where $X^- = \frac{1}{2}\,CO_3^{2-}$ or OH^-, were prepared by hydrothermal syntheses at $P_{H_2O} = 100$ MPa and $T = 100°–350°C$. Starting materials were MgO, γ-Al_2O_3, H_2O, and $MgC_2O_4 \cdot 2H_2O$. The synthesis depended on temperature, pressure, the $Al/(Al + Mg)$ ratio x, and the CO_2 content of the starting material. Previously an Al content of x = 0.33 was thought to be the upper limit in these double-layer compounds, but by using pressure the Al-content was increased to x = 0.44. Up to x = 0.33, a_0 decreased linearly to about 3.04 Å, but for x $\geq$ 0.33, a_0 remained nearly constant at this value. For the synthesized products the layer thickness c' varied between 7.40 and 7.57 Å in contrast to the natural phases wherein c' varies from 7.60 to 7.80 Å. At higher temperatures CO_2-free syntheses, i.e., those without Mg-oxalate, resulted in a disordered hydrotalcite-like phase. The transition temperature between the ordered and the disordered hydrotalcite-like phase depended on the Al-content, x.

INTRODUCTION

The carbonate-hydroxide $[Mg_{1-x}Al_x(OH)_2]^{x+}$ $[xX^- \cdot n\,H_2O]^{x-}$, where $X^- = \frac{1}{2}\,CO_3^{2-}$ or OH^-, occurs in two dimorphic forms, rhombohedral hydrotalcite and hexagonal manasseite. Both are double-layer structures. Reviews of commonly non-stoichiometric double-layer structures were made by Allmann (1970) and Taylor (1973). Hydrotalcite and manasseite are actually stacking polymorphs that have the same basic substructure. They consist of brucite-like layers $Me(OH)_2$, in which Mg^{2+} and Al^{3+} are randomly distributed among the octahedral positions. In minerals, the value $x = Al/(Al + Mg)$ varies between about 0.22 and 0.33. Because of the different size of the Mg^{2+} and Al^{3+} ions, the lattice parameter a is controlled by x ($a = 3.14$ Å for x = 0 in brucite, and $a = 3.05$ Å for x = 0.33). The brucite-like layers are separated by disordered (nearly liquid) interlayers of water molecules, CO_3^{2-}, and/or OH^- anions.

Charge compensation between the brucite-like layers and interlayers is realized by hydrogen bonds, which also exist within the interlayer. In the hydrotalcite structure the layers are stacked with rhombohedral symmetry (BC . . . CA . . . AB . . . BC . . . for the brucite-like mainlayers), and three double-layers are present per unit cell ($c = 3c' = 23.4$ Å); in the manasseite structure they are stacked with hexagonal symmetry (BC . . . CB . . . BC . . .), and two double-layers are present per unit cell ($c = 2c' = 15.6$ Å). For hydrotalcite from Snarum, Norway, where x $\approx$ 0.25, Roy *et al.* (1953) reported $c' = 7.63$ Å, whereas we found for the same material $c' = 7.80$ Å. For hydrotalcite from Vezna, Czechoslovakia, where x = 0.33, Černý (1963) reported $c' = 7.62$ Å. The single crystals of this material yielded $c' = 7.603$ Å (Allmann and Jepsen, 1969).

In nature hydrotalcite and manasseite are commonly intergrown. Manasseite generally forms the core and hydrotalcite the outer part of a grain. Thus, hydrotalcite appears to form later than the coexisting manasseite and, presumably, at lower temperatures. To date, synthetic hydrotalcite-like compounds have been prepared hydrothermally (Roy *et al.,* 1953), by coprecipitation from mixed $MgCl_2$-$AlCl_3$-solutions (Feitknecht and Gerber, 1942; Gastuche *et al.,* 1967), and from MgO-Al_2O_3-suspensions (Mascolo and Marino, 1980). Hydrotalcite always formed at lower temperatures; in some experiments a disordered phase was reported (Gastuche *et al.,* 1967), but manasseite was never synthesized.

EXPERIMENTAL

In the present study hydrotalcite-like compounds were prepared hydrothermally at temperatures between 100° and 350°C and a water pressure of 100 MPa. Alumina gel (γ-Al_2O_3), MgO (freshly annealed at 1050°C), $MgC_2O_4 \cdot 2H_2O$, and distilled and boiled H_2O were used as starting materials. From these oxides, mixtures with different Mg:Al ratios were prepared. Two series of experiments were carried out: one with mixtures containing CO_2, and the other free from CO_2, i.e., without $MgC_2O_4 \cdot 2H_2O$. In both series the Mg:Al ratio was varied between x = 0.25 and x = 0.60. The reaction times varied from 7 to 42 days. Experiments were carried out in welded gold tubes of about 4 mm internal diameter in Tuttle-type cold-seal pressure vessels. At temperatures above 200°C, Morey-type pressure vessels were also used. After the runs, the vessels were cooled to room temperature within 10 to 15 min. For the CO_2-free series the gold tubes were opened in a glove-box containing dry nitrogen. The products were
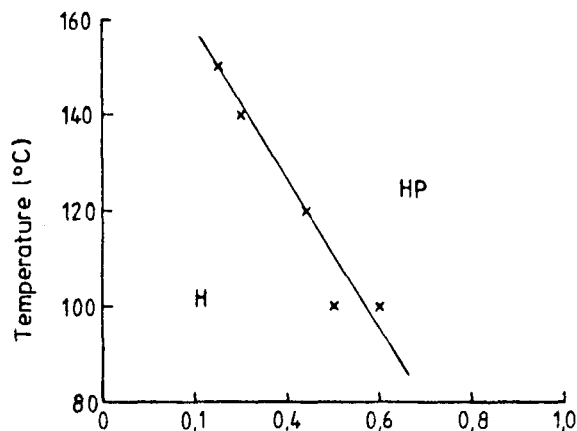
Figure 1. Transition temperature for hydrotalcite (H) to hydrotalcite-like phase with disordered stacking of the layers (HP) as a function of the initial composition $x = Al/(Al + Mg)$ in the CO_2-free system at 100 MPa.

immersed in nujol and immediately checked by IR spectroscopy. In all samples very minor amounts of CO_3^{2-} were detected, but the intensity of these bands was less than 5% as compared with natural hydrotalcite. Thereafter, the examples were examined by X-ray powder diffraction (XRD) on a Philips X-ray diffractometer using CuKα radiation and, if possible, the measured lines were used for an LQ refinement of the lattice constants a_0 and c_0.

RESULTS

For the system $MgO-Al_2O_3-H_2O-CO_2$ no new results were obtained, and the products were similar to those reported by Roy *et al.* (1953). The only double-layer structure found was hydrotalcite. In the system $MgO-Al_2O_3-H_2O$, hydrotalcite-like phases (hydrotalcite and a hydrotalcite-like phase having no defined stacking order, herein called HP) were formed in all runs, in contrast to Roy *et al.* (1953), who found no hydrotal-

Table 1. X-ray powder diffraction diagram of disordered hydrotalcite-like phase synthesized at 150° and 1 kbar[1] and CO_2-containing precipitation product of Gastuche *et al.* (1967)[2].

hk*l*	I	d_{obs}	hk*l*	I	d_{obs}
003	100	7.40	003	100+	7.63
	30	4.57		5 br	4.57
006	70	3.71	006	100+	3.81
	40 br	2.61	101	75 br	2.60
			009	10	2.532
	70 br	2.37	105	27 vbr	2.36–2.20
	40 br	2.00	108	22 vbr	2.01–1.91
			0012	5	1.897
	25 br	1.68			
110	40	1.52	110	60	1.523
113	30	1.49	113	60	1.493

[1] Al(Al + Mg) = 0.33; a_0 = 3.04 Å, c' = 7.40 Å.
[2] Al/(Al + Mg) ≈ 0.30, a_0 = 3.048 Å, c' = 7.68 Å (Table 2, pattern 2). br = broad; vbr = very broad; for indexing, c is assumed to equal 3c'.
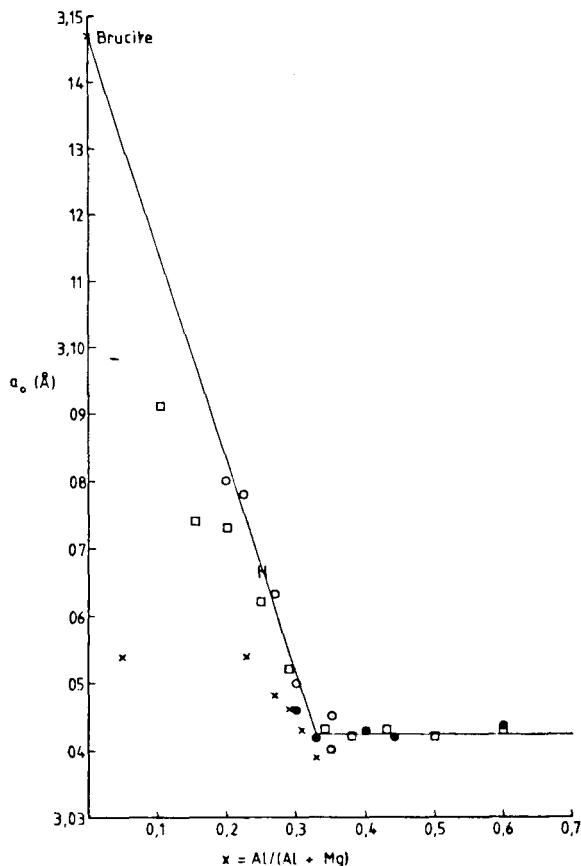

Figure 2. a_0 of natural and synthetic hydrotalcite-like phases as a function of the Al-contents $x = Al/(Al + Mg)$. O = Brindley and Kikkawa (1979); × = Mascolo and Marino (1980) (only the Al-contents of the initial composition are given, not that of the synthesized phases); □ = Miyata (1980); H = natural hydrotalcite from Snarum, Norway; ● = this study.

cite-like phase in this system. In nature a nearly CO_2-free hydrotalcite, meixnerite, has been reported (Koritnig and Süsse, 1975). A nearly CO_2-free hydrotalcite with x between 0.23 and 0.33 was also prepared by Mascolo and Marino (1980).

In the present experiments using pressure, hydrotalcite was preferentially formed at values of x between 0.25 and 0.44. At higher levels of Al and at higher temperatures disordered phase HP was formed instead of hydrotalcite. The transition temperature for hydrotalcite → HP thus appears to depend on the Mg:Al ratio of the starting material (see Figure 1). For x = 0.25, the transition hydrotalcite → HP took place at 150°C and 100 MPa. At higher Al-contents, the transition temperature decreased to 100°C for x = 0.50. Because the disordered phase HP has a somewhat smaller c_0 lattice constant than the coexisting hydrotalcite, both phases could be identified simultaneously (split 003 and 006 reflections, no difference in a_0). Apart from the region near the transition line, mostly one phase only (hydrotalcite or HP) was found. Only for x = 0.25

was some brucite found in addition to hydrotalcite or HP. For $x > 0.25$, only the double-layer phases hydrotalcite or HP were obtained; but for $x > 0.44$, a diffuse hump in the XRD background at about $37°2\theta$ indicated some unreacted noncrystalline γ-Al_2O_3.

The hydrotalcite and HP products differed only in their XRD patterns. The XRD pattern of the synthetic hydrotalcite was identical to that of natural hydrotalcite (JCPDS card 22-700), whereas the XRD pattern of HP (Table 1) showed fewer reflections, some of which were broad and diffuse. Only the 001 and hk0 reflections were sharp. This pattern is presumably due to a disordered stacking of the layers, i.e., only those reflections common to the hydrotalcite and manasseite stacking sequence ($-h + k = 3n$) were sharp. The basal reflections gave only the layer thickness c', and evidence for a well-defined supercell was not seen. The c' value of the synthetic CO_2-free hydrotalcites was always found to be near 7.57 Å, whereas the c' value of the HP was 7.40 Å. The c' values of natural hydrotalcites are 7.60 to 7.80 Å. The c' value of the CO_2-containing precipitation products of Gastuche et al. (1967) varied from 7.63 to 7.94 Å. Inasmuch as $a_0 = 2d(110)$, the value of a_0 was calculated from the 110 reflection = 3.04 Å for HP. HP therefore appears to be a transitional phase between hydrotalcite and manasseite. The formation of HP was favored by higher temperature and higher Al content of the starting material. It was hindered by the presence of CO_2, in which case, only hydrotalcite was formed.

Al-rich hydrotalcites

Previously it was assumed that Mg in the brucite-like layers of hydrotalcite could be replaced by Al only from 22 to a maximum of 33%. In this range, the lattice constant a_0 decreases linearly with increasing Al contents (Brindley, 1980). Figure 2 gives a review of the lattice constants a_0 of different authors and our own results.

In previous syntheses at normal pressure (0.1 MPa) with starting materials containing higher Al contents than $x = 0.33$, an additional Al-hydroxide phase has always been formed (e.g., Gastuche et al., 1967; Mascolo and Marino, 1980). In the CO_2-free system such a phase was not formed in the pressure experiments of the present study. In all runs at 100 MPa and about 100°C, with x varying from 0.25 to 0.44, only hydrotalcite-like compounds were detected in the XRD patterns. The only difference between these and earlier syntheses was the use of a water pressure of 100 MPa, which may be the reason for the complete accommodation of all Al in the double-layer compound. To exclude the possibility of noncrystalline Al-hydroxide phases the products of runs where $x = 0.44$ were analyzed by atomic absorption after they were washed for 1 hr in 0.1 N NaOH at 100°C. The weight change during washing was about ±3%. The chemical analysis of the

so-washed material confirmed Al-contents of $x = 0.42$–0.44. Some Na (1.2%) was found too. Surprisingly the a_0 value of 3.04 Å was about the same as for $x = 0.33$.

For values of $x \leq 0.33$ each $Al(OH)_6$-octahedron is surrounded by six $Mg(OH)_6$-octahedra, but for $x > 0.33$ $Al(OH)_6$-octahedra must be directly adjacent to each other, the smaller ionic radius of Al^{3+} probably being compensated for by the increasing electrostatic repulsion within the brucite-like layer. This statement is supported by the results of Serna et al. (1982) on hydrotalcite-like compounds $[Al_2Li(OH)_6]^+$ $[X^- \cdot n\,H_2O]$. These structures are built of octahedral sheets in which the Al ions are arranged as in gibbsite and the vacancies are filled with lithium cations. They can be regarded as hexagonal superlattices with $a = \sqrt{3} \cdot a' = \sqrt{3} \cdot 3.07$ Å (Serna et al., 1982). Theoretically, Li^+ can be replaced by Mg^{2+}, which leads to a hydrotalcite-like layer with $x = 0.66$. Because of the smaller ionic radius of Mg^{2+} the value of a' should decrease from $a' = 3.07$ Å for Li to $a' = 3.04$ Å for Mg. This latter value is exactly the value which was found in the present experiments for hydrotalcite (and HP) with $x = 0.33$ and greater. Thus, the lattice constant a_0 of hydrotalcite-like compounds does appear to not decrease further if the Al-content exceeds $x = 0.33$ (see Figure 2), i.e., a lattice constant of $a_0 = 3.05$–3.04 Å indicates only $x \geq 0.33$, but does not allow the exact x-value to be deduced.

Using pressure, we succeeded in synthesizing hydrotalcite or HP from starting materials in which x was as great as 0.44. Possibly in some former syntheses, hydrotalcite with $x > 0.33$ was formed, but not recognized by the authors because a_0 was not below 3.04 Å.

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