

A crystal-chemical study of Mg,Al and Ni,Al hydroxy-perchlorates and hydroxy-carbonates

G. W. BRINDLEY AND S. KIKKAWA¹

Mineral Sciences Building, The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract

Synthetic products of the form $M_{1-x}Al_x(OH)_2R_{x/n}^{-n} \cdot yH_2O$, with $M = Mg, Ni$ and $R = CO_3$ and/or ClO_4 have been prepared, with x ranging from about 0.33 to 0.20, by precipitation from mixed perchlorate solutions by addition of NaOH; the carbonate ion is present owing to solution of atmospheric CO_2 . The two kinds of anions show a strong tendency to segregate into separate crystals or, under particular conditions, into separate layers within the same crystals, forming an alternating sequence of carbonate and perchlorate layers. Pure carbonate and pure perchlorate phases were obtained by anion exchange reactions. The parameter c' , layer thickness, diminished with increase in Al^{3+} ions due to increase in electrostatic attraction between positive layers and negative interlayers. The parameter a for a hexagonal cell also diminished with increase of Al^{3+} ions because of their smaller size. The observed change $\Delta a/\Delta x$ agrees semi-quantitatively with calculated values. Reasons are suggested for the range of Al^{3+} ions which can substitute in mixed hydroxide phases and for the commonly observed value of $x \approx 0.25$ in natural minerals, based on possible supercell arrangements of the Al^{3+} and M^{2+} ions.

Introduction

The hydroxy compounds studied have compositions of the type $[R_{1-x}^{2+}R_x^{3+}(OH)_2]^{+x}R_{x/n}^{-n} \cdot yH_2O$. Many minerals and synthetic compounds have compositions of this type with $R^{2+} = Mg, Fe, Ni, \dots$, $R^{3+} = Al, Fe, Cr, \dots$, $R^{-n} = CO_3, SO_4, NO_3, \dots$. The structures consist of brucite-like octahedral layers with a net positive charge x per formula unit balanced by an equal negative charge from interlayer anions; water molecules occupy remaining interlayer space. The layers can be stacked with hexagonal symmetry and two layers per unit cell, with rhombohedral symmetry and three layers per unit cell, or with less symmetrical arrangements.

The proportion of R^{3+} ions varies, but in natural minerals is often near 0.25, so that the ratio R^{2+}/R^{3+} is near 3; hydrotalcite, for example, has a composition near $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$. An extensive literature exists on the compositions and structures of these materials. The early history dating back to the

middle of the last century was surveyed by Frondel (1941), who clearly recognized the hexagonal and rhombohedral forms. Structural studies have been carried out by Allmann and Lohse (1966), Ingram and Taylor (1967), Allmann and Jepsen (1969), Taylor (1969), and Bish (1977, 1978a, b). Synthetic products were studied by Feitknecht and his colleagues (Feitknecht, 1942), Gastuche *et al.* (1967), Brown and Gastuche (1967), Miyata (1975, 1977), and Bish (1977, 1978a, b). General discussions have been given by Allmann (1970) and Taylor (1973).

The present study is concerned with the range of Mg/Al and Ni/Al ratios compatible with this type of structure, the variation of the layer (basal) spacing with layer charge, and the spacings developed with different interlayer anions.

Experimental

Product preparation

Preliminary experiments using mixed chloride solutions and slow addition of NaOH followed closely the previous work of Gastuche *et al.* (1967). Uncertainty regarding the role of Cl^- ions, which conceiv-

¹ Present address: Institute for Scientific and Industrial Research, Osaka University, Yamadakami, Suita, Osaka 565, Japan.

ably might occupy positions in the octahedral layers as well as in the interlayers, led us to prefer perchlorate solutions. The perchlorate ion is detected readily by infrared spectroscopy and can be expected to occur only in interlayer positions. Experiments were carried out in plastic vessels to avoid contamination with silica when glass vessels were used.

Mixed solutions of Mg (or Ni) and Al perchlorates, 0.1 M in total cation content, were reacted at about pH 10 with NaOH solutions added drop-wise and with vigorous stirring. To reduce (or eliminate) the adventitious role of dissolved CO_2 , solutions were prepared with boiled distilled water cooled in stoppered flasks opened only to add NaOH and to check pH. Reactions were continued for periods of 5–7 days. Products were washed with boiled distilled water after centrifugation, dried overnight at 55°C in normal atmosphere, and stored in stoppered tubes. The precautions taken reduced but did not eliminate CO_3 anions from the products. The results, however, proved interesting in other respects.

The products, which contained both ClO_4^- and CO_3^{2-} anions, were treated with 0.1 M sodium carbonate solution or with 1/100 perchloric acid solution to obtain single-anion products.

Product examination

Products were examined by X-ray powder diffraction using filtered $\text{CuK}\alpha$ radiation and diffractometer

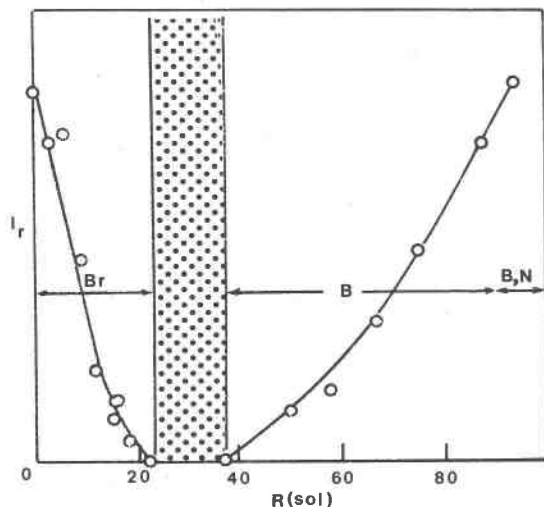


Fig. 1. I_r , X-ray intensity relative to the highest recorded intensity, plotted against $R(\text{sol}) = [\text{Al}/(\text{Al} + \text{Ni})] \times 100$ for the hydroxide phases Br = $\text{Ni}(\text{OH})_2$ with brucite structure and B = $\text{Al}(\text{OH})_3$ with bayerite structure. In the composition range B,N a mixture of bayerite and nordstrandite was observed. Stippled area = composition range where only mixed Ni,Al hydroxy phases were formed.

recording at $1^\circ(2\theta)/\text{min}$ and a chart speed to give $2^\circ(2\theta)/\text{inch}$. Thin layers of oriented powder on glass slides were used to emphasize basal 00l reflections. These reflections correspond to successive orders from the layer spacing c' . The true c parameter is a multiple of c' and depends on the layer stacking sequence. General reflections were recorded from randomly oriented powders but were not defined sufficiently well to provide unique indexing. A prominent reflection with a spacing near 1.5A, however, can be indexed as 110 with respect to hexagonal axes (see Brown and Gastuche, 1967) and with $l = 0$ this reflection is not dependent on the layer stacking arrangement. The hexagonal a parameter is $2d(110)$.

Transmission infrared spectra were obtained using the KBr pellet technique with 2 mg of sample in 200 mg KBr in vacuum-pressed pellets.

Atomic absorption analysis was used to determine Mg/Al and Ni/Al ratios in the prepared materials and in the initial solutions.

Results

Composition ranges of Mg,Al and Ni,Al double hydroxides

The proportions of Al in the initial solutions and in the resulting products are conveniently represented by the mole fractions $R(\text{sol})$ and $R(\text{cryst})$, $R = \text{Al}/(\text{Al} + \text{M})$ with $\text{M} = \text{Mg}$ or Ni . $R(\text{cryst})$ is identical with x as used in the general formula given previously.

Double-cation hydroxides are formed when $R(\text{sol})$ lies in the range approximately 20%–35% and are recognized easily in X-ray diffraction patterns by distinctive basal reflections at about 7.5–8.0A or larger values determined by the anions and water molecules present. Outside this composition range, single-cation hydroxides also appear. Figure 1 shows results for the Ni,Al system; similar results for the Mg,Al system were obtained which confirmed the earlier results of Gastuche *et al.* (1967). In Figure 1, the intensities of the strong 001 reflections of nickel hydroxide at $d = 4.61\text{A}$ and of bayerite at $d = 4.71\text{A}$ are shown relative to their maximum intensities when $R(\text{sol})$ is zero or approaches 100% respectively. At the highest values of $R(\text{sol})$, some nordstrandite also was observed. In the stippled range of Figure 1, only double-hydroxide reflections were recorded, but (as discussed later) the situation is more complex than can be attributed simply to the variation of the Ni:Al ratio. Outside the stippled area, the double-cation

hydroxide reflections became weaker as those of the single-cation hydroxides became stronger, but the results did not conform to clearly defined curves and the reasons for this behavior remained obscure.

In the composition range where only double hydroxides are obtained, it is of interest to compare $R(\text{cryst})$ and $R(\text{sol})$ values, since these are not necessarily the same. Figure 2 shows the results together with corresponding data of Gastuche *et al.* (1967; their data for products B and G in Table 4 of their paper). The dashed line corresponds to $R(\text{cryst}) = R(\text{sol})$. Our data indicate that $R(\text{cryst}) < R(\text{sol})$ for both systems studied, which means that there is less preference for Al ions in the crystalline products than in the coexisting solutions. The data points of Gastuche *et al.* indicate $R(\text{cryst}) > R(\text{sol})$. We have no explanation for the difference between our results and theirs beyond the possibility that they arise from the particular experimental conditions. Gastuche *et al.* used chloride solutions and long periods of washing by dialysis, thereby ensuring a predominance of interlayer carbonate anions; we used shorter washing periods and perchlorate solutions with only partial replacement of perchlorate by carbonate anions, as discussed later.

The composition range of Mg,Al hydroxides after carbonation (see later) extends from $R(\text{cryst})$ 23%–35% in our experiments and 21.5%–35% in those of Gastuche *et al.* For the Ni,Al system, the range is 17%–28%. We do not claim high accuracy for these limiting compositions because of the uncertainty in determining exactly where the X-ray intensities I_i (see Fig. 1) fall to zero.

Mg,Al hydroxy phases with ClO_4 and CO_3 anions

Relevant parts of the X-ray diffraction and infrared patterns of representative samples are shown in Figure 3. The products are specified by values of $R(\text{cryst}) \times 100$. As stated earlier, $R(\text{cryst})$ is identical with x , the layer charge per $[\text{R}_{1-x}\text{R}_x^{3+}(\text{OH})_2]$.

The products change progressively from mainly perchlorate to mainly carbonate forms in passing from $R(\text{cryst})$ 23% to 37%. The infrared peaks near 1100 and 1355 cm^{-1} are attributable to the ν_3 frequencies of the ClO_4 and CO_3 ions respectively. The absorption band near 1625 cm^{-1} arises from water molecules, and for the most part diminishes as the ClO_4 absorption diminishes.

The X-ray patterns in Figure 3 were obtained with oriented samples. With $R = 23, 27, 30\%$, we see two sets of basal reflections. One set from a basal spacing

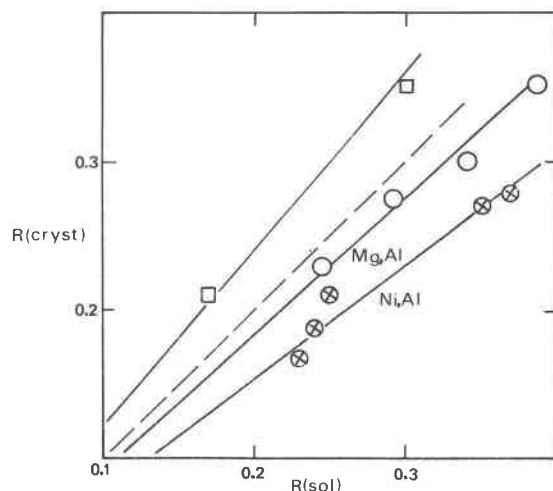


Fig. 2. $R(\text{cryst})$ vs. $R(\text{sol})$. $R = \text{Al}/(\text{Al} + \text{M})$ and $\text{M} = \text{Mg}$ or Ni . Squares indicate data of Gastuche *et al.* (1967) for Mg,Al system. Dashed line corresponds to $R(\text{cryst}) = R(\text{sol})$. All data are for carbonate-saturated systems. Straight lines are drawn to pass through the origin of coordinates.

of about 9.2Å diminishes in intensity with little change of spacing as the 1100 cm^{-1} absorption diminishes, and therefore is associated with a hydroxy-perchlorate form. The other set, with a spacing near 7.8Å, increases in intensity with little change of spacing as the 1355 cm^{-1} absorption increases, and therefore is associated with a hydroxy-carbonate form. The results indicate that two phases are present with dominantly perchlorate forms when R has smaller values and dominantly carbonate forms when R has larger values. The fact that we have two sets of basal reflections is an indication of a segregation of the two kinds of anions, but at present we cannot say if there is a variation of R , *i.e.*, of layer charge, from crystal to crystal within a given sample. However, results discussed in the next section for carbonated forms do not support such a variation of R but indicate uniformly charged particles within a given preparation.

When $R = 37\%$, an additional phase is seen in the X-ray pattern. A third sequence of basal reflections, stippled in Figure 3, corresponds to a superlattice with a spacing of about $16.8\text{Å} = 9.2 + 7.6\text{Å}$, which appears to be due to a regular alternation of perchlorate and carbonate layers. The three diffraction peaks marked in Figure 3 have spacings near 8.5, 5.5, and 4.2Å, corresponding to 002, 003, and 004 diffractions from a total spacing of 16.8Å; the 001 diffraction has not been observed. Turning again to the infrared patterns, we see that the absorptions associated with the perchlorate and carbonate anions and the water

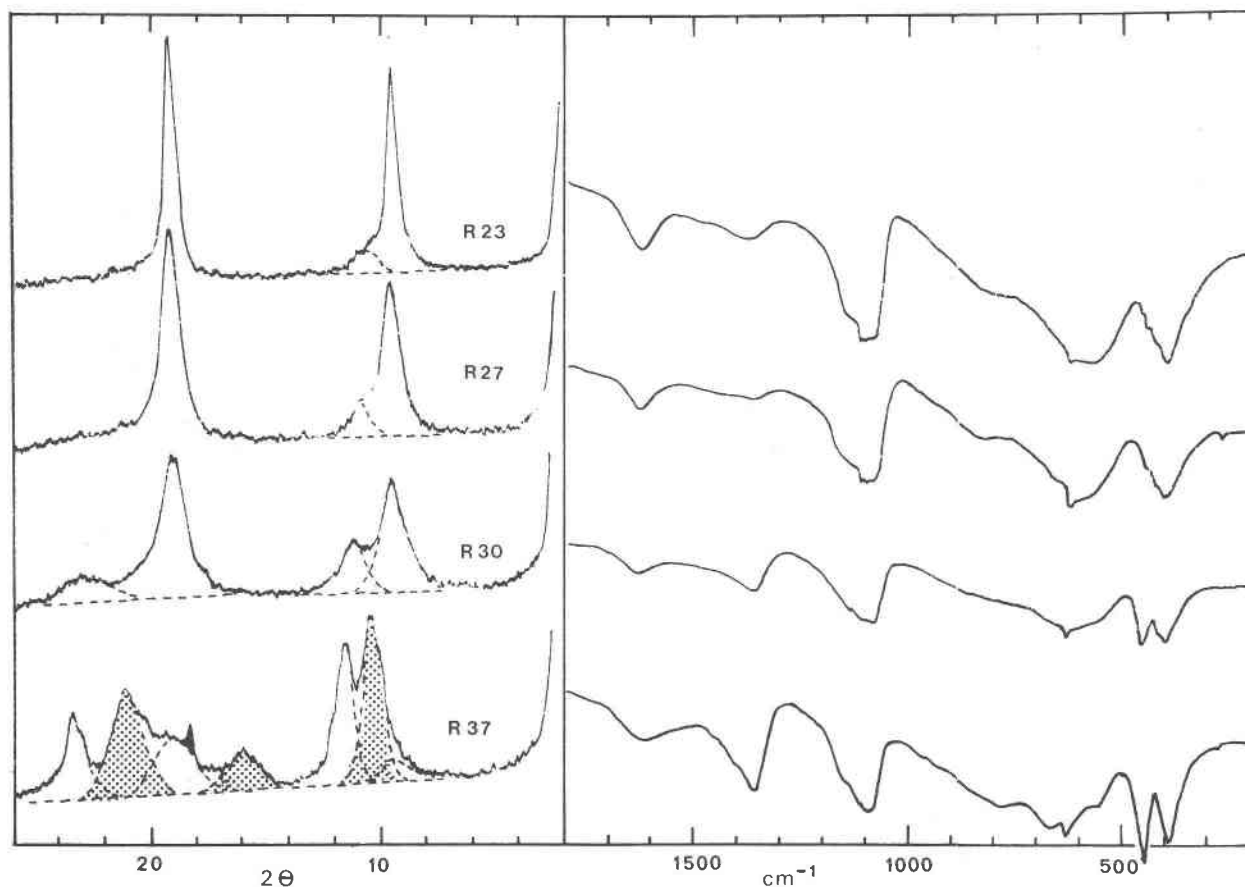


Fig. 3. X-ray diffraction ($\text{CuK}\alpha$ radiation) and infrared absorption patterns for Mg,Al products prepared from perchlorate solutions. R values relate to crystalline products. $R = [\text{Al}/(\text{Al} + \text{Mg})] \times 100$. Stippled X-ray diffraction peaks from an interstratified phase. A peak shaded black is due to a trace of bayerite.

molecules change in an orderly way as R varies from 23, to 27, to 30%, but the data for $R = 37\%$ do not fit well into the sequence; the probable explanation is the appearance of the additional phase when $R = 37\%$. We note also a trace of bayerite in the $R = 37\%$ product, which is indicated by a small peak marked black in Figure 3. Evidently $R(\text{cryst})$ for the limiting composition must be somewhat less than 37%.

Mg,Al hydroxy-carbonates

Treatment of the initial products with 0.1 M sodium carbonate solution readily exchanged CO_3 ions for ClO_4 ions, as shown by the X-ray diffraction and infrared patterns in Figure 4. The diffraction peaks are now sharp and symmetrical, and for any given value of R only one set of basal reflections is observed. The basal spacing becomes smaller as R, *i.e.*, layer charge, increases. These results indicate homogeneously charged layers. The infrared adsorption

near 1350 cm^{-1} also increases progressively with the value of R, as would be expected. The values of R in Figure 4 differ slightly from those in Figure 3 because the products after sodium carbonate treatment were re-analyzed; the small changes are believed to be experimental and to have no basic significance. It may be pointed out that the sample which previously showed superlattice reflections shows no abnormalities after carbonation.

Mg,Al hydroxy-perchlorates

To avoid reproduction of numerous X-ray diffraction and infrared patterns, it will suffice to describe the results obtained. Most of the carbonate anions were removed with a 5-hr treatment with 1/100 perchloric acid solution. At the higher values of $R(\text{cryst}) \approx 30\%$, the product initially had a basal spacing of 11.7–11.8 Å, probably due to water molecules associated with perchlorate ions between the hydrox-

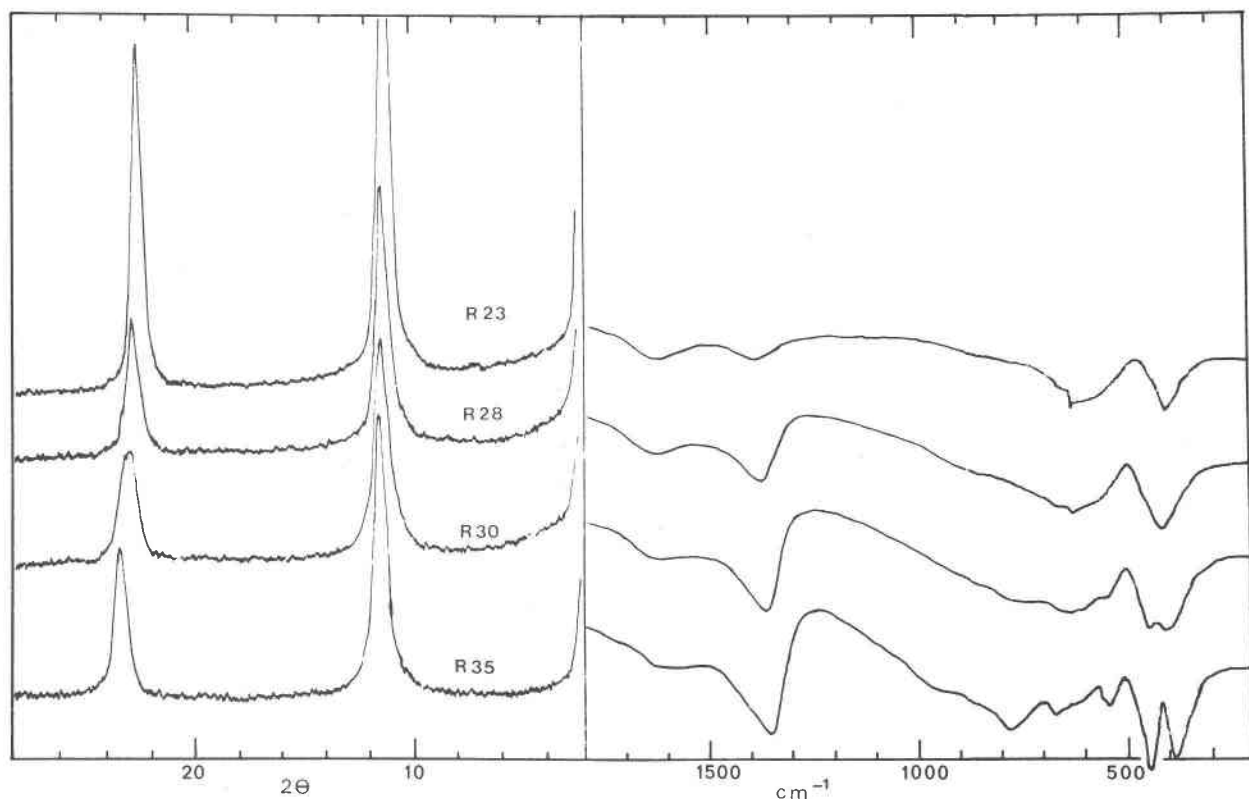


Fig. 4. X-ray diffraction ($\text{CuK}\alpha$ radiation) and infrared absorption patterns for Mg,Al hydroxy-carbonate phases.

ide layers. At relative humidities less than about 50% the spacing diminished to about 9.2Å, in agreement with the data in Figure 3. Bish (1978b) reported similar observations with SO_4 -exchanged products.

Products with values of $R(\text{cryst}) \approx 25\%$ gave poor X-ray patterns after treatment with 1/100 perchloric acid solution. Only one broad basal reflection with a spacing near 9Å was obtained. It appears that treatment with perchloric acid solution not only exchanged CO_3 anions with ClO_4 ions, but also, because of the acidic environment, caused some general destruction of the crystalline product.

Ni,Al hydroxy phases

The results were generally very similar to those for the Mg,Al system, but the diffraction patterns usually were less clearly defined. The initial products contained both perchlorate and carbonate ions; the perchlorate content decreased and the carbonate content increased as $R(\text{cryst})$ increased. The range of $R(\text{cryst})$ values in which only Ni,Al hydroxy products were formed, about 17–28%, was somewhat different from that for the Mg,Al system, about 23–35%. After sodium carbonate treatment, the products con-

tained only CO_3 anions and the X-ray patterns showed sharper and more symmetrical peaks.

Lattice parameters a and c' of Mg,Al and Ni,Al hydroxy-carbonate phases

Values of c' obtained from the first and second basal reflections give the combined thickness of the hydroxide layers and the interlayer anions and water molecules. The hexagonal a parameter is obtained from a prominent reflection with $d \approx 1.50\text{Å}$, which can be indexed as 110 (see previous discussion under "Product examination").

The results for the Mg,Al and Ni,Al hydroxy-carbonates are shown in Figure 5. Also shown are results for two Mg,Al products prepared by Gastuche *et al.* (1967), results for a natural hydrotalcite from Snarum, Norway, analyzed for Mg and Al in the present studies, and data for takovite, a mainly Ni,Al hydroxy-carbonate studied by Bish and Brindley (1977). For the most part the data for the natural minerals agree well with the values for the prepared products.

The decrease of the layer spacing, c' , with increase of the ratio R can be attributed to the increase in

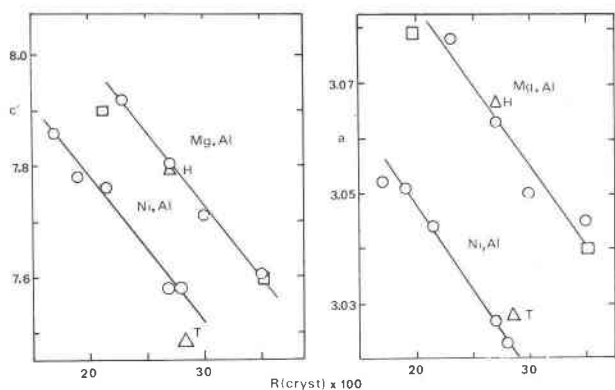


Fig. 5. Lattice parameters, c' and a , for Mg,Al and Ni,Al hydroxy-carbonate phases. Circles show present experimental data. Squares show data of Gastuche *et al.* (1967) for the Mg,Al system. Triangles marked H, data for hydrotalcite; triangles marked T, data for takovite.

electrostatic attraction between the positive hydroxide layers and negative interlayers. The separation of the Ni,Al and Mg,Al lines is about the same as that between the c parameters of $\text{Mg}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$. When the straight line relations are extrapolated to $R = 0$, the resulting values of c' are 8.52 and 8.37Å and the difference is 0.15Å. The c parameters of $\text{Mg}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$, taken from the X-Ray Powder Diffraction File, are 4.769 and 4.605Å and the difference is 0.164Å. In other words, when the electrostatic attraction is reduced to zero, the difference in the c' parameters is essentially the same as that between the c parameters of the single hydroxides.

The a parameters also decrease as R increases, mainly because of the substitution of the smaller Al^{3+} ion for the larger Mg^{2+} and Ni^{2+} ions. The change of

a with R , $\Delta a/\Delta R$, can be considered as follows: for an ideal octahedral layer the a parameter equals $\sqrt{2}$ ($M-O$), where $M-O$ is the metal ion-oxygen ion distance. The mean metal ion radius, \bar{r} , is given by:

$$\bar{r} = (1 - x)r(M) + xr(\text{Al}) = r(M) - x[r(M) - r(\text{Al})]$$

where $M = \text{Mg}$ or Ni . The negative slope of a with R , or with x , is given by:

$$\Delta a/\Delta x = -\sqrt{2}[r(M) - r(\text{Al})]$$

With the Shannon-Prewitt (1969) ionic radii, Mg^{2+} 0.720Å, Ni^{2+} 0.700Å and $\text{Al}^{3+}(\text{VI})$ 0.530Å, the calculated values of $\Delta a/\Delta x$ are 0.269 and 0.240 for the Mg,Al, and Ni,Al systems respectively. The experimental values from the data in Figure 5 are respectively 0.300 and 0.310. The agreement is as good as we can expect from the simple calculation and the accuracy of the experimental a parameters.

The a vs. R relations, extrapolated to $R = 0$, *i.e.*, zero Al substitution, give extrapolated a values of 3.144 and 3.110 for the Mg,Al and Ni,Al systems respectively. The former agrees very well with the a parameter of $\text{Mg}(\text{OH})_2$, 3.147Å; the latter agrees less well with the value 3.126Å for $\text{Ni}(\text{OH})_2$. Small changes in the slope of the observed lines, however, have large effects on the extrapolated values.

The range of R^{2+} , R^{3+} cation proportions in mixed hydroxide structures

We have seen that the highest proportion of R^{3+} ions is near 33% or a ratio $R^{2+}:R^{3+} = 2:1$. The lowest proportion is known with less certainty, but is probably near 20% or a ratio of about 4:1 or 5:1. These results can be considered in relation to possible distributions of Al^{3+} ions replacing Mg^{2+} ions in a brucite-type hydroxide layer. Figure 6a shows the distribution of Mg ions, and the positions labelled 1, 2, 3... are at progressively larger distances from the zero position.

Substitution of an Al^{3+} ion for a Mg^{2+} ion creates a resultant charge of +1. Therefore Al substitutions are likely to be as far apart as possible because of mutual repulsions; substitutions in adjacent sites will be the least likely to occur unless accompanied by vacant cation sites, *i.e.*, a gibbsite 'unit' within a brucite layer. If the first substitution occurs at the zero position in Figure 6a, then the next substitution is likely to be no nearer than position 2. If this arrangement is continued, the distribution of Figure 6b is obtained. Each Al position is now surrounded by six Mg positions and the ratio Mg:Al in the unit cell outlined is

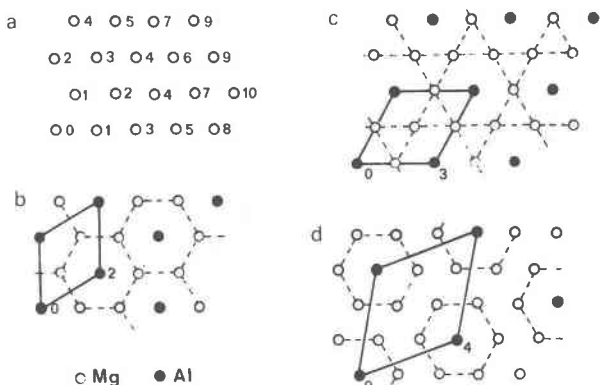


Fig. 6. Possible distributions of Mg^{2+} ions, open circles, and Al^{3+} ions, solid circles, in octahedral layer structure. (a) Arrangement in brucite; (b) Mg:Al = 2:1; (c) Mg:Al = 3:1; (d) Mg:Al = 6:1.

2:1. The hexagonal a parameter is $\sqrt{3} a'$, where a' refers to the sub-cell which makes no differentiation between the cations. This distribution corresponds to the maximum observed substitution of Mg by Al. Evidence for such a supercell with $a = \sqrt{3} a'$ has been obtained (Taylor, 1969; Bish, 1977) and recognized as corresponding to a 2:1 ratio of $R^{2+}:R^{3+}$.

Although each Al ion in the arrangement of Figure 6b is ringed by six Mg ions, the Al ions are not fully screened from each other. The next-nearest distribution of Al ions is developed from positions zero and 3, as shown in Figure 6c. The Mg:Al ratio is 3:1, the supercell parameter $a = 2a'$, and a Mg ion is now located between every pair of Al ions. This ratio corresponds to that found in many natural minerals and therefore is perhaps a more stable arrangement than that of Figure 6b.

The next-nearest distribution of Al ions, shown in Figure 6d, starts from positions zero and 4. The Mg:Al ratio is now 6:1, corresponding to a value of $R = 14.3\%$, which is less than the minimum found experimentally. With this low concentration of Al^{3+} ions there are six Mg^{2+} ions within the unit cell outlined in Figure 6d, and such groups may well act as nuclei for the development of brucite. In fact, there are bands of Mg^{2+} ions at 120° to each other running continuously through the structure.

From these considerations we conclude that the maximum substitution of Al^{3+} ions in a Mg^{2+} hydroxide layer corresponds to a Mg:Al ratio 2:1 or $R = 33\%$; any larger substitution places Al ions in adjacent octahedral groups and may thereby lead to nucleation of an $Al(OH)_3$ phase. The lowest substitution, corresponding to $R \approx 17\text{--}20\%$ or a Mg:Al ratio 4:1–5:1, occurs when groups of Mg^{2+} -occupied octahedra come together in sufficient numbers to develop nuclei of normal $Mg(OH)_2$. Within this range of composition, the preferred ratio of $R^{2+}:R^{3+}$ appears to be 3:1 or $R = 25\%$, as shown by its frequent occurrence in minerals such as hydrotalcite, pyroaurite, and sjögrenite.

In the preceding discussion, only short-range order has been considered. Evidently long-range disorder could occur such that supercell reflections would be difficult to observe or not observable. In a study of cation segregation and cation ordering in sjögrenite and pyroaurite, $Mg_{1-x}Fe_x(OH)_2(CO_3)_{x/2} \cdot yH_2O$ with x mainly ≈ 0.33 , Taylor (1969) cited evidence for superlattice with $a = \sqrt{3} a'$ and $\sqrt{13} a'$. The latter corresponds to a cell developed with Fe^{3+} in positions zero and 7 in Figure 6a, with a ratio $R^{2+}:R^{3+}$ of 12:1 or R

$= 7.7\%$. This low concentration of trivalent cations is considerably smaller than the minimum value found by Gastuche *et al.* (1967) and in the present study for Mg,Al mixed hydroxides, and it is difficult to see what ordering mechanism could lead to a $\sqrt{13} a'$ supercell.

Conclusions

Crystalline materials of the form $M_{1-x}Al_x(OH)_2R^{-n} \cdot yH_2O$ with $M = Mg, Ni$, and $R^{-n} = CO_3^{2-}$ and/or ClO_4^- have been prepared, with x ranging from a maximum value near 0.33 to a less well-defined minimum value near 0.20. Preparations using mixed Mg,Al perchlorate solutions yield mixed perchlorate, carbonate products, because atmospheric CO_2 in solution enters into the reactions. With higher values of x , the carbonate anion is predominant, and with lower values of x , the perchlorate ion. A regularly interstratified hydroxy-carbonate, perchlorate also has been prepared. Single-anion products are prepared by anion exchange reactions. The layer spacing c' and the hexagonal a parameter diminish with increasing value of x , the former because of increasing electrostatic attractions, the latter because of the smaller size of the Al^{3+} ions. Reasons are suggested for the observed upper and lower limits of x .

Acknowledgments

We are indebted to the National Science Foundation for grant EAR 74-02821 which has supported this research. We thank Dr. David L. Bish for useful discussion and also acknowledge some initial experiments on mixed cation hydroxides by Ms. Christie Bell.

References

- Allmann, R. (1970) Doppelschichtstrukturen mit brucitähnlichen Schichtionen $[Me(II)_{1-x}Me(III)_x(OH)_2]^{x+}$. *Chimia*, 24, 99–108.
- and H. P. Jepsen (1969) Die Struktur des Hydrotalkits. *Neues Jahrb. Mineral. Monatsh.*, 544–551.
- and H. H. Lohse (1966) Die Kristallstruktur des Sjögrenits und eines Umwandlungsproduktes des Koenenits (= Chlor-Mannasseits). *Neues Jahrb. Mineral. Monatsh.*, 161–181.
- Bish, D. L. (1977) *The Occurrence and Crystal Chemistry of Nickel in Silicate and Hydroxide Minerals*. Ph.D. Thesis, The Pennsylvania State University, University Park, Pennsylvania.
- (1978a) Deviations from the ideal disordered structure in minerals of the pyroaurite group (abstr.) *Sixth Int. Clay Conf., Oxford, England, Abstracts*, 612.
- (1978b) Anion exchange in takovite; applications to other hydroxide minerals (abstr.) *Colloque sur la Minéralogie, Géochimie, et Géologie des Minéraux Nickelifères Latéritiques, Orléans, France, Abstracts*, 35,36.

- and G. W. Brindley (1977) A reinvestigation of takovite, a nickel aluminum hydroxy-carbonate of the pyroaurite group. *Am. Mineral.*, 62, 458–464.
- Brown, G. and M. C. Gastuche (1967) Mixed magnesium–aluminum hydroxides. II. Structural chemistry of synthetic hydroxy-carbonates and related minerals and compounds. *Clay Minerals*, 7, 193–201.
- Feitknecht, W. (1942) Über die Bildung von Doppelhydroxyden zwischen zwei- und dreiwertigen Metallen. *Helv. Chim. Acta*, 25, 555–569.
- Frondel, C. (1941) Constitution and polymorphism of the pyroaurite and sjögrenite groups. *Am. Mineral.*, 26, 295–315.
- Gastuche, M. C., G. Brown and M. M. Mortland (1967) Mixed magnesium–aluminum hydroxides. I. Preparation and characterization of compounds formed in dialysed systems. *Clay Minerals*, 7, 177–192.
- Ingram, L. and H. F. W. Taylor (1967) The crystal structures of sjögrenite and pyroaurite. *Mineral. Mag.*, 36, 465–479.
- Miyata, S. (1975) Synthesis of hydrotalcite-like compounds and their structures and physico-chemical properties—I: The systems $Mg^{2+}-Al^{3+}-NO_3^-$, $Mg^{2+}-Al^{3+}-Cl^-$, $Mg^{2+}-Al^{3+}-ClO_4^-$, $Ni^{2+}-Al^{3+}-Cl^-$, and $Zn^{2+}-Al^{3+}-Cl^-$. *Clays and Clay Minerals*, 23, 369–375.
- and A. Okada (1977) Synthesis of hydrotalcite-like compounds and their physico-chemical properties—the systems $Mg^{2+}-Al^{3+}-SO_4^{2-}$ and $Mg^{2+}-Al^{3+}-CrO_4^{2-}$. *Clays and Clay Minerals*, 25, 14–18.
- Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, B25, 925–946.
- Taylor, H. F. W. (1969) Segregation and cation-ordering in sjögrenite and pyroaurite. *Mineral. Mag.*, 37, 338–342.
- (1973) Crystal structures of some double hydroxide minerals. *Mineral. Mag.*, 39, 377–389.

*Manuscript received, November 2, 1978;
accepted for publication, March 9, 1979.*