THERMAL BEHAVIOR OF HYDROTALCITE AND OF ANION-EXCHANGED FORMS OF HYDROTALCITE

G. W. Brindley and S. Kikkawa[1]

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

Abstract—Chloride-, sulfate-, and perchlorate-exchanged forms of hydrotalcite have been prepared and their layer spacings determined after equilibration in hydrous atmospheres and after heat-treatments up to the temperature of decomposition in the range 300–400°C. The initial carbonate form of hydrotalcite and also brucite, for purposes of comparison, have been similarly studied. Only chloride-hydrotalcite and brucite exhibit a single phase stable to the decomposition temperature. The other anionic forms exhibit various phases with different layer spacings which are interpreted in terms of the size, orientation, and stability of the anions and, in some cases, the presence of additional water. A regularly interstratified form of sulfate-hydrotalcite (layer spacing = 19.80 Å) is obtained at room temperature and relative humidity <50%; at higher humidities, a fully hydrated phase is obtained, and at 50°C a collapsed form is obtained. In the preparation of perchlorate-hydrotalcite, an interstratified phase (layer spacing = 17.0 Å) was recognized with alternating carbonate and perchlorate layers, although the evidence is less certain.

Key Words—Anion exchange, Brucite, Hydrotalcite, Interstratification, Perchlorate, Thermal reaction.

INTRODUCTION

An extensive literature exists on natural and synthetic materials having compositions of the form $[R^{2+}_{1-x}R^{3+}_x(OH)_2]^{+x}R^{-n}_{x/n} \cdot yH_2O$, where R^{2+} = Mg, Fe, Ni, . . . , R^{3+} = Al, Fe^{3+}, . . . , R^{-n} = OH^-, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-} . . . and x lies mainly in the range 0.20–0.33. Among natural minerals, hydrotalcite is typical with the approximate formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ which corresponds with x = 0.25 in the general formula. Anion exchange reactions are possible as Bish (1977, 1978) especially has emphasized.

The structures of these materials consist of positively charged, brucite-like hydroxide layers, with negatively charged interlayers. The layer spacings depend on the nature of the interlayer anions and the state of hydration, and to a lesser extent on the magnitude of the electrostatic attraction between layers and interlayers. The variation of layer spacing with layer charge has been studied previously (Brindley and Kikkawa, 1979), and in the present paper the variation with different anions in relation to temperature and relative humidity is examined. Anion-exchanged forms of the natural mineral hydrotalcite provide better X-ray powder diffraction patterns than wholly synthesized materials.

EXPERIMENTAL

An essentially pure sample of hydrotalcite from Snarum, Norway, was ground to pass a 120 mesh sieve. The powdered material was treated for periods of several hours to several days at room temperature with 1:100 HCl, 1:1000 $HClO_4$, 1:100 and 1:1000 H_2SO_4 to prepare chloride-, perchlorate-, and sulfate-exchanged forms. After washing, samples in the form of thin layers on glass slides were prepared for X-ray diffraction examination. A high degree of basal plane orientation ensured that basal reflections were obtained prominently and other reflections were largely absent. Under these conditions, mixtures of phases, including any unreacted hydrotalcite, were easily recognized. Samples were examined after exposure for several days to various relative humidities, controlled by saturated salt solutions, and after heating in air at temperatures of 55°, 110°C, and higher temperatures, mainly at intervals of about 25°C, until decomposition occurred usually in the range 300–375°C. Samples were examined in a closed chamber on the diffractometer, and heated samples were cooled to room temperature prior to X-ray diffraction examination. The original hydrotalcite and also a sample of brucite were examined in the same manner. Diffraction patterns were recorded at 1° 2θ/min with filtered CuKα radiation and with a chart speed to give 2° 2θ/inch in the recording.

RESULTS

The layer spacings of the observed phases are plotted against relative humidity and temperature of heat-treatment in Figures 1–3. The layer spacings are obtained directly from the recorded basal reflections; true basal spacings are multiples of the layer spacings and depend on the layer stacking arrangement. The present study considers only the layer spacings and their dependence on the humidity and temperature conditions.

---

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

87
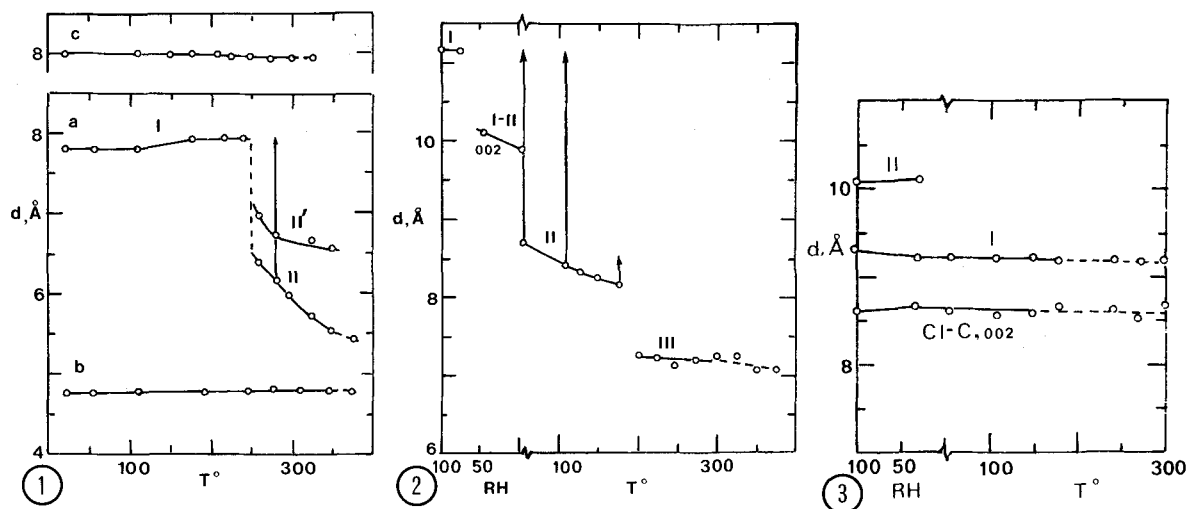
Figures 1–3.   (1) Layer spacing, d, in Å vs. temperature T, °C, for (a) hydrotalcite, (b) brucite, (c) chloride-hydrotalcite. Arrow indicates change of spacing of phases II and II′ when material is rehydrated. (2) Layer spacing, d, in Å vs. relative humidity RH and temperature T, °C, for sulfate-hydrotalcite. Vertical arrows indicate changes of spacing by rehydration. For the inter-stratified phase marked I–II, the spacing d(002) is plotted. Although a break is shown in the horizontal scale, 50°C is essentially coincident with 0% RH. (3) Layer spacing, d, in Å vs. relative humidity RH and temperature T, °C, for perchlorate-hydrotalcite. For the interstratified perchlorate-carbonate phase marked Cl–C, the spacing d(002) is plotted. Although a break is shown in the horizontal scale, 50°C is essentially coincident with 0% RH.

Hydrotalcite

The layer-spacing data are shown in Figure 1. No hydration effects were observed. The spacing of the original material, called phase I, increased slightly from 7.80 to 7.90 Å after heating to 150°C and persisted to 240°C; the reflections remained sharp with no obvious changes of intensity. An abrupt change occurred at 260°C when the spacing decreased abruptly to 6.4 Å forming phase II, which gave similarly sharp and strong basal reflections. There was also evidence for a less well-crystallized phase II′ giving a broad, weak reflection with a spacing near 7 Å. With continued heating the spacings of phases II and II′ diminished to 5.45 and 6.5 Å, respectively, at 375°C. Rehydration experiments showed that phases II and II′ re-expanded readily to about 7.9 Å when heated to 280°C, but did not rehydrate after being heated to higher temperatures.

Brucite and chloride-hydrotalcite

The layer-spacing data are presented in Figure 1. No changes were observed in hydrous atmospheres. The spacings remained essentially constant at 4.75 Å for brucite and 8.00 Å for chloride-hydrotalcite until decomposition occurred at about 350°C and 300°C, respectively.

Sulfate-hydrotalcite

The results are shown in Figure 2 where four phases, I, I–II, II, and III, are recognized. Phase I, with basal spacing 11.15 Å, gave sharp basal reflections and was obtained only at room temperature and with relative

humidities greater than about 50%. Phase II was formed at 50°C with a spacing of 8.65 Å which diminished progressively to 8.15 Å at 175°C. An abrupt contraction to a spacing near 7.2 Å occurred at 200°C, and the product, phase III, persisted to 325°C with little change of spacing but the reflections became increasingly weaker. Phase III was decomposed at 400°C.

The phase labelled I–II was obtained at room temperature with relative humidities less than 50%. It is a regularly interstratified phase with an alternating sequence of layers corresponding to phases I and II. The overall spacing is the sum of the component spacings, 11.15 + 8.65 = 19.80 Å. For convenience the second order spacing near 10 Å is plotted in Figure 2. Basal 00ℓ reflections with ℓ = 2, 3, 4, and 5 were obtained with moderately sharp peaks indicating a considerable degree of order in the alternating layer sequence. No first order reflection was obtained.

Phase II formed at 50°C and at 110°C it easily rehydrated to phase I in humid atmospheres, RH > 50%, but when heated to higher temperatures, rehydration did not expand the spacing beyond about 8.5 Å.

Perchlorate-hydrotalcite

Two product phases I and II are shown in Figure 3, together with a third phase marked Cl–C, 002. Phase I with a layer spacing of 9.2 Å was the major phase and gave strong, sharp basal reflections up to 200°C which became progressively weaker at higher temperatures and disappeared at 300°C. Phase II, with a spacing of about 10.1 Å, was a very minor phase and was obtained

only at room temperature and in humid atmospheres. It may be similar to the interstratified sulfate phase with d(002) ≃ 10 Å, but the experimental data were insufficient to establish this result with certainty.

The third phase, Cl–C, was observed during the preparation of the perchlorate-hydrotalcite, and it decreased in amount as the period of treatment increased. A similar phase was produced in synthesis experiments using mixed solutions of magnesium and aluminum perchlorates when CO_2 was not excluded from the solutions (Brindley and Kikkawa, 1979). This phase appears to be a regular interstratification of perchlorate and carbonate layers with a combined spacing of 9.2 + 7.8 = 17.0 Å. In Figure 3, d(002) is plotted for this phase, which remained stable to about 175°C.

DISCUSSION

Hydrotalcite

The spacing changes of normal hydrotalcite (see Figure 1) are similar to those observed by Rouxhet and Taylor (1969) for the analogous minerals pyroaurite and sjögrenite. They established that interlayer molecular water was lost between room temperature and about 200–250°C with little change in layer spacing, and that the progressive decrease of spacing above this temperature was due to the combined decomposition of the CO_3 anions and the hydroxide layers.

In the case of hydrotalcite, the X-ray diffraction pattern shows little or no change up to 240°C, but at 260°C there is an abrupt decrease of spacing, more abrupt than Rouxhet and Taylor recorded, which is followed by a continued decrease until complete decomposition occurs around 370°C.

Following the abrupt decrease of spacing to 6.4 Å at 260°C, and a further decrease to 6.2 Å at 280°C, the mineral can be rehydrated to give the initial spacing. It seems likely that the initial collapse is due to decomposition of the CO_3 groups, $CO_3^{2-} \rightarrow CO_2 + O^{2-}$; the oxygen anions remain between the hydroxide layers and are more closely packed than the bulky CO_3 groups. At this stage the layers are sufficiently separated to permit penetration of water molecules and re-expansion to the original spacing. The continued decrease to about 5.5 Å at higher temperatures must be attributed to decomposition of the hydroxide layers and accommodation of the O^{2-} anions more or less within these layers. The minimum spacing of 5.5 Å approaches that of brucite; Rouxhet and Taylor (1969) found a minimum spacing of 5.1 Å, even nearer to that of brucite, 4.75 Å.

Chloride-hydrotalcite

Figure 1 shows that the thermal stability of chloride-hydrotalcite is very similar to that of brucite. Evidently the Al for Mg replacements in the hydroxide layers have little effect on the thermal stability. The spacing of the chloride form, about 8.0 Å, is only slightly greater than that of hydrotalcite, 7.6 Å, which suggests that single chloride anions can be more efficiently packed between hydroxide layers than the bulky CO_3 anions.

XO_4-substituted forms of hydrotalcite

The spacings of these forms of hydrotalcite depend on the number, size, and orientation of the XO_4 anions involved.

The sizes of ClO_4^- and SO_4^{2-} anions are very similar. Louisnathan et al. (1972, 1977) compiled dimensional data for tetrahedral XO_4 groups, and their results show that Cl–O distances lie mainly in the range 1.40–1.46 Å and S–O distances lie in the range 1.43–1.49 Å. In the present context, it is unnecessary to make any differentiation between these size ranges and it will suffice to take a value for X–O = 1.45 ± 0.05 Å to cover both anions.

Orientation of the XO_4 groups with respect to the planes of hydroxyl ions is probably more important than their precise dimensions in determining the spacing of XO_4-substituted hydrotalcites. Two cases can be considered, (1) with three oxygens adjacent to one hydroxyl plane and the fourth pointing to the opposite hydroxyl plane, and (2) with two oxygens pointing to each of the adjacent hydroxyl planes. These arrangements correspond to (1) the maximum and (2) the minimum thickness of the interlayer anions with respect to the separation of successive brucite-like layers. For regular tetrahedral groups with X–O = 1.45 Å, the separation of the anion oxygen planes with arrangement (1) is (4/3)(X–O) = 1.93(5) Å, and with arrangement (2) is (2/√3) (X–O) = 1.67(5) Å. It is evident that the separation of the hydroxide layers depends much more on the orientation of the tetrahedral anionic groups than on small differences in their dimensions.

The phases to be considered are those which are stable between 50° and 200°C, phase I of the perchlorate form with d = 9.20 Å and phase II of the sulfate form with d ≃ 8.4 Å at 110°C. The difference between these spacings, about 0.8 Å, is greater than can be attributed to different orientations of the anions, which cannot account for more than about 0.3 Å. If arrangement (1) for perchlorate anions and arrangement (2) for sulfate anions is assumed, a difference of about 0.5 Å remains which may be attributed to the packing of the anionic groups against the brucite-like layers. To account for the observed layer spacings, the separation of oxygen and hydroxyl planes must be about 2.6 Å for the perchlorate form and about 2.4 Å for the sulfate form. The spacing of the hydroxyl planes in the hydrotalcite structure is close to 2.00 Å (Allmann and Jepson, 1969). With these data the layer spacings are as follows:

Perchlorate form: 2.0 + 2.6 + 1.93 + 2.6 = 9.13 Å
Sulfate form: 2.0 + 2.4 + 1.67 + 2.4 = 8.47 Å

It is therefore concluded that the difference in the spacings of the perchlorate and sulfate forms can be

attributed about equally to a different orientation of the tetrahedral groups and a different packing of the anions against the brucite-like layers.

It is of interest now to consider if there are any supporting arguments or evidence in favor of orientation (1) for the perchlorate groups and orientation (2) for the sulfate groups. In fact, two lines of argument point in this direction.

In the first place the ClO_4^- anions are twice as numerous as the SO_4^{2-} anions. Arrangement (1) for the ClO_4^- anions favors the packing of this larger number of anions between the brucite-like layers. With fewer SO_4^{2-} anions involved, they can be arranged with their minimum dimension normal to the brucite-like layers and thereby bring the layers closer together, an arrangement which minimizes the potential energy of the system.

Secondly certain features of the Na^+ and Ca^{2+} forms of montmorillonite should be recalled. Mering and Glaeser (1954) and Pezerat and Mering (1967) showed that in the early stages of hydration, the monovalent ions tended to retain positions adjacent to the silicate layers and the divalent ions tended to occupy central positions where they can satisfy layer charges in opposite layers. Analogously, arrangement (1) for ClO_4 ions brings the centers of the anionic groups nearer to the hydroxide layers than arrangement (2), while arrangement (2) places the centers of the SO_4^{2-} ions in a central position between successive hydroxide layers.

Hydrated phases and interstratified phases

Phase I of sulfate-hydrotalcite (Figure 2) has a spacing of 11.15 Å which is 2.8 Å greater than the spacing 8.4 Å of phase II at 110°C. The expanded phase is obtained only under humid conditions and the wider spacing is sufficient to accommodate additional water molecules. Bish (1978) recorded a similar spacing and noted the similarity to spacings recorded by Nickel and Clarke (1976) for a related mineral, carrboydite. The perchlorate form did not give a corresponding hydrated phase. Again, there is a partial similarity to the hydration behavior of smectites where divalent ion forms hydrate more readily in the initial stages of hydration than monovalent ion forms.

The formation of interstratified phases is particularly interesting. Sulfate-hydrotalcite gives reflections showing very clearly an alternating sequence of hydrated layers (11.15 Å) and non-hydrated layers (8.65 Å) with a combined layer spacing of 11.15 + 8.65 = 19.8 Å. A corresponding phase may be formed by perchlorate-hydrotalcite but the evidence is less clear because a fully hydrated phase is not obtained. A similar interstratified phase is formed by the mineral motukoreaite which has a fully hydrated phase (d = 11.1 Å), a dehydrated phase (d = 8.7 Å), and an interstratified phase with d ≃ 11.1 + 8.7 Å (Brindley, 1979). This mineral has a mainly Mg, Al hydroxide layer structure,

with interlayer sulfate and carbonate anions and water molecules, and has been described by Rodgers· *et al.* (1977).

These results are interesting because of their similarity to phases observed with layer silicates. Thus, for example, Walker (1956) recognized in the last stages of dehydration of vermiculite a regular interstratifed phase of 11.59 Å hydrated layers and 9.02 Å dehydrated layers with an overall spacing of 11.59 + 9.02 = 20.6 Å. Other examples could be cited. The mechanism controlling these long-range ordering processes still remains obscure; a possible mechanism involving interactions of OH dipoles has been suggested (Bassett, 1960; Norrish, 1972), and this could be operative in structures of the type considered here.

REFERENCES

Allmann, R. and Jepson, H. P. (1969) Die Struktur des Hydrotalkits: *Neues Jahrb. Mineral. Monatsh.* 544–551.

Bassett, W. A. (1960) Role of hydroxyl orientation in mica alteration: *Bull. Geol. Soc. Amer.* **71**, 449–456.

Bish, D. L. (1977) Occurrence and Crystal Chemistry of Nickel in Silicate and Hydroxide Minerals: Ph.D. Thesis, Pennsylvania State University, University Park, Pennsylvania, 152 pp.

Bish, D. L. (1978) Anion exchange in takovite. Applications to other hydroxide minerals: *Bull. du B.R.G.M. (2nd Series)* Sect. 2, 293–301.

Brindley, G. W. (1979) Motukoreaite—Additional data and comparison with related minerals: *Mineral. Mag.* **43**, 337–340.

Brindley, G. W. and Kikkawa, S. (1979) A crystal-chemical study of Mg,Al and Ni,Al hydroxy-perchlorates and hydroxy-carbonates: *Amer. Mineral.* **64**, 836–843.

Louisnathan, S. J. and Gibbs, G. V. (1972) Bond length variation in TO_4^{n-} tetrahedral oxyanions of the third row elements: T = Al, Si, P, S, Cl: *Mater. Res. Bull.* **7**, 1281–1292.

Louisnathan, S. J., Hill, R. J., and Gibbs, G. V. (1977) Tetrahedral bond length variations in sulfates: *Phys. Chem. Mineral.* **1**, 53–69.

Mering, J. and Glaeser, R. (1954) Sur la rôle de la valence des cations échangeables dans la montmorillonite: *Bull. Soc. fr. Minéral. Cristallogr.* **77**, 519–530.

Nickel, E. H. and Clarke, R. M. (1976) Carrboydite, a hydrated sulfate of nickel and aluminum: a new mineral: *Amer. Mineral.* **61**, 366–372.

Norrish, K. (1972) Factors in the weathering of mica to vermiculite: In J. M. Serratosa, Ed., *Proc. Int. Clay Conf., Madrid,* Division de Ciencias, C.S.I.C., Madrid, 417–432.

Pezerat, H. and Mering, J. (1967) Recherches sur la position des cations échangeables et de l'eau dans les montmorillonites: *C. R. Acad. Sci., Paris, Ser. D,* **265**, 529–532.

Rodgers, K. A., Chisholm, J. E., Davis, R. J., and Nelson, C. S. (1977) Motukoreaite, a new hydrated carbonate, sulphate, and hydroxide of Mg and Al from Auckland, New Zealand: *Mineral. Mag.* **41**, 389–390, M21–M23.

Rouxhet, P. G. and Taylor, H. F. W. (1969) Thermal decomposition of sjögrenite and pyroaurite: *Chimia* **23**, 480–485.

Walker, G. F. (1956) Mechanism of dehydration of Mg-vermiculite: *Clays & Clay Minerals* **4**, 101–115.

(Received 9 August 1979, accepted 22 September 1979)

Резюме—Приготавливались хлоридные, сульфатные, и перхлоратные обменные формы гидроталькита, и после уравновешивания в водной атмосфере и тепловой обработки до температуры разложения в пределах 300–400°C определялись их межслойные промежутки. Аналогичным образом в целях сравнения изучалась начальная карбонатная форма гидроталькита, а также брусит. Только хлорид-гидроталькит и брусит выявили единственную фазу, устойчивую к температуре разложения. Другие анионные формы выявили различные фазы с разными межслойными промежутками, которые зависят от размера, направления, и устойчивости анионов и, в некоторых случаях, от присутствия добавочной воды. Регулярно переслаивающаяся форма сульфата-гидроталькита (межслойное расстояние = 19,80 Å) образуется при комнатной температуре и относительной влажности <50%; при более высоких влажностях, образуется полностью гидратированная фаза, а при 50°C образуется слипшаяся фаза. При приготовлении перхлората-гидроталькита, была обнаружена переслаивающаяся фаза (межслойное расстояние = 17,0 Å) счередующимися карбонатными и перхлоратными слоями, но доказательства этого обнаружения не вполне надежны. [N. R.]

Resümee—Es wurden mit Chlorid, Sulfat, und Perchlorat ausgetauschte Formen von Hydrotalkit hergestellt und ihre Schichtabstände bestimmt. Die Bestimmung dieser Werte erfolgte nach der Gleichgewichtseinstellung in einer wasserhaltigen Atmosphäre und nach dem Erhitzen bis zur Zersetzungstemperatur im Bereich von 300° bis 400°C. Die ursprüngliche Karbonatform des Hydrotalkits und auch der Brucit wurden zu Vergleichszwecken in gleicher Weise untersucht. Nur der Chlorit-Hydrotalkit und der Brucit ergeben eine einzige Phase, die bis zur Zerfallstemperatur stabil ist. Die übrigen anionischen Formen ergeben verschiedene Phasen mit unterschiedlichen Schichtabständen, die durch die Größe, die Orientierung und die Stabilität des Anions und in manchen Fällen durch zusätzliches Wasser erklärt werden können. Eine regelmäßige Wechsellagerungsform von Sulfat-Hydrotalkit (Schichtabstand 19,80 Å) erhielt man bei Raumtemperatur und einer relativen Feuchtigkeit von <50%; bei größerer Feuchtigkeit erhält man eine voll hydratisierte Phase und bei 50°C eine kollabierte Phase. Bei der Präparation von Perchlorat-Hydrotalkit wurde eine Wechsellagerungsform (Schichtabstand = 17,0 Å) mit abwechselnd Karbonat- und Perchloratschichten erkannt, obwohl der Nachweis weniger sicher ist. [U. W.]

Résumé—Des formes d'hydrotalcite échangées au chloride, au sulphate et au perchlorate ont été préparées, et l'espacement de leurs couches déterminé après équilibration dans des atmosphères hydrées et après des traitements d'échauffement jusqu'à la température de décomposition dans la gamme de 300–400°C. Les formes carbonées initiales d'hydrotalcite et aussi de brucite ont été étudiées de la même manière pour des raisons de comparaison. Seuls l'hydrotalcite-chloride et la brucite montrent une seule phase stable jusqu'à la température de décomposition. Les autres formes anioniques exhibent des phases variées avec des espacements intercouche différents qui sont interprétés d'après la taille, l'orientation, et la stabilité des anions, et dans certains cas, d'après la présence d'eau ajoutée. Une forme régulièrement interstratifiée d'hydrotalcite-sulphate (espacement inter-couche = 19,80 Å) est obtenue à température ambiante et humidité <50%; à de plus hautes humidités, une phase totalement hydratée est obtenue, et à 50°C, une forme effondrée est obtenue. Dans la préparation d'hydrotalcite-perchlorate, une phase interstratifiée (espacement inter-couche = 17,0 Å) a été reconnue avec des couches alternantes de carbonate et de perchlorate, quoique cette évidence est moins certaine. [D. J.]