MORPHOLOGY OF NORDSTRANDITE

P. VIOLANTE,[1] A. VIOLANTE,[1] AND J. M. TAIT[2]

Abstract—Nordstrandite was obtained synthetically by precipitation of $Al(OH)_3$ at pH 9.0 to 11.0 in citrate or malate systems with Al : carboxylic acid molar ratios of 10–100 in the absence and in the presence of montmorillonite. Examination by transmission and scanning electron microscopy showed that the nordstrandite had a tabular morphology in the clay-free systems with Al : carboxylic acid ratio >50. Because the inhibiting effect on crystallization of the citrate or malate anion decreases with increase in pH, the crystal size varied from <2 μm at pH 10 to 5 μm at pH 11. With increasing concentration of citrate or malate, the nordstrandite crystals became more elongated in the c-direction probably due to organic anion occupation of the coordination sites of Al on the edge faces parallel to the c-axis. Irregular growth along the c-axis was probably due to steric hindrance by the organic ligands distorting the arrangement of the unit layers of nordstrandite.

The catalytic effect of montmorillonite on the formation of nordstrandite was confirmed. Nordstrandite synthesized in the presence of montmorillonite at pH 9.0 presented an ill-defined ovoidal outline (0.2–0.5 μm), some showing shafts of bayerite growing from the center. At higher pH, where conditions for crystalline growth were again more favorable, nordstrandite crystals nucleated on the montmorillonite surfaces and condensed in clusters of weak face-to-face associations of plates.

Key Words—Carboxylic acid, Electron diffraction, Electron microscopy, Montmorillonite, Morphology, Nordstrandite, Synthesis.

INTRODUCTION

Van Nordstrand *et al.* (1956) identified a third crystalline form of $Al(OH)_3$ as a synthetic product in admixture with gibbsite and bayerite. Papée *et al.* (1958) obtained the new material in essentially pure form by ageing Al gels at high pH and named it nordstrandite. Nordstrandite has since been synthesized in a pure state by reacting slightly amalgamated Al foil or noncrystalline, precipitated aluminum hydroxide gel in an ethylenediamine solution (Hauschild, 1963), or by ageing hydrolytic precipitation products of aluminum with aqueous ethylene glycol (Aldcroft and Bye, 1967). Recently, organic chelating anions and clay mineral surfaces, particularly at pH >8.0, have been shown to play important roles in favoring the crystallization of pure nordstrandite (Violante and Jackson, 1979, 1981; Violante and Violante, 1980).

Well-documented occurrences of natural nordstrandite have also been reported. The mineral has been identified in microscopic solution cavities in upper Miocene limestone on the island of Guam (Hathaway and Schlanger, 1962, 1965), in karst limestone Terra Rossa in West Sarawak, Borneo (Wall *et al.*, 1962), in Montenegro (Tertian, 1966), in the Dinaric Alps of Croatia (Maric, 1967), in Hungary (Naray-Szabo and Peter, 1967), and in Jamaica (Davis and Hill, 1974). Nordstrandite has also been found closely associated with dawsonite nodules in Permian marine strata of the Syd-

ney Basin in New South Wales, Australia (Goldberry and Loughnan, 1970) and as fillings in thin fissures in dolomitic marlstone of the Green River Formation in northwestern Colorado (Milton *et al.*, 1975).

The synthetic (Lippens, 1961; Bosmans, 1970; Schoen and Roberson, 1970) and natural forms of nordstrandite have usually been characterized by X-ray powder diffractometry, but difficulties have arisen due to the general similarity of the diffraction patterns of the several $Al(OH)_3$ polymorphs. Moreover, nordstrandite and gibbsite cannot be distinguished easily by their thermal behavior, and their differential thermal curves are of limited diagnostic value (Barnhisel and Rich, 1965; Hsu, 1977). According to Milton *et al.* (1975), the similarity of many of the properties of nordstrandite to those of gibbsite suggest that nordstrandite is probably "an unrecognized constituent" in many natural environments.

The electron microscope has been used for distinguishing gibbsite, bayerite, and nordstrandite, because particles of these polymorphs can be differentiated with a fair degree of confidence by their morphology (Aldcroft and Bye, 1967; McHardy and Thompson, 1971). However, no detailed electron micrographs of natural nordstrandite have been published, and only a few electron-optical investigation have included synthetic mixtures containing this phase. Lippens (1961), Hauschild (1963), and Schoen and Roberson (1970) claimed that nordstrandite occurs as rectangular plates or in the form of elongate, platy parallelograms. However, Violante and Jackson (1979, 1981) and Violante and Violante (1980) found that the synthesis of nordstrandite in the presence of chelating carboxylic acid anions produced

[1] Istituto di Chimica Agraria, Universita di Napoli, 80055 Portici, Italy.
[2] The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen AB9 2QJ, Scotland, United Kingdom.
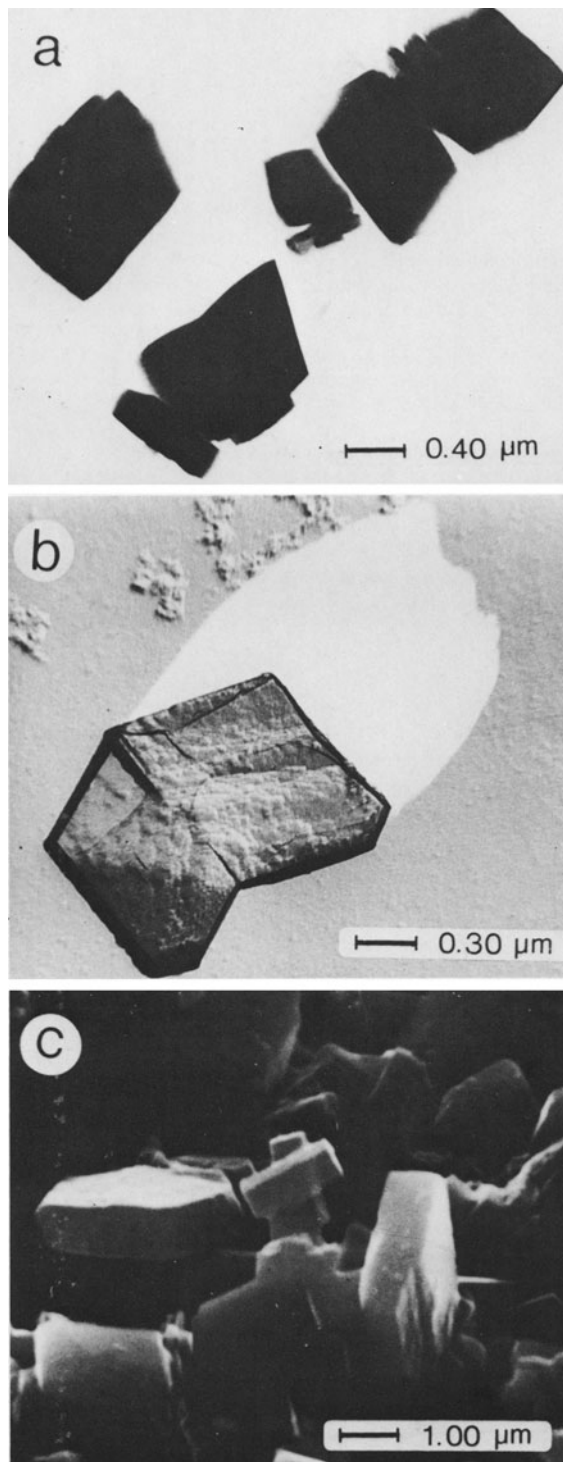
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Figure 1.   (a) Transmission electron, (b) Pt/C-shadowed replica, and (c) scanning electron micrographs of nordstrandite synthesized at pH 10.0 and Al : citric acid molar ratio = 50.
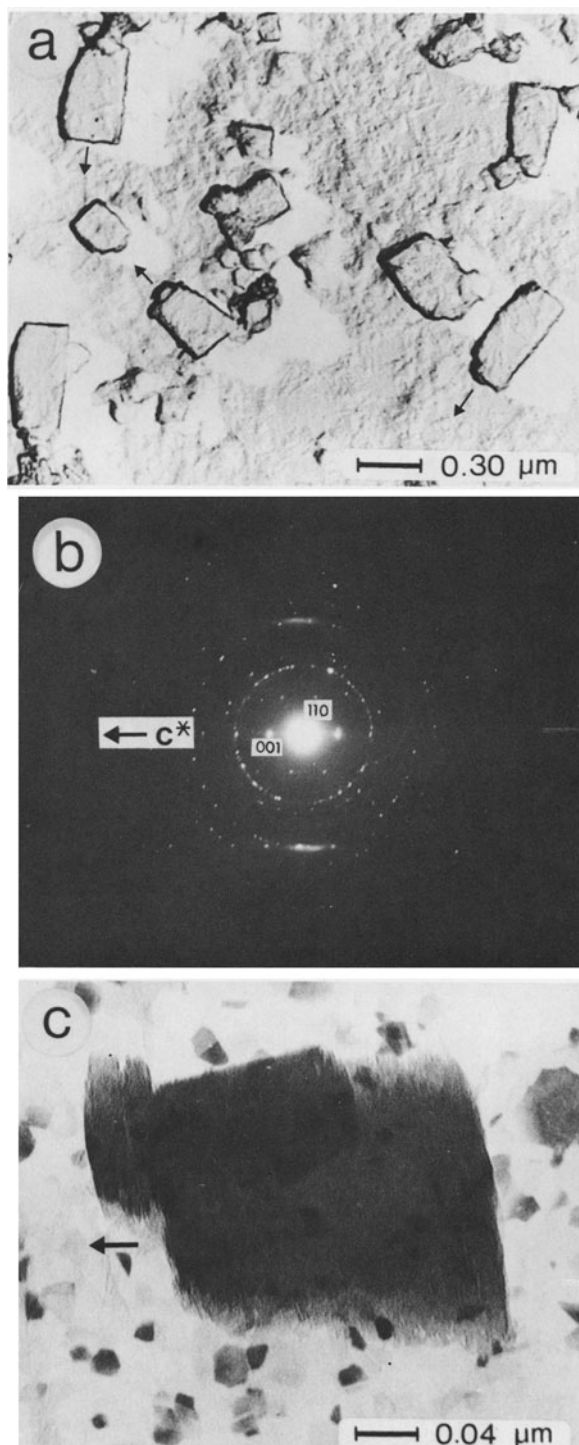

Figure 2.   (a) Transmission electron micrograph of Pt/C-shadowed replica and (c) transmission electron micrographs of nordstrandite (pH 10.0 and Al : malic acid molar ratio = 10) with crystal shape more elongated parallel to the c-axis; (b) electron diffraction pattern from particle in (c). The arrows in (a) and (c) indicate the direction of the c-axis. The diffraction rings in (b) are from aluminum used as an internal standard.
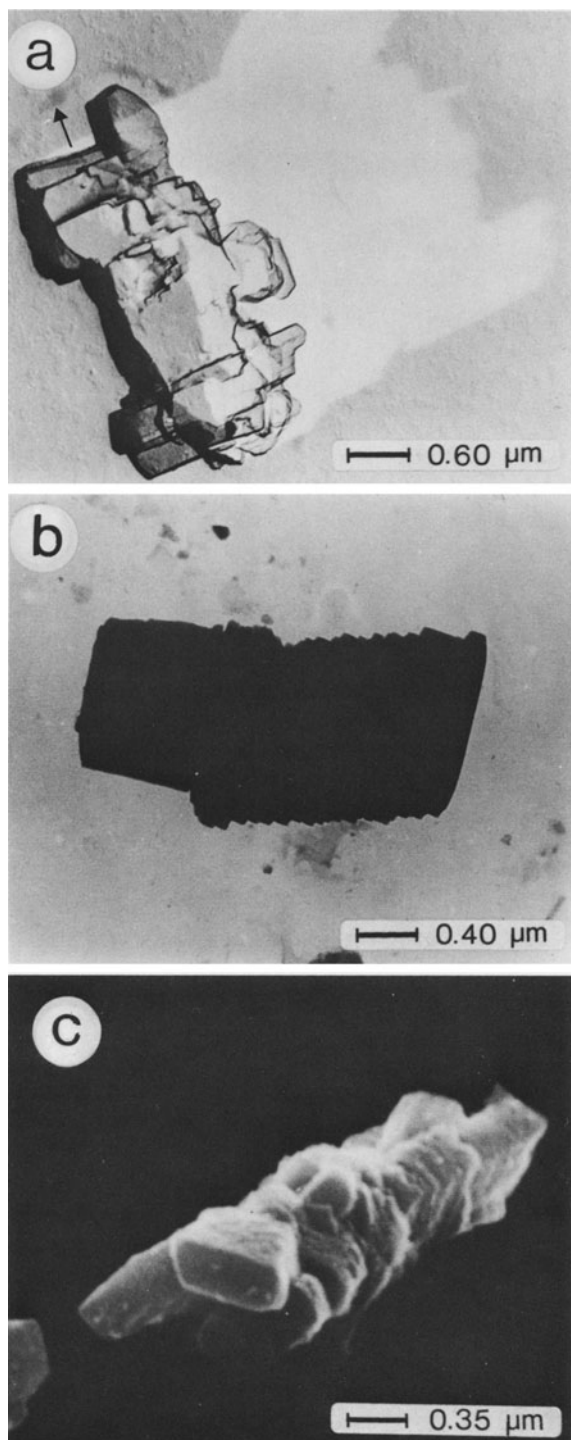
Figure 3. (a) Transmission electron micrograph of Pt/C-shadowed replica of complex nordstrandite crystal (pH 10.3 and Al : citric acid molar ratio = 10) showing growth in the c-direction (arrowed) with irregular extent of growth in the (001) plane; (b) transmission and (c) scanning electron micrographs of nordstrandite (pH 11.0 and Al : citric acid molar ratio = 10) showing distortion of the arrangement of unit layers.
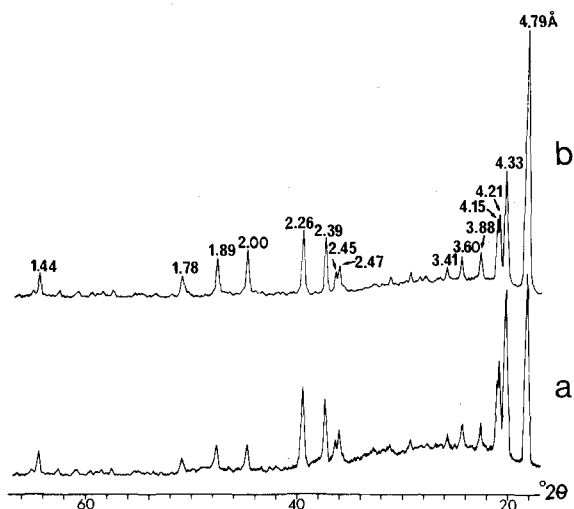

Figure 4. X-ray powder diffractograms of oriented aggregates showing variation in relative intensity of the 4.79-Å peak (001) due to modification of crystal shape of nordstrandite synthesized: (a) at pH 10.0 and Al : malic acid molar ratio = 10, and (b) at pH 10.0 and Al : citric acid molar ratio = 50.

roughly rectangular crystals and that, with the addition of clay to the system, either ovoidal particles or clusters of acicular crystals were obtained, depending on pH.

The aim of the present work was to determine by electron microscopy the crystal morphology of nordstrandite synthesized under different conditions, so that the mechanisms of formation of this mineral in soils and sediments may be better understood.

MATERIALS AND METHODS

Nordstrandite was synthesized using the method described by Violante and Jackson (1979). Aluminum hydroxide was precipitated between pH 9.0 and 11.0 by adding 0.1 M NaOH with stirring to a mixture of $AlCl_3$ and citric or malic acid in the absence or presence of montmorillonite (16 meq Al/g clay) at 25°C. The montmorillonite used was from Upton, Wyoming, and was pretreated as described by Violante and Jackson (1981). The final concentration of Al was 0.01 M; the citrate or malate concentration was varied to give Al : carboxylic anion molar ratios of 10–100. The samples were aged in polyethylene bottles for 60 days during which time the pH was held constant by the addition of 0.1 M NaOH or HCl. The material was washed free of chloride with deionized water and examined by X-ray powder diffraction and electron microscopy.

X-ray powder diffraction (XRD) was carried out using an Ital-Structures diffractometer with Ni-filtered CuKα radiation generated at 40 kV and 26 ma. The samples were prepared as orientated aggregates by sedimentation onto glass slides. Transmission electron microscope (TEM) specimens were prepared by drying a
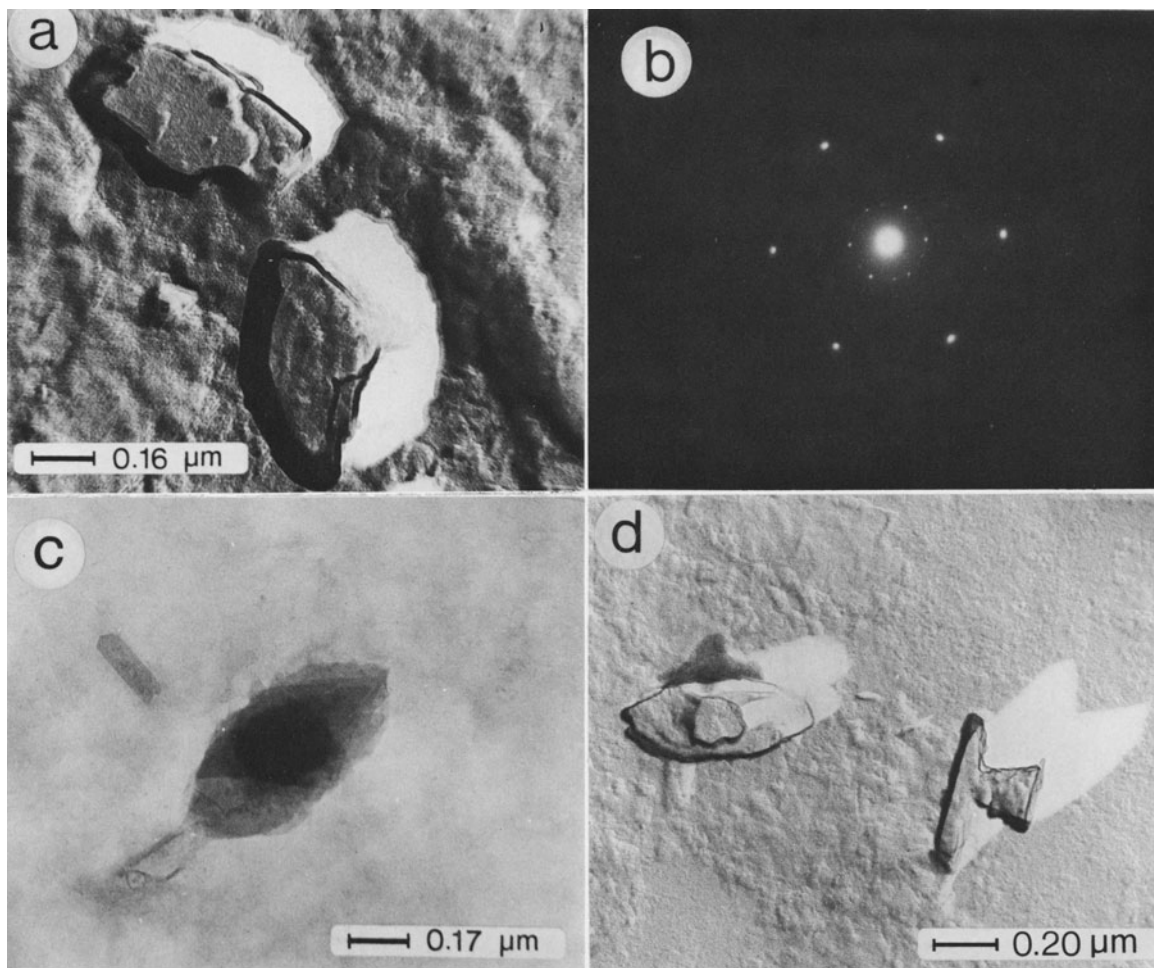
Figure 5.   Nordstrandite synthesized at pH 9.0 and Al : citric acid molar ratio = 100, in the presence of montmorillonite: (a) transmission electron micrograph of Pt/C-shadowed replica of ovoidal particles; (b) electron diffraction pattern from ovoidal particle; (c) transmission electron micrograph of ovoidal particle with electron dense center; (d) transmission electron micrograph of Pt/C-shadowed replica of ovoidal particles with projections.

drop of dilute suspension onto a carbon or carbon-aluminum film supported on a copper grid. Carbon replicas were prepared from material dried from suspension onto a glass slide, shadowed with Pt/C at $\tan^{-1}$ 1/3, then backed with a film of carbon. The slide was placed gently into a HF/HCl bath where the carbon film floated off the slide and the sample dissolved from the replica film. After washing, the film was picked up on a specimen grid. For scanning electron microscope (SEM) studies, the samples, dried on glass cover slips, were mounted on aluminum stubs and sputter-coated with gold. TEM and SEM instruments used were a Philips EM 300, a Siemens Elmiskop 102 and a Cambridge S4 stereoscan.

RESULTS AND DISCUSSION

The synthesis of pure nordstrandite by the above method proved difficult. The particular examples quoted are those which yielded a high percentage (>90%) of nordstrandite and only a small percentage of gibbsite and/or bayerite. Citric acid more effectively inhibits the crystallization of $Al(OH)_3$ than malic acid because of its slightly higher chelating power for Al ions (Violante and Violante, 1980). However, under the conditions employed here, the resulting morphology was independent of whether malic or citric acid was used.

Nordstrandite synthesized in clay-free systems

A nearly rectangular outline (length <2 μm) characterizes nordstrandite synthesized at pH 10 and at an Al : citric acid ratio =50 (Figure 1a). TEM micrographs of Pt/C-shadowed replicas (Figure 1b) and SEM micrographs (Figure 1c) of the same sample show that the crystals have a tabular morphology. The crystals formed at pH 11.0 were usually larger (as large as 5 μm) than those obtained at lower pH because the inhibiting effect on crystallization of the chelating carboxylic acid anion

decreased as the pH increased (Violante and Violante, 1980).

With increasing concentration of chelating organic anions (Al : carboxylic acid ratio <50) and at pH ≤10.0, the nordstrandite crystals were more distinctly elongated. For example, Figure 2a shows the morphology of small particles (<1 μm) of nordstrandite synthesized at an Al : malic acid ratio =10 and pH 10.0. A typical selected area electron diffraction (SAD) pattern (Figure 2b) from one of these nordstrandite particles (Figure 2c) gave a repeat distance of 4.79 Å in the direction of elongation of the crystal. This pattern was indexed on the basis of the simple unreduced triclinic unit cell (as described by Bosmans, 1970) which allows direct comparison of the basal spacing d(001) =4.79 Å of nordstrandite with those of the other Al(OH)$_3$ polymorphs, viz. d(002) =4.85 Å for gibbsite and d(001) =4.72 Å for bayerite. Therefore, these nordstrandite crystals are elongated in the crystallographic c-direction with the c-axis parallel to the plane of the supporting film. Parfitt *et al.* (1977) identified the active sites for anion adsorption on gibbsite as being on edge faces rather than (001) faces. Because nordstrandite has essentially the same structure on the (001) face as gibbsite, the active coordination sites on the former are also likely to be on edge faces parallel to the c-axis. If the chelating organic anions occupied these edge sites during nordstrandite crystallization then growth in the (001) plane could be inhibited and growth in the c-direction favored. Nordstrandite synthesized at an Al : citric acid ratio =10 at pH 10.3 (Figure 3a) and at pH 11.0 (Figure 3c) produced some complex crystals with the same general growth in the c-direction but with the extent of growth in the (001) planes quite irregular. This irregular and, on certain crystals, step-wise growth (Figure 3b) along the c-axis could be due to steric hindrance by the organic ligands distorting the arrangement of the unit layers (Ng Kee Kuang and Huang, 1979).

The nordstrandite crystals with distinct elongation in the c-direction gave a much lower relative intensity for the 4.79 Å reflection (001) in the XRD pattern (Figure 4a) compared with nordstrandite crystals of tabular morphology (Figure 4b). This lower intensity was due to the preferred orientation adopted by the elongated crystals during sedimentation of the material on to the glass slides.

Nordstrandite synthesized in the presence of montmorillonite

The catalytic effect of montmorillonite on the formation of nordstrandite and its influences on the crystal habit (Violante and Jackson, 1979, 1981) have been confirmed. An ill-defined ovoidal outline characterizes nordstrandite crystals (usually 0.3–0.5 μm) synthesized at pH 9.0 and at an Al : carboxylic acid ratio >50 in the presence of montmorillonite (Figure 5a). Electron dif-
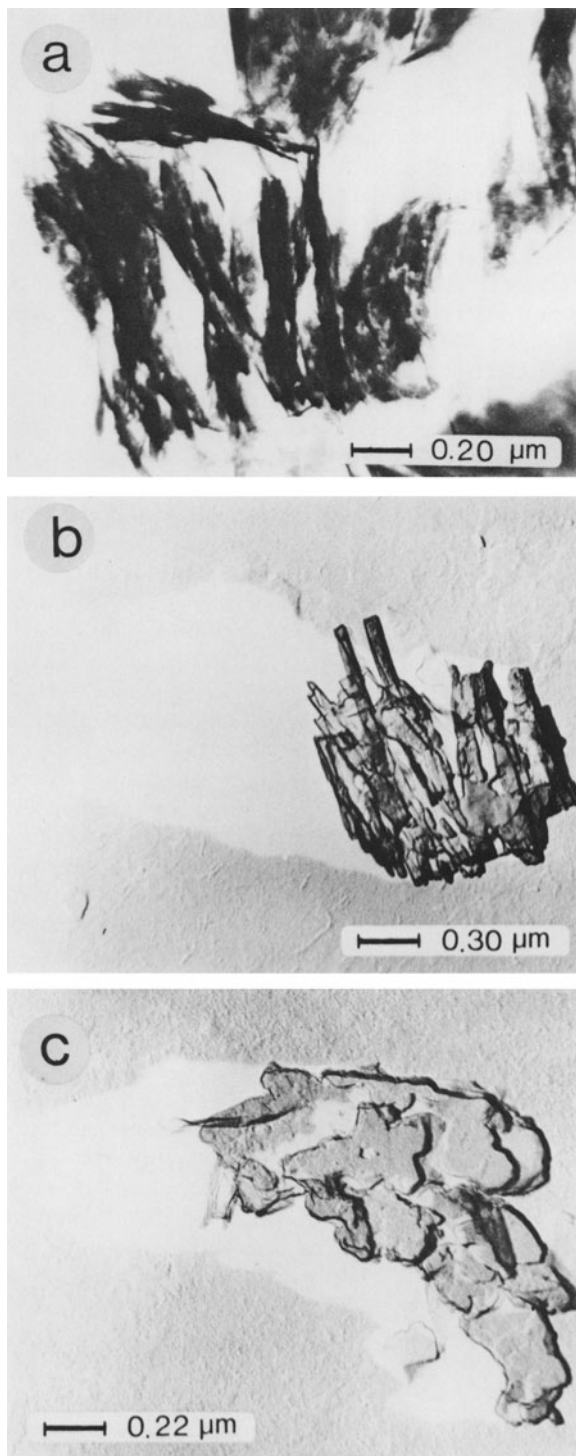

Figure 6.   Nordstrandite synthesized at pH 10.0 and Al : citric acid molar ratio = 80, in the presence of montmorillonite: (a) transmission electron micrograph and (b) transmission electron micrograph of Pt/C-shadowed replica of clusters of elongated crystals of nordstrandite; (c) transmission electron micrograph of Pt/C-shadowed replica of aggregate of gibbsite crystals.

fraction patterns from these particles gave a hexagonal network of spots with a repeat spacing of 4.33 Å (Figure 5b), representing the *ab* plane of nordstrandite. The preferred orientation for these ovoids is thus approximately perpendicular to that of the c-elongated nordstrandite crystals discussed above.

Some of the ovoidal particles are more electron dense in the center than at the edges (Figure 5c). Pt/C replications best show their exact morphology. Particles of varying length and thickness project from the center of the ovoids (Figure 5d). The T-shaped particle to the right in Figure 5d is an edge-on ovoid with projection. These projections are roughly cone-shaped (height <0.3 μm) with their apexes toward the adjoining ovoids. Other work in this laboratory suggests that the cone-shaped material may be bayerite that has co-crystallized with the ovoidal nordstrandite. Larger grains, commonly >5 μm, are also present in some samples and appear to be polycrystalline aggregates similar to the "round pellets" in the soil from West Sarawak (Wall *et al.,* 1962).

At pH 10–11, where the inhibiting effect of the chelating organic anions on crystallization was decreased, particles of nordstrandite nucleated on the montmorillonite surfaces and condensed to form polycrystalline units. The clusters of nordstrandite particles appear to be formed by a weak face-to-face association of thin plates (Figures 6a and 6b) whose principal faces are probably (001) planes. In this same sample, aggregates of small, platy crystals (Figure 6c) have been identified as gibbsite and are clearly distinct from the nordstrandite clusters. Violante and Jackson (1979) also identified gibbsite and nordstrandite by XRD in samples synthesized under similar conditions.

The different morphologies presented here are similar to those observed in nordstrandite from natural environments. For example, Hathaway and Schlanger (1962) and Milton *et al.* (1975) reported nordstrandite in the form of radiating clusters of platy or bladed crystals. The present study and those by Violante and Jackson (1979, 1981) confirm the suggestion by Hathaway and Schlanger (1965) that clay surfaces may act as nucleation centers for the growth of radiating clusters of nordstrandite crystals. The latter authors also noted the presence of several nordstrandite crystals which were not in contact with clay coatings. These crystals had tabular morphology with well-defined faces and would therefore appear to be similar to the nordstrandite observed in the present study in the clay-free preparations.

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Резюме—Нордстрандит был получен синтетически путем осаждения $Al(OH)_3$ при pH от 9 до 11 в цитратных и малатных системах с молярными отношениями Al : карбоксиловая кислота порядка 10–100 при отсутствии и в присутствии монтмориллонита. Исследования при помощи электронной и сканирующей микроскопии показали, что нордстрандит имеет пластинчатую морфологию в глино-свободных системах с отношением Al : карбоксиловая кислота >50. Тормозящий эффект на кристаллизацию цитратных и малатных анионов уменьшается с ростом величины pH и поэтому размеры кристаллов изменялись от <2 μм при pH =10 до 5 μм при pH =11. С увеличением концентрации цитрата или малата кристаллы нордстрандита становились более вытянутыми в с-направлении, вероятно, за счет занятия органическими анионами координационных мест Al на крайних гранях, параллельных к с-оси. Нерегулярный рост вдоль с-оси был, вероятно, результатом пространственного затруднения органическими лигандами, нарушающими расположение элементарных слоев нордстрандита. Подтверждено каталитическое влияние монтмориллонита на образование нордстрандита. Нордстрандит, синтезированный в присутствии монтмориллонита при pH =9, представлял плохо-определенный яйцеобразный контур (0,2–0,5 μm), некоторый имеющий колонки баиерита, вырастающие из центра. При больших pH, когда условия кристаллического роста были снова более благоприятные, кристаллы нордстрандита начинались на поверхностях монтмориллонита и конденсировались в кластеры со слабыми связями грань к грани. [E.C.]

Resümee—Nordstrandit wurde durch Ausfällung von $Al(OH)_3$ bei pH 9,0 bis 11,0 in Citrat- oder Malatsystemen mit Molverhältnissen Al : Carboxylsäure von 10–100 in Abwesenheit und Anwesenheit von Montmorillonit synthetisiert. Untersuchungen mittels Transmissions- und Rasterelektronenmikroskopie zeigen, daß der Nordstrandit in Ton-freien Systemen mit einem Al : Carboxylsäure-Verhältnis >50 eine tafelige Morphologie hat. Da der Inhibitationseffekt der Citrat-, oder Malationen auf die Kristallisation mit zunehmendem pH abnimmt, schwankt die Kristallgröße von <2 μm bei pH 10 bis 5 μm bei pH 11. Mit zunehmender Citrat- oder Malatkonzentration sind die Nordstranditkristalle mehr langgestreckt in Richtung der c-Achse, was wahrscheinlich darauf zurückzuführen ist, daß die organischen Anionen die Koordinationsplätze von Al auf den Randflächen parallel zur c-Achse besetzen. Das unregelmäßige Wachstum in Richtung der c-Achse ist wahrscheinlich auf sterische Hinderung durch die organischen Liganden zurückzuführen, was zu einer Störung der Anordnung der Einheitsschichten von Nordstrandit führt.

Der katalytische Effekt von Montmorillonit auf die Bildung von Nordstrandit wurde bestätigt. Nordstrandit, der in der Anwesenheit von Montmorillonit bei pH 9,0 synthetisiert wurde, zeigt einen schlecht ausgebildeten eiförmigen Umriß (0,2–0,5 μm), einige zeigen Bayeriteinlagerungen, die vom Zentrum aus wachsen. Bei hohen pH-Werten, wo die Bedingungen für das Kristallwachstum wieder günstiger waren, wuchsen die Nordstranditkristalle auf den Montmorillonitoberflächen auf und verdichteten sich zu Aggregaten aus schwachen Fläche zu Fläche Assoziaten der Blättchen. [U.W.]

Résumé—La nordstrandite a été obtenue synthétiquement par la précipitation d'$Al(OH)_3$ à un pH de 9,0 à 11,0 dans des systèmes citrate ou malate avec des proportions molaires d'Al : acide carbolyxique égales à 10–100 en l'absence et en la présence de montmorillonite. L'examen par microscopie à transmission, et balayante à électrons a montré que la nordstrandite avait une morphologie tabulaire dans les systèmes sans argile avec la proportion Al : acide carboxylique >50. Parce que l'effet inhibant de l'anion citrate ou malate sur la cristallisation décroit avec une augmentation de pH, la taille du cristal a varié de <2 μm au pH 10 à 5 μm au pH 11. Avec l'accroissement de la concentration de citrate ou de malate, les cristaux de nordstrandite sont devenus plus allongés dans la direction-c, probablement à cause de l'occupation par l'anion organique des sites de coordination d'Al sur les faces de bordure parallèles à l'axe-c. La croissance irrégulière le long de l'axe-c était probablement due à un empêchement stérique par les ligands organiques déformant l'arrangement de couches unitaires de nordstrandite.

On a confirmé l'effet catalytique de la montmorillonite sur la formation de nordstrandite. La nordstrandite synthétisée en présence de montmorillonite au pH 9,0 a présenté un contour ovoïde mal défini (0,2–0,5 μm), montrant en partie des tiges de bayerite croissant à partir du centre. A un pH plus élevé, lorsque les conditions pour la croissance cristalline étaient à nouveau plus favorables, les cristaux de nordstrandite ont nuclée sur les surfaces de montmorillonite et se sont condensés en groupes de faibles associations de plaques face à face. [D.J.]