HYDROTHERMAL SYNTHESES OF AMINO ACID–MONTMORILLONITES AND AMMONIUM–MICAS

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Abstract—An attempt has been made to synthesize nitrogenous clay minerals hydrothermally from silica–alumina gels in the presence of amino acids, namely glycine and lysine. The products have been characterized by X-ray powder diffraction, by analyses for C and N contents, and by their infrared spectra.

Amino acid–montmorillonites have been prepared under hydrothermal conditions of 200–250°C and 1000 atm. Above 250°C the amino acids were degraded to ammonium ions, and ammonium–micas were obtained. Syntheses without the addition of amino acids to gels yielded kaolinite.

The role of organic compounds in the formation of clay minerals seems to be of considerable geochemical significance.

INTRODUCTION

The presence of NH_4^+ as interlayer ions has been demonstrated for some natural muscovites by Vedder (1965) and it has been discovered by Barrer *et al.* (1961, 1966, 1967) that layer silicates can be synthesized hydrothermally from aluminosilicate gels in the presence of ammonium or alkylammonium ions of various kinds and in the absence of inorganic cations normally required for their syntheses. These facts indicate that organic compounds, which are formed by a biochemical process of the partial decomposition of organic vegetable and animal matter, may play an important role in the formation of clay minerals during the stages of sedimentation and successive diagenesis.

In this work amino acids were chosen as organic compounds, and an attempt has been made to synthesize nitrogenous layer silicates from silica–alumina gels in the presence of amino acids.

EXPERIMENTAL

Gels as the source of silica and alumina were prepared as follows: appropriately concentrated aluminum nitrate solution was stirred in the correct proportion with "Snowtex" silica sol; the mixture was evaporated to dryness and fired to about 600°C until the nitrate was completely decomposed. The product was ground to fine powder.

The calculated amount of each amino acid was then mixed with the silica–alumina gel to obtain the batch composition. The amino acids used were glycine and lysine hydrochloride.

The materials were enclosed in small silver tubes to prevent selective leaching. The weight of sample per charge was about 0·1 g and a small amount of distilled water was added before the tube was sealed. The weight of each sealed tube containing the specimen

and water was measured before and after heating to detect any leakage. Standard hydrothermal equipment was used throughout the investigation. The capacity of test-tube pressure vessels was 5 ml. The vessel was brought up to the desired temperature as rapidly as possible. In every heating, the pressure was maintained at 1000 atm. After reaction the charge was quenched by removing the furnace from around the vessel and immediately placing the vessel into cold water. Upon removal from the tube, the sample was thoroughly washed with distilled water and dried at room temperature.

The product then was examined by X-ray powder diffraction. Phases such as montmorillonite were further identified by their swelling characteristics. The presence of organic ions in the product was established by means of i.r. spectra, and estimated by analyses using the C.H.N. analyzer made by Yanagimoto Co. Ltd., Kyoto, Japan. The theory and use of the instrument have been described by Hozumi (1966).

RESULTS AND DISCUSSION

X-ray powder diffraction studies

The phases obtained at various temperature from the different starting materials are listed in Tables 1 and 2. Clay minerals did not crystallize at 150°C, and above this temperature up to 400°C micaceous minerals were produced from silica–alumina gels in the presence of amino acids. Syntheses without adding amino acids to gels yielded kaolinite in the temperature range from 200 to 400°C.

Montmorillonite was synthesized hydrothermally from the starting materials at the lower temperature range. The basal spacing of these well-crystallized products were 12·6 and 13·5 Å, when the amino acids

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Table 1. Representative runs of silica–alumina gels with glycine

Starting material $SiO_2:Al_2O_3:$glycine			Time (days)	Temp. (°C)	Products*
2	1	1	7	150	gel
3	1	1	7	150	gel
4	1	1	7	150	gel
3	1	1	11	200	v.p. mont.($\sim$15)†
3	1	2	11	200	m. mont.(12·6)
4	1	1	10	200	g. mont.(12·6)
4	1	2	10	200	m. mont.(12·6)
4	2	1	8·5	250	g. mont.(12·6)
2	1	1	8·5	250	mica
4	2	3	8·5	250	mica
3	1	1	4	250	mica
3	1	2	4	250	mica + g. mont.(12·6)
4	2	1	8	300	mica
2	1	1	8	300	mica
4	2	3	8	300	mica
3	1	1	6	300	mica
3	1	2	6	300	mica
4	1	1	4	300	mica
4	1	2	4	300	mica
2	1	1	5	400	mica
3	1	1	5	400	mica
4	1	1	5	400	mica

* Abbreviation used: mont. = montmorillonite, v. = very, p. = poor, m. = moderate, g. = good.
† The basal spacings of montmorillonites are shown in parentheses with Å values.

added were glycine and lysine, respectively. The basal spacing was about the same as that obtained for natural montmorillonite treated with glycine or lysine solution. When the products were treated with barium chloride solution, the basal spacings increased to 15·5 Å and then the exchanged products swelled in ethylene glycol to 17 Å.

For clay minerals prepared at the higher temperature range, X-ray patterns resembled that of mica and showed moderate crystallinity. The basal spacing was 10·5 Å, and clays did not change the basal spacing in ion-exchange experiments and in ethylene glycol. These products are best described as mica.

Chemical analyses of interlayer organic ions

For some representative products the interlayer organic ions of montmorillonites and micas were esti-

Table 2. Representative runs of silica–alumina gels with lysine

Starting material $SiO_2:Al_2O_3:$lysine			Time (days)	Temp. (°C)	Products*
4	2	1	10	150	gel
6	2	1	10	150	gel
4	1	1	10	150	gel
6	2	1	11	200	p. mont.($\sim$14)†
3	1	1	11	200	m. mont.($\sim$14)
4	1	1	10	200	p. mont.($\sim$14)
4	1	2	10	200	m. mont.($\sim$14)
4	2	1	8·5	250	g. mont.(13·5)
2	1	1	8·5	250	g. mont.(13·5) + mica
6	2	1	4	250	m. mont.(13·5)
3	1	1	4	250	m. mont.(13·5)
4	1	1	4	250	m. mont.(13·5)
2	1	1	8	300	mica
3	1	1	6	300	m. mont.(12·5) + mica
4	1	1	4	300	mica
4	1	2	4	300	mica
4	2	1	6	400	mica
6	2	1	6	400	mica
4	1	1	6	400	mica

* Abbreviation used: mont. = montmorillonite, p. = poor, m. = moderate, g. = good.
† The basal spacings of montmorillonites are shown in parentheses with Å values.

Table 3. C and N analyses of some montmorillonites and micas

Starting material	Time (days)	Temperature (°C)	C (%)	N (%)	Atomic ratio C:N	N retained (m-equiv/100 g clay)
$4SiO_2 \cdot 2Al_2O_3 \cdot glycine$	8·5	250	1·0	0·7	1·7	50
$2SiO_2 \cdot Al_2O_3 \cdot glycine$	5	400	0·1	1·8	0·1	130
$4SiO_2 \cdot 2Al_2O_3 \cdot lysine$	8·5	250	4·9	2·2	2·6	160
$4SiO_2 \cdot 2Al_2O_3 \cdot lysine$	6	400	0·2	2·0	0·2	150

mated by means of C and N analyses. Results are listed in Table 3.

The montmorillonites prepared in the presence of glycine or lysine gave C:N atomic ratios of 1·7 and 2·6, respectively. Although the ratio was a little below the appropriate value to be compared with 2 for glycine and 3 for lysine, the results suggest that the interlayer ions of the montmorillonites may consist mostly of amino acids.

On the other hand, the C:N atomic ratios of micas were negligibly small. It is considered, therefore, that amino acids might be thermally degraded to form ammonium ions which might act as the interlayer ions of micas. At present, the reaction involved in the degradation of amino acids is uncertain.

Assuming that the products are completely free from amorphous phases, the amount of interlayer organic ions on the clay minerals can be estimated from the N content retained in the products; that is, 50 m-equiv/100 g clay for glycine–montmorillonite, 80 m-equiv/100 g clay for lysine–montmorillonite and 140 m-equiv/100 g clay for ammonium–mica.

I.R. spectra

Figure 1 shows the i.r. spectra observed for montmorillonites and micas. Band assignments for amino
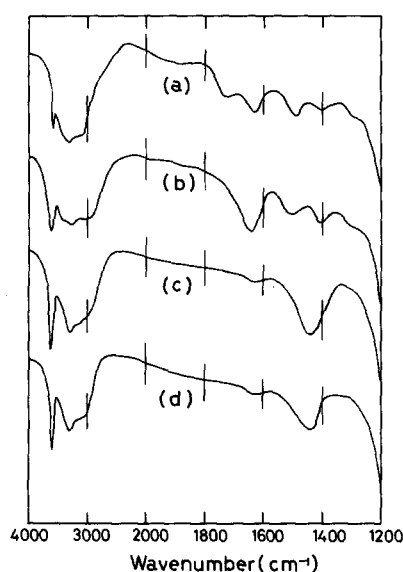

Fig. 1. I.R. spectra of montmorillonites and micas. (a) $4SiO_2 \cdot 2Al_2O_3 \cdot glycine$, 250°C, 8·5 days; (b) $4SiO_2 \cdot 2Al_2O_3 \cdot lysine$, 250°C, 8·5 days; (c) $2SiO_2 \cdot Al_2O_3 \cdot glycine$, 400°C, 5 days; (d) $4SiO_2 \cdot 2Al_2O_3 \cdot lysine$, 400°C, 6 days.

acids were made by considering the results obtained by Tsuboi *et al.* (1963).

The strong band at *ca.* 3630 cm^{-1} is due to the lattice hydroxyl stretching mode for montmorillonite or mica. The broad bands in the upper region (3500–2500 cm^{-1}) are due to NH stretching and OH stretching, but are difficult to assign.

In the lower region (1800–1200 cm^{-1}) several bands due to organic ions are observed. For the montmorillonite prepared in the presence of glycine at 250°C, the bands at 1730, 1630 and 1490 cm^{-1} may be assigned to COOH stretching, H_2O deformation and NH_3^+ symmetric deformation, respectively. The band due to NH_3^+ degenerate deformation may overlap that of H_2O deformation at 1630 cm^{-1}. The montmorillonite prepared with lysine at 250°C has bands at 1640, 1505 and 1405 cm^{-1} which may be assigned to COO^- asymmetric stretching accompanied by H_2O deformation, NH_3^+ deformation and COO^- symmetric stretching, respectively.

The spectra of micas show only the band at 1440 cm^{-1} which can be readily assigned to NH_4^+ deformation.

From the results of i.r. analyses it may be confirmed that the organic interlayer ions of montmorillonites are amino acids, and that the micas synthesized in this investigation contains ammonium ions.

CONCLUSIONS

Amino acid–montmorillonites were synthesized from silica–alumina gels in the presence of amino acids under hydrothermal conditions of 200–250°C and 1000 atm, and ammonium–micas were obtained in the temperature range from 250 to 400°C. Syntheses without adding amino acids to gels yielded kaolinite at 200–400°C.

It is observed within the limits of the present experiments that the phases obtained are scarcely affected by $SiO_2:Al_2O_3$ molar ratios or reaction times. The conclusive factor is the reaction temperature reflecting the thermal stability of the amino acids. According to the results of Abelson (1959) the degradation of amino acids with comparable stability requires almost a year at 200°C but a few minutes at 300°C in aqueous solutions.

It is concluded, therefore, that most amino acids exist stably during the crystallization of montmorillonite at temperature 200–250°C, but that above 250°C amino acids are degraded to form ammonium ions which become the interlayer ions in the formation of mica.

The role of organic compounds as interlayer organic ions in the formation of clay minerals seems to be of considerable geochemical significance.

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