SPHERICAL KAOLINITE: SYNTHESIS AND MINERALOGICAL PROPERTIES

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Abstract—Spherical kaolinite has been synthesized for the first time from noncrystalline aluminosilicate material in hydrothermal experiments conducted between 150° and 250°C and under autogenous vapor pressure. Spherules, whose mean diameters depended on growth conditions (0.1–0.6 μm), were formed surrounding the noncrystalline aluminosilicate in all products of 150° and 200°C runs and coexisted with platy or lath-shaped kaolinite in the products of 250°C runs. The estimated percentages of spherules in the products increased from about 1% in the 150°C-15 days product to about 74% in 200°C-8 days product, and decreased from about 21% in 250°C-2 days product to 0% in 250°C-8 days product. Lattice images by high-resolution electron microscope indicated that the spherules consisted of nearly concentric stackings of layers with a unit spacing of 7Å, which were sectored by radiating boundaries. The mean chemical composition of the spherules ($Al_2O_3/SiO_2 = 0.58$) analyzed by the analytical electron microscope is similar to that of kaolinite ($Al_2O_3/SiO_2 = 0.5$). Even in the case of the product abundant in spherule (200°C-8 days), X-ray powder diffraction patterns of the wetted products, e.g., of the 200°C-8 day run, showed the 7.14-Å (001) reflection of kaolinite. The 020 reflection was broad, indicating the existence of abundant (001) layer displacements. The b axis (8.94 Å) were within the kaolinite range (8.93–8.94 Å). No infrared absorption peaks were observed at 3550 cm^{-1} which would correspond to halloysite. The differential thermal analysis slope ratios of the endothermic peak at about 550°C (1.4–2.3) were in the kaolinite range (0.78–2.39).

Key Words—Halloysite, High resolution electron microscopy, Infrared spectroscopy, Kaolinite, Spherules, Synthesis, X-ray powder diffraction.

INTRODUCTION

Kaolinite and halloysite[1] are common members of the kaolin group of 1:1 dioctahedral phyllosilicates. Allophane also can be treated as a mineral related to this group. Ideal chemical compositions and basal spacings of these minerals are $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ and a 10-Å spacing for halloysite(10Å), $Al_2Si_2O_5(OH)_4$ and a 7.2-Å spacing for both halloysite(7Å) and kaolinite, and $Al_{2-4}Si_2O_5(OH)_n \cdot mH_2O$ and noncrystalline diffraction for allophane. The species are also distinguished by their distinctive morphologies, i.e., tubes or spheres for halloysite(10Å), polygonized tube or polygonized spheres for haolloysite(7Å), plates for kaolinite, and minute spheres about 50 Å in diameter for allophane. Spherules with kaolinite composition and 7-Å basal spacing have not previously been found or synthesized. Although tubular halloysite(10Å) has been synthesized in the laboratory (Parham, 1969), the synthesis of spherical halloysite has not been reported.

Spherical aluminosilicate minerals, which were either described as noncrystalline or not characterized, have been synthesized by several investigators (DeKimpe *et al.*, 1964; Trichet, 1969; Rodrique *et al.*, 1972).

Inasmuch as morphological aspects are of fundamental importance to the mineralogy of the kaolin group, it is worthwhile to prepare these materials experimentally so that their origin and conditions of formation in nature may be understood. In the course of our investigations of clay mineral formation, we have synthesized for the first time a kaolinite with spherical morphology. In this paper, the growth conditions and mineralogical properties of this material are discussed.

EXPERIMENTAL

Starting materials

A mixed sol of colloidal silica (Snowtex-O)[2] and alumina (Aluminasol-200)[2] was prepared in a molar ratio of $Al_2O_3/SiO_2 = 0.5$. The sol was spray-dried to form

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[1] The 1975 AIPEA Nomenclature Committee recommended the term halloysite(10Å) for halloysite with the basal spacing of 10 Å and the term halloysite(7Å) for material with a spacing of 7 Å.

[2] Snowtex-O and Aluminasol-200 are trade names of the Nissan Chemical Industries, Ltd. for soda-stabilized silica and alumina sols of high purity. The dominant impurity is 0.11% Na_2O in each.

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noncrystalline aluminosilicate particles having a mean diameter of about 5 μm and heated at 600°C for 8 hr to decompose the acetic acid which was included as a deflocculant in both sols. The product was powdery and amorphous to X-rays.

Hydrothermal synthesis

The starting material (1 g) and distilled water (4 ml) were sealed in a 50-ml, stainless steel, nonlined Morey-type pressure vessel. The pressure vessel was held at constant temperatures from 150° to 350°C ($\pm$ 2°C) at intervals of 50°C. The pressure was the equilibrium water pressure at the corresponding temperature. All runs above 200°C were made for 2, 4, and 8 days; runs at 150°C were made for 15, 30, 40, 50, and 62 days. After each run, the pressure vessel was quenched and the product removed and dried in an oven at 40°C for one day.

The products of 150° and 200°C runs were investigated in a moist condition by X-ray powder diffraction to check for the presence of halloysite(10Å). Other experiments were carried out using gold tubes and Teflon pressure vessels at 200°C. Inasmuch as no essential difference was found in the results between the two types of pressure vessels, only the results obtained by the Morey-type, stainless steel pressure vessels are described below.

Analytical measurements

Two types of sample preparation were used for electron microscopic study using a JEOL-JEM 200CX electron microscope. The specimens were either dispersed on a carbon-coated microgrid or embedded in an epoxy resin, from which ultrathin sections were prepared. Chemical analyses of the products were carried out using the HITACH 700H analytical electron microscope with the analytical mode (AEM) installed at Kyoto University, based on the method described by Morimoto and Kitamura (1981).

All products were examined by X-ray powder diffraction (XRD) method using a Simazu VD-2 diffractometer with Ni-filtered CuKα radiation. Infrared absorption (IR) spectra of the oriented specimen on Au-coated slide glass were recorded on a Simazu IR-430 spectrophotometer in the same manner as described by Kato *et al.* (1981). Differential thermal analysis (DTA) and thermogravimetry (TGA) were carried out using a Rigaku thermoflex micro TG-DTA apparatus. The specific surface area was obtained by the N_2 gas adsorption (BET) method of Brunauer *et al.* (1938).

RESULTS

Electron microscopy

Various morphologies were observed depending on growth conditions. The most striking was a spherulitic morphology (Figure 1). Such spherules were observed
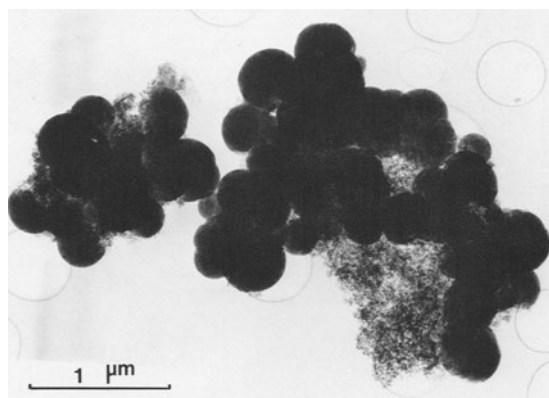

Figure 1. Electron micrographs of spherulitic kaolinite products (200°C, 8 days).

in all products of the 150° and 200°C runs and in some of the 250°C runs (Figure 2), but not in products of higher temperature runs. In the 150° and 200°C products, spherules were formed around the periphery of noncrystalline aluminosilicate (Figure 3). Their size ranged from 0.1–0.6 μm and increased with the duration and temperature of runs at 150° and 200°C, but decreased with duration of the runs at 250°C (Figure 4). The electron diffraction patterns of the spherules smaller than 0.1 μm across gave distinct halos, whereas those of larger spherules gave a halo of 7 Å with spots. High-resolution electron microscopy of a spherule produced well-resolved lattice images with 7-Å spacings, together with stacking disorders (Figure 5). The lattice images appear concentric, but closer investigation shows that they consist of radiating domains having straight lattice images. The domains are slightly inclined to each other. The domain boundaries are shown schematically in Figure 6.

Although spherules were formed in the 250°C runs, they were slightly different from those observed in the lower temperature runs in that platy or lath-shaped kaolinite crystallites protruded from the spherules formed in 2 and 4 days duration (Figure 2). Their sizes decreased as the duration increased, and after 8 days, no spherules were found. The kaolinite crystallites formed above 250°C were hexagonal and platy in habit, and their sizes increased slightly as the duration increased, but they became rounded platy or irregular platy at 350°C in runs that lasted more than 4 days. This change in the morphology of kaolinite corresponds to the transformation from kaolinite to pyrophyllite as seen on the XRD diagrams (Figure 7).

The spherule/plate ratios were estimated from electron micrographs, and the kaolinite/noncrystalline aluminosilicate ratios were estimated from the weight loss in TGA between 450° and 600°C. These data are compiled in Table 1 by assuming that all of the spherules
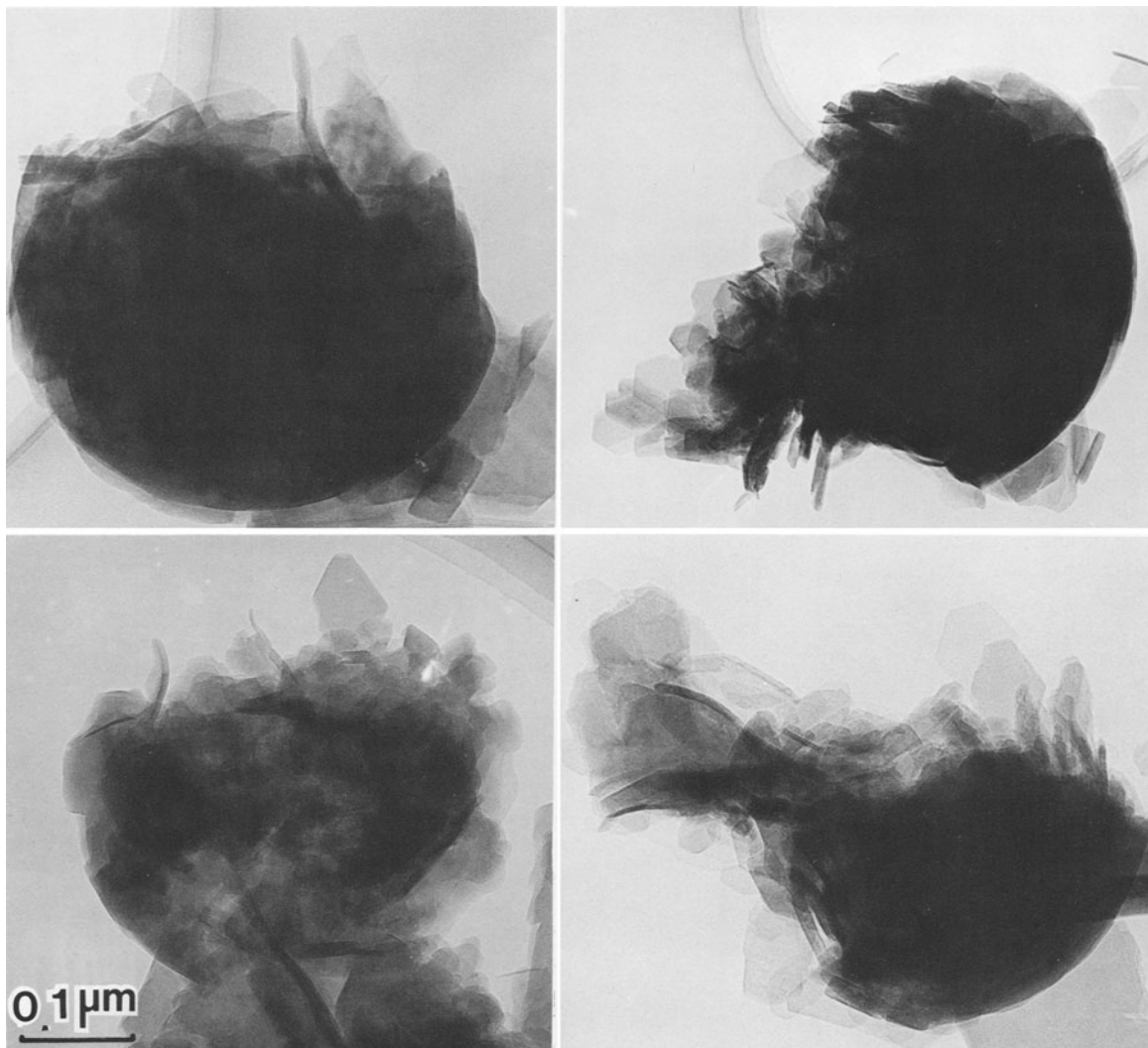
Figure 2.   Transmission electron micrographs of kaolinite spherules surrounded by platy kaolinite (250°C, 4 days).

and plates are kaolinite. The spherules increased from about 1% in the 150°C-15 days product to about 74% in the 200°C-8 days product, and decreased from about 21% in the 250°C-2 days product to 0% in the 250°C-8 days product.

The above observations are summarized in Figure 8, from which it appears that: (1) the aluminosilicate used as the starting material was noncrystalline; (2) spherules formed around the starting aluminosilicate at 150°–200°C; (3) platy or lath-shaped kaolinite grew at the expense of the spherules at 250°C; (4) platy or lath-shaped kaolinite formed at 300°C; and (5) platy or lath-shaped kaolinite decomposed and pyrophyllite grew at 350°C.

From the results of analytical electron microscopy, the Al_2O_3/SiO_2 molar ratio of the spherule formed in the 200°C-8 days runs ranged from 0.52 to 0.63 and averaged 0.57. The Al_2O_3/SiO_2 molar ratio of lath or platy kaolinite ranged between 0.42 and 0.52 and averaged 0.46.

X-ray powder diffraction

Dried samples. The XRD patterns of the products of the 150°C runs of more than 30 days duration showed the sharp 001 reflection of kaolinite at 7.14 Å. The sharp reflection at 6.15 Å ($2\theta = 14.4°$, Figure 8) was asigned to the 001 reflection of MoS_2 used as sealing grease. Broad reflections were also observed at 4.5 and 2.4 Å corresponding to the hk bands of phyllosilicates. The XRD patterns of the 200°C products of 4 and 8 days duration showed the 001 reflections of kaolinite at 7.14 Å ($2\theta = 12.38°$) and weak $11\bar{1}$ and $1\bar{1}0$ reflections corresponding to kaolinite hk bands. The XRD patterns of the 250° and 300°C products were essen-
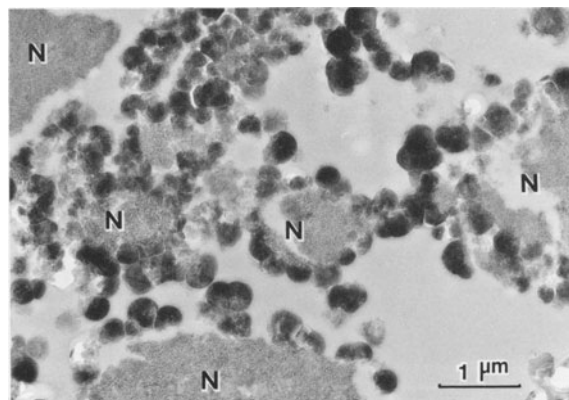
Figure 3. Electron micrograph (ultrathin section technique) of the product synthesized at 150°C for 62 days. Note that spherules are formed on the surface of a particle of the noncrystalline aluminosilicate. N = noncrystalline aluminosilicate.

Figure 4. Mean diameter of spherules vs. run time.

tially similar to those of the 200°C products, although the (*hkl*) reflections were stronger. The intensity of the 001 reflection of kaolinite in the 350°C product gradually decreased, whereas that of the 9.4-Å reflection of pyrophyllite increased as the duration increased.

To evaluate the stacking disorders in the kaolinite products, Hinckley's crystallinity indexes (Hinckley, 1963; intensity ratios of non-basal reflections of kaolinite) were calculated for each product (Table 1). The Hinckley indexes increased as temperature increased, and the 150°C products appeared to be highly disordered. The b-axis parameter (8.94 Å) calculated from
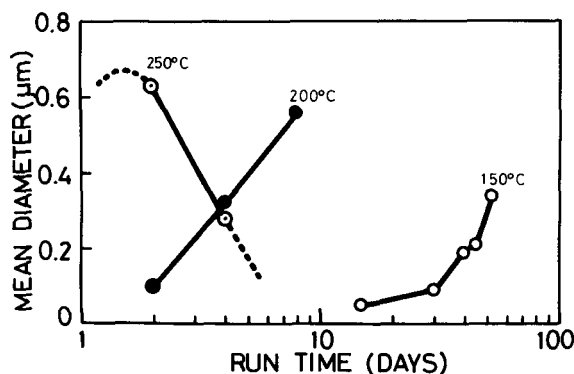
the d(060) value of 1.49 Å is within the kaolinite range (8.93–8.94 Å) and not within the halloysite range (8.88–8.93 Å), as suggested by Nagasawa (1969).

Moist samples. The XRD patterns of the products synthesized at 150°C and 200°C but not subsequently dried also showed the sharp 7.14-Å reflection of kaolinite and not the 10-Å reflection of halloysite(10Å).

Infrared spectroscopy

The IR spectra of the products formed at 150°C in 30-day runs and at 200°C in 2-day runs showed only the very broad peak of adsorbed water. The other products formed at 150°, 200°, 250°, and 300°C showed the 3700-cm^{-1} peak characteristic of the kaolin-group minerals. The intensity of the peak at 3700 cm^{-1} decreased and that of the 3685-cm^{-1} peak characteristic of py-

Table 1. Summary of hydrothermal run results.

Run temp. (°C)	Run time (days)	Run products[1]	Specific surface area (m²/g)	Estimated amount of observed particles			Kaolinite		
				NC (%)	Sphere (%)	Plate (%)	b axis (Å)	CI[2]	DTA[2] S.R.
150	15	NC	207	99	1	0	—	0	—
150	30	NC + K	207	96	2	2	—	0	—
150	40	NC + K	206	88	6	6	8.94	0	1.41
150	50	NC + K	208	80	16	4	8.94	0	2.33
150	62	NC + K	165	61	34	5	8.94	0	2.29
200	2	NC	170	95	2	3	—	0	—
200	4	NC + K	150	81	15	3	8.94	0.44	1.40
200	8	K + NC	135	22	74	4	8.94	0.34	1.75
250	2	K	55	6	21	73	8.94	0.91	3.00
250	4	K	30	3	17	80	8.93	0.91	3.29
250	8	K	35	0	0	100	8.93	0.88	2.84
300	2	K	28	0	0	100	8.93	0.87	2.52
300	4	K	33	0	0	100	8.93	0.98	2.38
300	8	K	32	0	0	100	8.93	0.98	2.41
350	2	K + (P + B)	44	0	0	100[3]	8.93	0.95	1.43
350	4	K + P + B	43	0	0	100[3]	8.93	0.75	1.51
350	8	K + P + B	43	0	0	100[3]	8.93	0.43	1.01

[1] NC = noncrystalline aluminosilicate; K = kaolinite; P = pyrophyllite; B = boehmite.
[2] CI = Hinckley's crystallinity index; S.R. = slope ratio of kaolinite endothermic peak.
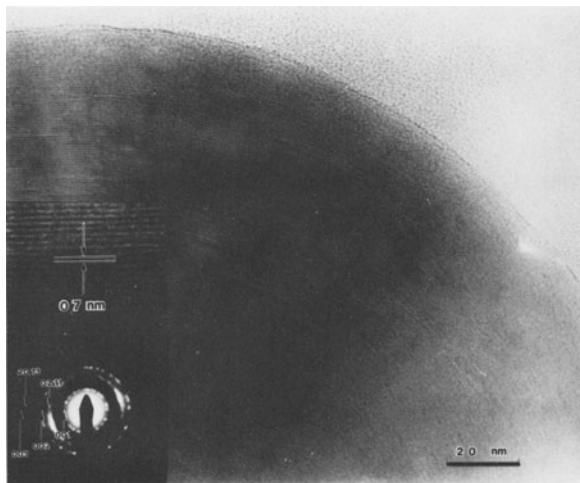[3] Pyrophyllite or boehmite like materials are included in the value.

Figure 5.   Lattice image of a spherule synthesized at 150°C for 62 days. Note the lattice image with 7-Å spacing and the corresponding electron diffraction pattern inserted.

rophyllite increased with run duration for the 350°C products.

A small peak at 3450 cm^{-1} in the IR patterns of the products of the 150° and 200°C runs was also observed by Kato *et al.* (1977) in b-axis disordered kaolinite and by DeKimpe *et al.* (1981) in synthetic disordered kaolinite. No peak was observed at 3550 cm^{-1} which corresponds to halloysite according to Farmer (1974).

Thermal analysis

The DTA curves of the products showed that the endothermic peak at about 550°C increased in intensity with an increase in run length, and shifted towards higher temperature as the run temperature increased from 150° to 250°C. The endothermic peak at about 550°C increased with run temperature up to 300°C, but decreased for the 350°C product, for which a weak endothermic peak appears at about 700°C.

The slope ratios of endothermic peak around 550°C, which were proposed by Bramao *et al.* (1952) as a
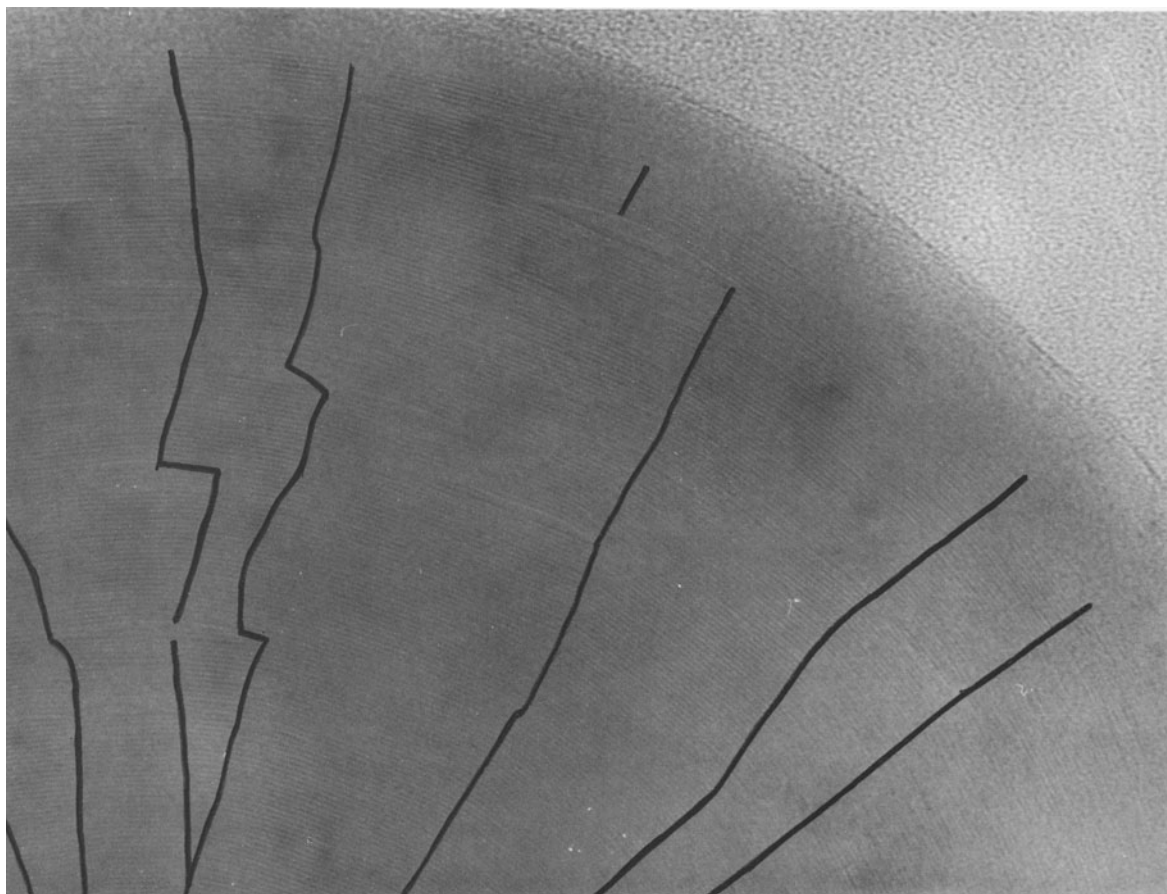

Figure 6.   Indicating the boundaries between the neighboring columns on the lattice image of a spherule shown in Figure 5.
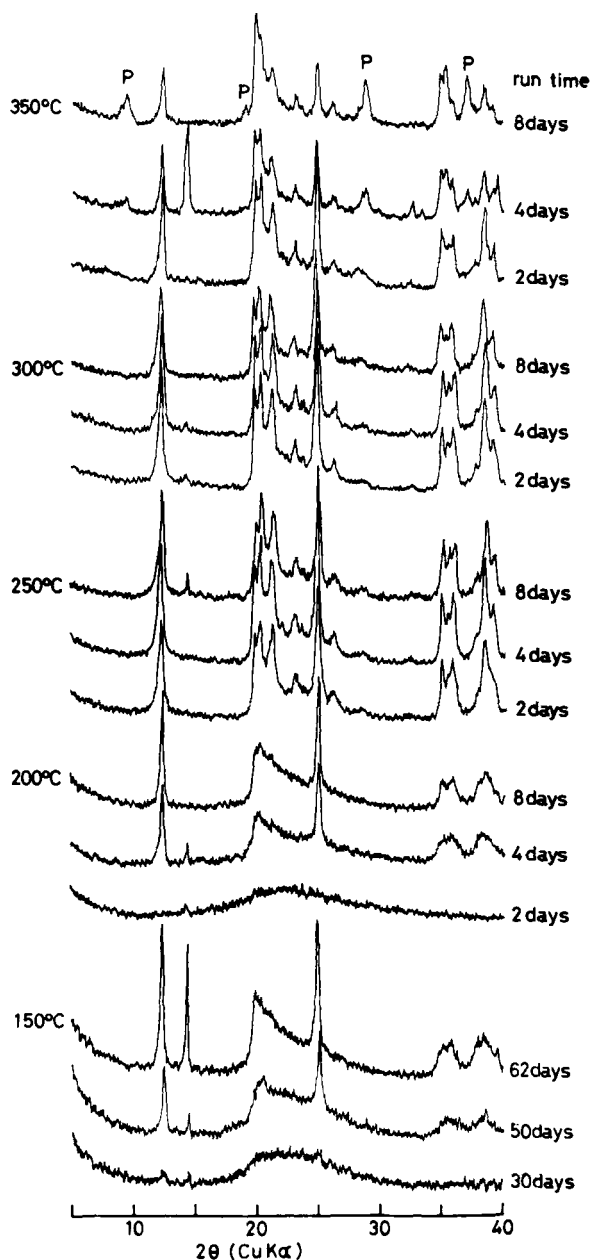
Figure 7. X-ray powder diffraction patterns of products synthesized under different conditions.

Figure 8. Morphological phase diagram of products obtained in the present study.

criterion to distinguish kaolinite from halloysite(7Å), ranged from 1.4 to 2.3, except for the 250°C products (2.8–3.3). These values fall in the kaolinite range (0.78–2.39), rather than the halloysite range (2.5–3.8). These data are consistent with electron microscopic observations and XRD data.

Specific surface area

The specific surface area of the product was approximately proportional to the percentage of the remaining noncrystalline aluminosilicate (Table 1).
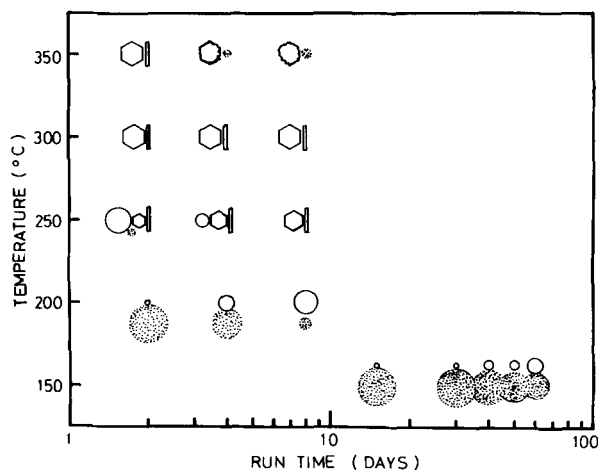
DISCUSSION

The present study strongly suggests that the spherules formed between 150° and 250°C are kaolinite and not halloysite, which lies within the stability field of kaolinite according to the phase diagram of Roy and Osborn (1954). At higher run temperatures, spherulitic kaolinite became unstable and hexagonal platy kaolinite was produced. Aluminosilicate minerals with similar spherulitic morphology have been synthesized by several workers (DeKimpe *et al.*, 1964; Rodrique *et al.*, 1972), although they did not identify the mineral. The starting materials and the containers were different in these studies. Our work shows that spherulitic aluminosilicate minerals can be formed, irrespective of containers or starting materials, in the Al_2O_3-SiO_2-H_2O system under certain hydrothermal experimental conditions.

Although the distinction among kaolinite, halloysite, and allophane is often made on the basis of their morphologies, the present results suggest that the difference in morphologies among spherulitic kaolinite, spherulitic or tubular halloysite, and spherical allophane should be studied more carefully. Table 2 summarizes the present work and the data on natural kaolinite, halloysite, and allophane. Because of a large size difference (spherulitic kaolinite is 200 times larger than allophane), there is no difficulty in distinguishing between these two spherulitic minerals. There is no problem also in distinguishing between spherulitic kaolinite and tubular halloysite because halloysite contains interlayer water, which is easily dehydrated, and the morphological changes from water-containing to dehydrated halloysite (tubular and spherical) has been studied by Kohyama *et al.* (1978) and Kirkman (1981). In these studies, it was demonstrated that both tubular and spherical halloysites change their original morpholo-
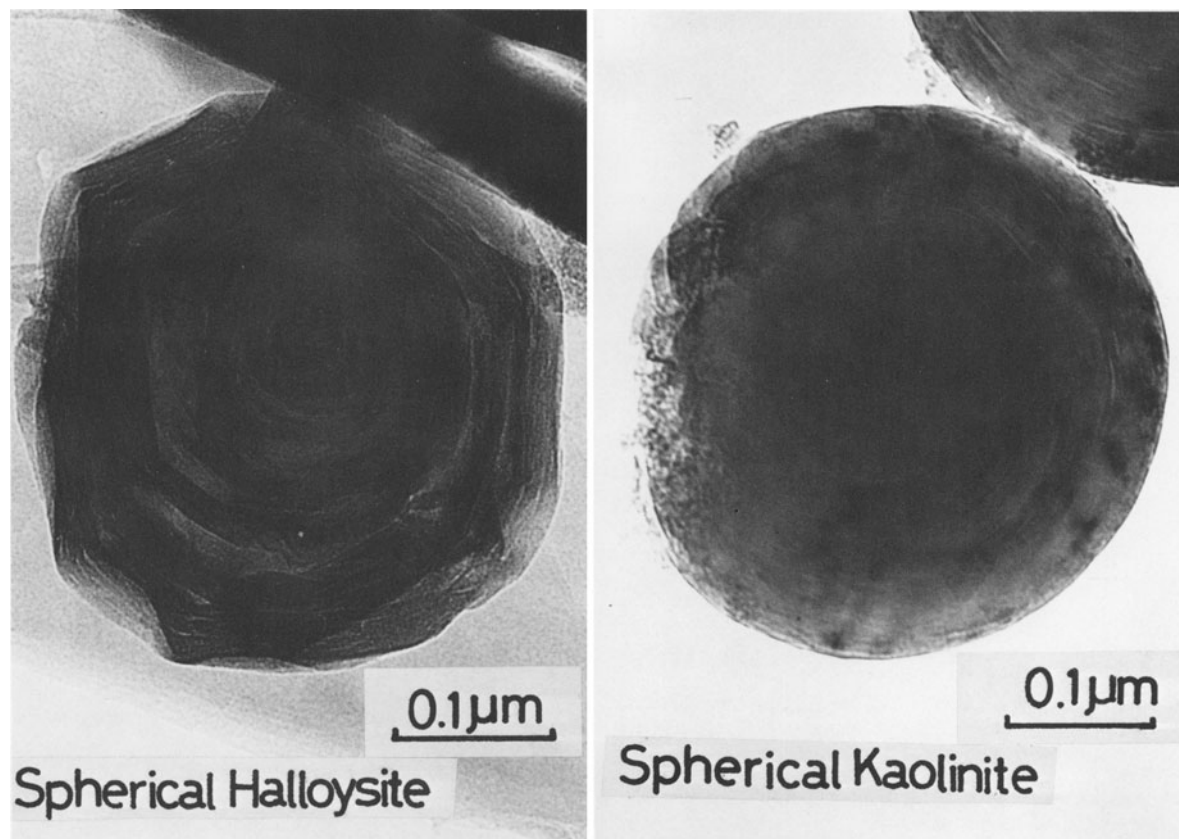
Figure 9.   A comparison of dehydrated spherical halloysite (A) from Ina mine, Nagano prefecture, Japan; (B) spherical kaolinite synthesized at 200°C, 4 days.

Table 2.   Mineralogical properties of synthetic spherical kaolinite compared with natural kaolinite, halloysite, and allophane.

	Synthetic spherical kaolinite	Natural platy kaolinite	Natural halloysite 10-Å form	Natural halloysite 7-Å form	Natural allophane
Morphology	sphere	plate	tube or sphere	polygonized tube or sphere	sphere
Dehydrated morphology	sphere	plate	polygonized tube or polygonized sphere		sphere
Particle size (μm)	0.1–1.5	0.1–1000[1]	0.1–2.0[1]	0.1–2.0[1]	0.005[1]
XRD d(001) (Å)	7.14	7.15[2]	10.0–10.1[2]	7.2–7.5[2]	—
b axis (Å)	8.94	8.93–8.94[3]	8.88–8.93[3]	8.88–8.93[3]	—
IR 3450 cm^{-1}	present	sometimes[4] present	absent[4]	?	—
3550 cm^{-1}	absent	absent[5]	present[5]	?	—
DTA slope ratio	1.4–2.3	0.78–2.39[6]	2.5–3.8[6]	?	—
Molar ratio of Al_2O_3/SiO_2	0.58	0.50[7]	0.46[7]	?	0.5–1.0

[1] Bates (1971).
[2] Brindley and Brown (1980).
[3] Nagasawa (1969).
[4] Kato et al. (1977).
[5] Farmer (1974).
[6] Bramao et al. (1952).
[7] Tomura et al. (1982).

gies with smoothly curved surfaces to polyhedral morphologies consisting of depressed facets due to dehydration. With spherical kaolinite, such a morphological change due to dehydration was not noted. In Figure 9, electron micrographs of dehydrated spherical halloysite and spherical kaolinite are compared. We therefore conclude that kaolinite without interlayer water can assume a spherulitic morphology, resembling very closely spherical halloysite in appearance.

ACKNOWLEDGMENTS

REFERENCES

Bates, T. F. (1971) The kaolin minerals: in *The Electron-Optical Investigation of Clays*, J. A. Gard, ed., Mineralogical Society, London, 109–158.

Bramao, L., Cady, J. G., Hendricks, S. B., and Swerdlow, M. (1952) Criteria for the characterization of kaolinite, halloysite, and a related mineral in clays and soils: *Soil Sci.* **73**, 273–287.

Brindley, G. W. and Brown, G., eds. (1980) *Crystal Structures of Clay Minerals and Their X-ray Identification:* Mineralogical Society, London, 495 pp.

Brunauer, S., Emmett, P. H., and Teller, E. (1938) Adsorption of gases in multi-molecular layers: *J. Amer. Chem. Soc.* **60**, 309–319.

DeKimpe, C. R., Gautuche, M. C., and Brindley, G. W. (1964) Low-temperature syntheses of kaolin minerals: *Amer. Mineral.* **49**, 1–16.

DeKimpe, C. R., Kodama H., and Rivard R. (1981) Hydrothermal formation of kaolinite material from aluminosilicate gels: *Clays & Clay Minerals* **29**, 446–450.

Farmer, V. C., ed. (1974) *The Infrared Spectra of Minerals:* Mineralogical Society, London, 539 pp.

Hinckley, D. N. (1963) Variability in "crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina: in *Clays and Clay Minerals, Proc. 11th Natl. Conf., Ottawa, Ontario, 1962,* Ada Swineford, ed., Pergamon Press, New York, 229–235.

Kato, E., Kanaoka, S., and Inagaki, S. (1977) Infrared spectra of kaolin minerals in OH region (I); on the glass slide method for the measurement of the infrared spectra in OH region of clay minerals: *Rept. Govt. Industr. Res. Inst. Nagoya* **26**, 203–210 (in Japanese).

Kato, E., Kanaoka, S., and Kato, S. (1981) On the glass-slide reflection method for infrared adsorption spectra measurement of clay minerals: *J. Clay Sci. Soc. Japan* **21**, 19–25 (in Japanese).

Kirkman, J. H. (1981) Morphology and structure of halloysite in New Zealand tephras: *Clays & Clay Minerals* **29**, 1–9.

Kohyama, N., Fukushima, K., and Fukami, A. (1978) Observation of the hydrated form of tubular halloysite by an electron microscope equipped with an environmental cell: *Clays & Clay Minerals* **26**, 25–40.

Morimoto, N. and Kitamura, M. (1981) Applications of 200 kV analytical electron microscopy to the study of the textures of minerals: *Bull. Mineral.* **104**, 241–245.

Nagasawa, K. (1969) Kaolin minerals in Cenozoic sediments of central Japan: in *Proc. Int. Clay Conf., Tokyo, 1969,* **1**, L. Heller ed., Israel University Press, Jerusalem, 15–30.

Parham, W. E. (1969) Formation of halloysite from feldspar: low temperature, artificial weathering versus natural weathering: *Clays & Clay Minerals* **17**, 13–22.

Rodrique, L., Poncelet, G., and Herbillon, A. (1972) Importance of the silica subtraction process during the hydrothermal kaolinitization of amorphous silico-aluminas: in *Proc. Int. Clay Conf., Madrid 1972,* J. M. Serratosa, ed., Div. Ciencias C.S.I.C., Madrid, 187–198.

Roy, R. and Osborn, E. F. (1954) The system Al_2O_3-SiO_2-H_2O: *Amer. Miner.* **39**, 853–885.

Tomura, S., Kitamura, M., Shibasaki, Y., and Maeda, T. (1982) Iron in gairome clay—analytical electron microscopic study: *J. Ceram. Soc. Japan* **90**, 28–32 (in Japanese).

Trichet, J. (1969) Study of the structure of volcanic glass and its relation to the alteration of vitreous rocks: in *Proc. Int. Clay Conf., Tokyo 1969,* **1**, L. Heller, ed., Israel University Press, Jerusalem, 443–453.

Резюме—Сферический каолинит был первый раз синтезирован из некристаллического алюмино-силикатного материала путем гидротермических экспериментов, проведенных при температурах от 150°C до 250°C и при автогенном давлении пара. Шарики, средние диаметры которых зависили от условий роста (0,1–0,6 µм), были образованы вокруг некристаллических алюмосиликатов во всех продуктах экспериментов при 150°C и 200°C и существовали с пластинчатым каолинитом в продуктах экспериментов при 250°C. Определенное процентное содержание шариков увеличивалось от 1% в продуктах, образованных при 150°C в течение 15 дней, до около 74% в продуктах, образованных при 200°C в течение 8 дней, а также уменьшалось от около 21% в продуктах при условиях 250°C–2 дня до 0% в условиях 250°C–8 дней. Отображения решетки при помощи электронного микроскопа с высокой равщиряющей способностью указывают на то, что эти шарики состояли из почти концентрических групп слоев с элементарным расстоянием 7 Å, которые были расчленены излучающими границами. Средний химический состав шариков (Al_2O_3/SiO_2 = 0,58), анализированный при помощи аналитического электронного микроскопа, был похож на состав каолинита (Al_2O_3/SiO_2 = 0,5). Даже в случае наличия избытка шариков в продуктах (200°C–8 дней), образы рентгеновской порошковой дифракции влажных продуктов экспериментов показали отражение 7,14 Å (001) каолинита. 020 отражение было широким, указывая на существование перемещений слоев 001. Оси b (8,94 Å) находились в каолинитовом диапазоне (8,93–8,94 Å). Не наблюдалось полос инфракрасной абсорбции при 3550 цм⁻¹, которые соответствовали бы галлоизиту. Отнощения наклонов эндотермических пиков дифференциального термического анализа при около 550°C (1,4–2,3) находились в каолинитовом диапазоне (0,78–2,39). [E.G.]

Resümee—Kugeliger Kaolinit wurde zum ersten Mal aus nichtkristallinem Alumosilikatmaterial in hydrothermalen Experimenten synthetisiert, die zwischen 150° und 250°C und unter autogenem Dampfdruck durchgeführt wurden. Die Kugeln, deren durchschnittlicher Durchmesser von den Wachstumsbedingungen abhing (0,1–0,6 μm), umgaben in allen zwischen 150° und 200°C gebildeten Produkten das nichtkristalline Alumosilikat. In den bei 250°C entstandenen Produkten bildeten sie sich neben plattigen und leistenförmigen Kaoliniten. Der geschätzte Anteil der Kugeln in den Produkten nahm von etwa 1% in den bei 150°C nach 15 Tagen entstandenen Produkten auf etwa 74% in den bei 200°C nach 8 Tagen enstandenen Produkten zu. Weiters nahmen sie von etwa 21% in den bei 250°C nach 2 Tagen entstandenen Produkten auf 0% in den bei 250°C nach 8 Tagen entstandenen Produkten ab. Die Gitterbilder mittels hochauflösender Elektronenmikroskopie zeigten, daß die Kugeln aus einer nahezu konzentrischen Anordnung von Schichten mit einem Schichtabstand von 7 Å bestehen, die durch radiale Grenzen unterteilt sind. Der Durchschnittschemismus der Kugeln (Al_2O_3/SiO_2 = 0,58), der mittels Mikrosonde bestimmt wurde, ist ähnlich dem von Kaolinit (Al_2O_3/SiO_2 = 0,5). Selbst wenn in dem Produkt die Kugeln überwiegen (200°C, 8 Tage), zeigen die Röntgenpulverdiffraktometeraufnahmen der feuchten Produkte, z.B. das aus dem Experiment bei 200°C und 8 Tagen, den 7,14 Å (001) Reflex von Kaolinit. Der 020 Reflex war breit, was auf eine häufige Fehlordnung der 001 Schichten hindeutet. Der Abschnitt auf der b-Achse (8.94 Å) war innerhalb der bei Kaoliniten üblichen (8,93–8,94 Å). Bei 3550 cm^{-1} wurden keine Infrarot-Absorptionspeaks gefunden, die auf Halloysit hingedeutet hätten. Die Neigungsverhältnisse des endothermen Peaks bei 550°C (1,4–2,3) der differentialthermoanalytischen Untersuchung lag im Bereich der Kaolinite (0,78–2,39). [U.W.]

Résumé—La kaolinite sphérique a été synthétisée pour la première fois à partir de matériel aluminosilicate non-cristallin dans des expériences hydrothermiques menées entre 150° et 250°C et sous une pression de vapeur autogène. Des sphérules dont les diamètres moyens dépendaient des conditions de croissance (0,1–0,6 μm) ont été formées autour de l'aluminosilicate non-cristallin dans tous les produits des expériences à 150° et 200°C, et coexistaient avec la kaolinite en plaquettes ou en forme de lattes dans les produits des expériences à 250°C. Les pourcentages de sphérules estimés dans les produits ont augmenté d'à peu près 1% dans le produit 150°C-15 jours à à peu près 74% dans le produit 200°C-8 jours, et a diminué d'à peu près 21% dans le produit 250°C-2 jours à 0% dans le produit 250°C-8 jours. Des images de lattice par microscope électronique à haute résolution ont indiqué que les sphérules consistaient d'empilement de couches presque concentriques avec un espacement d'unités de 7 Å, sectionnés par des limites radiantes. La composition chimique moyenne des sphérules (Al_2O_3/SiO_2 = 0,58) analysée par le microscope électronique analytique est semblable à celle de la kaolinite (Al_2O_3/SiO_2 = 0,5). Même dans le cas du produit abondant en sphérules (200°C-8 jours), les clichés de diffraction des rayons-X des produits mouillés, e.g., de l'expérience à 200°C-8 jours, ont montré la réflection 7,14-Å (001) de la kaolinite. La réflection 020 était large, indiquant l'existence d'abondants déplacements de couche (001). L'axe b (8,94 Å) est dans la gamme de la kaolinite (8,93–8,94 Å). Aucun sommet d'absorption infrarouge n'a été observé à 3550 cm^{-1}, ce qui corresponderait à l'halloysite. Les proportions de courbes d'analyse différentielle thermique du sommet endothermique à à peu près 550°C (1,4–2,3) étaient dans la gamme de la kaolinite (0,78–2,39). [D.J.]