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HYDROTHERMAL SYNTHESIS OF KAOLINITE, DICKITE, BEIDELLITE, AND NONTRONITE

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ABSTRACT

Kaolinite was synthesized by heating coprecipitated $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels and mixtures of Al_2O_3 and SiO_2 with water in a pressure bomb at 310°C . Similarly dickite was prepared by treating coprecipitated $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels at 350°C and 365°C , beidellite from mixtures of Al_2O_3 and SiO_2 at 350°C and 390°C , and also from coprecipitated gels and kaolinite at 390°C . Nontronite was made by treating a coprecipitated $\text{Fe}_2\text{O}_3\text{-2SiO}_2$ gel at 350°C . Beidellite was formed in these experiments in the presence of soda by transport of SiO_2 in solution to the Al_2O_3 and reaction with Al_2O_3 in situ.

The products were identified by X-ray patterns. Their optical properties were also consistent with those of the natural minerals. The stability ranges of kaolinite, dickite, and beidellite probably occur in the order named, with increasing temperature. This relation between kaolinite and dickite is consistent with geological evidence as to their formation in nature.

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I. INTRODUCTION

The formation of kaolin ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$) in nature and its possible synthesis in the laboratory have been a matter of much interest to geologists, chemists, and soil scientists for many years, and have been the subject of much speculation, but it has only been in the last decade that any successful experimental results have been obtained.

Schwarz and Brenner (1)¹ made coprecipitated gels of the composition $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ which were amorphous, but which after aging for 21 days at 20° C had a crystalline structure "related to that of kaolin" as shown by an X-ray pattern.

Van Nieuwenburg and Pieters (2), expressing doubts regarding the synthesis of kaolin claimed by Schwarz and Brenner, made a coprecipitated gel of composition $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ by a modification of Schwarz and Brenner's method and heated the gel in an autoclave for 12 days at 200 to 260 atmospheres steam pressure. This gave a product which was birefringent, had approximately the same mean index of refraction and density as kaolin, and from which a very small amount of Al_2O_3 was extracted by HCl. Their product was probably a kaolin mineral, but they did not make any X-ray patterns of it, and X-ray patterns constitute the only criterion of crystalline identity in such finely divided materials.

Noll (3) prepared a coprecipitated gel of composition $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot \text{aq.}$ by the method of Schwarz and Brenner, which was amorphous when first prepared and was still amorphous after standing 2 years in air. When this gel was heated with water in a pressure bomb for 5 days at 250 to 300° C (corresponding to 40 to 90 atmospheres steam pressure), there resulted a product which gave an X-ray pattern identical with that of kaolin. Noll made no reference to Van Nieuwenburg's work and had evidently not seen it. Noll made no attempt to distinguish between kaolinite, dickite, and nacrite, the three closely related kaolin minerals, although the paper by Ross and Kerr (4) describing the differences between them had been published at that time.

The present paper carries the work further and describes the synthesis of both kaolin and dickite in different temperature ranges, of beidellite, a related clay mineral, in still a third temperature range, and of nontronite, the iron analogue of beidellite.

II. DESCRIPTION OF PURE CLAY MINERALS USED AS COMPARISON MATERIALS

1. KAOLIN MINERALS—FORMULA $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$

Washed kaolinite from Zettlitz, distributed as an international standard by the Ceramic Society of Czechoslovakia, dickite from the National Belle mine, Red Mountain, Colo., and nacrite from St. Peters Dome, Colo., were used as reference materials. These minerals have been thoroughly described by Ross and Kerr (4). X-ray patterns of these minerals show significant differences. Patterns of kaolinite and dickite are shown in figure 1.

2. BEIDELLITE-NONTRONITE MINERALS—FORMULA $(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)\cdot 3\text{SiO}_2\cdot n\text{H}_2\text{O}$

Beidellite and nontronite are hydrous aluminum and iron silicates, respectively, with a $\text{SiO}_2\cdot \text{R}_2\text{O}_3$ ratio equal to 3. Both are orthorhombic minerals and have the same X-ray patterns, except that the lines of nontronite are all shifted towards the zero beam relative to those of beidellite (fig. 2). They are therefore thought to be members of a series of isomorphous solid solutions. Both minerals

¹ Figures in parentheses here and throughout the text refer to the references at the end of this paper, p. 185.

have the same dehydration characteristics. Since they do bear this close relationship and since both end-members were synthesized in this work, they will be considered together.

Three beidellites were used as comparison materials:

(a) Montmorillonite from Otay, San Diego County, Calif.

(b) Beidellite from Beidell, Colo.

(c) Pink clay from pegmatite, San Diego County, Calif.

In spite of the differences in nomenclature and chemical composition (table 1), all 3 minerals gave the same X-ray patterns (fig. 2), except that the patterns of (a) and (c) have a few faint lines which do not appear in the pattern of (b) and all the lines in the pattern of (b) and (a) are shifted slightly toward the zero beam relative to (c). Also, by comparison with a photograph published by Hofmann, Endell, and Wilm (6), another montmorillonite (probably from Montmorillon, France), has the same pattern. In addition, (b) and (c) gave the same heating curves and the same dehydration curves.

TABLE 1.—Chemical composition and optical constants for beidellites and nontronite

| Constituents | Al ₂ O ₃ - 3SiO ₂ - 4H ₂ O (theoretical) | San Diego pink clay | Otay mont- moril- lonite | Beidell beidellite | Sandy Ridge nontron- ite | Fe ₂ O ₃ - 3SiO ₂ - 4H ₂ O (theoretical) |
|--------------------------------------|---|------------------------------|-----------------------------------|-----------------------|-----------------------------------|---|
| | Percent | Percent | Percent | Percent | Percent | Percent |
| SiO ₂ | 50.85 | ^a 43.62 | ^b 50.30 | ^c 47.28 | ^d 41.38 | 43.69 |
| Al ₂ O ₃ | 28.81 | 35.55 | 15.96 | 20.37 | 9.84 | ----- |
| Fe ₂ O ₃ | ----- | .21 | .86 | 8.68 | 27.47 | 38.83 |
| CaO..... | ----- | 1.02 | 1.24 | 2.75 | Trace | ----- |
| MgO..... | ----- | .19 | 6.53 | .70 | do..... | ----- |
| K ₂ O..... | ----- | .03 | .45 | Trace | do..... | ----- |
| Na ₂ O..... | ----- | .19 | 1.19 | .97 | do..... | ----- |
| H ₂ O..... | 20.34 | 18.88 | 23.61 | 19.72 | 21.35 | 17.48 |
| Total..... | 100.00 | 99.69 | 100.14 | 100.47 | 100.04 | 100.00 |

Optical Constants

| | | | | | |
|-------------------------|--------------------|--------------------|--------------------|-------|-------|
| α | ^a 1.495 | ^b 1.492 | ^c 1.494 | 1.54 | ----- |
| γ | 1.518 | 1.513 | 1.536 | 1.57 | ----- |
| $\gamma - \alpha$ | .023 | .021 | .042 | .03 | ----- |
| 2V..... | ----- | 16 to 24° | Small | ----- | ----- |

^a W. T. Schaller, analyst, reference (5).

^b J. E. Whitfield, analyst, reference (8).

^c E. T. Wherry, analyst, reference (7).

^d L. T. Richardson, analyst, private communication from C. S. Ross.

^e Reference (8).

The nontronite used as a comparison material was from Sandy Ridge, N. C. It gave an X-ray pattern like that of the above beidellites, but with all the lines shifted toward the zero beam (fig. 2).

The true chemical composition of the minerals in this group is by no means as definitely known as in the case of the kaolin minerals. While the R₂O₃:SiO₂ ratios reported in the literature vary greatly (in beidellites from 1:2.1 to 1:3.6 (6, 7, 8, 9, 10); in nontronites from 1:2.5 to 1:3.5 (11, 12, 13, 14, 15, 16)), analyses of the purest materials indicate that 1:3 is the ratio most probably correct. Ratios of R₂O₃:H₂O also vary greatly (in beidellites from 1:3.5 to 1:5.6; in nontronites from 1:2 to 1:5.5), but 1:4 and 1:5 are mentioned most frequently as being the probably correct ratios.

As in the case of the zeolites, the dehydration curves of beidellite and nontronite are smooth curves without regions of rapid loss of water and the X-ray patterns do not change with loss of as much as three-fourths of the water. These data show that a large part of the water content of beidellite and nontronite is zeolitic in nature, and therefore has little meaning in a constitutional formula. Tammann and Grevemeyer (11) and Geilmann, Klemm, and Meisel (16) conclude that in nontronite one molecule of water is constitutional and is not lost until 300 to 500° C, whereas the other three or four molecules are lost below 200° C. The latter give no detailed data, and the data of the former, when plotted as a weight loss-temperature curve, offer small support for their conclusion. Our own dehydration experiments on beidellite and nontronite, and those of Larsen and Wherry (7) on beidellite, and of Larsen and Steiger (12) on nontronite fail to confirm this conclusion.

Ross and Shannon (8) conclude that at least some montmorillonites (including the one from Otay, Calif.) contain one molecule of constitutional RO (CaO + MgO), and Larsen and Steiger (12) believe the same to be true of some nontronites. However, this is certainly not a necessary part of the beidellite structure, as will be demonstrated in this paper.

To sum up this discussion, it may be stated that the probable formulas of the end members of the beidellite-nontronite series, whose synthesis will be described below, are $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$, where n is often 4 or 5 in natural minerals, but is variable as in zeolites.

Hofmann, Endell, and Wilm (6) have recently determined the crystal system of montmorillonite and a bentonite (localities not given) to be orthorhombic, a fact which several authors had previously surmised.

III. PREPARATION OF MATERIALS

Coprecipitated hydrogels of compositions $2\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$, $\text{Al}_2\text{O}_3\text{-}4\text{SiO}_2$ and $\text{Fe}_2\text{O}_3\text{-}2\text{SiO}_2$ were prepared by the method of van Nieuwenberg and Pieters (2). To a 4 percent solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in water, sufficient sodium silicate solution (containing 68 g of SiO_2 per liter) was added dropwise with constant stirring to give the desired molar ratios of alumina to silica. Then the solution was neutralized (to phenol red) by slowly adding 10 percent NaOH solution. The precipitate was filtered, dried at 110° C, ground to pass a no. 200 sieve, washed on a filter with hot water and again dried at 110° C. The $\text{Fe}_2\text{O}_3\text{-SiO}_2$ gel was similarly made from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and sodium silicate, using litmus paper as the indicator.

Schwarz and Brenner (1) and Schwarz and Walcker (17) found that an $\text{Al}_2\text{O}_3\text{:SiO}_2$ ratio of 1:5 was needed in the solutions to get a product $\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$. However, van Nieuwenburg and Pieters (2), using a slightly different procedure, found that the ratio in the precipitates was the same as the ratio in the solutions. Analyses of three of our 1:2 gel preparations gave $\text{Al}_2\text{O}_3\text{:SiO}_2$ ratios of 1:1.99, 1:1.90, and 1:1.88, respectively, which confirm van Nieuwenburg's findings. The other gels were not analyzed, but after the filtrates were evaporated to dryness on the steam bath they were found to be practically completely water-soluble in all cases. Any Al_2O_3 , Fe_2O_3 or SiO_2 in this

neutral filtrate would have precipitated in insoluble form on evaporation.

Amorphous SiO_2 gel was prepared by precipitating sodium silicate solution with HCl . The precipitate was filtered, dried, and washed as described above.

Amorphous Al_2O_3 gel was prepared by precipitating AlCl_3 solution with NaOH in iced solution at the neutral point. The gelatinous precipitate was filtered, dried, and washed as described above. Precipitation by NaOH at higher temperatures, or precipitation by NH_3 at any temperature failed to give a completely amorphous precipitate.

All these gels were found to consist of clear angular, isotropic grains when examined under the microscope, and X-ray photographs showed they were all amorphous.

The presence of soda in these preparations was not suspected until late in the investigation. The 1:1.88 coprecipitated gel mentioned above was analyzed for soda and found to contain 0.65 percent of Na_2O .²

All the other gels involving the use of either sodium silicate or sodium hydroxide were found to contain small amounts of soda, as indicated by testing with zinc uranyl acetate. This soda undoubtedly had some effect on the results given in this paper, as will be discussed later.

$\gamma\text{-Al}_2\text{O}_3$, a crystalline modification of anhydrous Al_2O_3 , was prepared by heating aluminum nitrate overnight at 750°C .

Böhmite, a crystalline modification of $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, was prepared by heating Al_2O_3 gel in an autoclave with water 18 hours at 350°C .

Each of these three forms of alumina was mixed with dried silica gel and also with finely powdered silica glass in proportions to give $\text{Al}_2\text{O}_3:\text{SiO}_2=1:2$. These mixtures were moistened and ground together in an agate mortar for 15 minutes and dried, and this process was repeated twice more, thus insuring uniform mixing and comparatively intimate contact.

IV. APPARATUS

A bomb, capable of withstanding 2,000 atmospheres pressure at 400°C , was constructed of tool steel according to the design of Morey and Fenner (18), with walls 12 mm thick and a capacity of 21 ml. The furnace used for heating the bomb was made of no. 16 nichrome wire wound on a mica-covered iron pipe and insulated with 4 inches of diatomaceous silica brick. The heating zone was twice as long as the bomb in order to insure uniform temperature distribution.

Temperatures were measured to $\pm 1^\circ\text{C}$ by means of a chromel-alumel thermocouple inserted in a well in the body of the bomb, and a portable potentiometer.

Identification of the crystalline compounds in the products was made by comparison of X-ray powder diffraction patterns, using either $\text{Mo } K\alpha$ radiation from a Coolidge tube and a camera of 20.8 cm radius, or $\text{Cu } K$ radiation from an ion tube and a camera of 4.1 cm radius. Both cameras were arranged for taking direct comparison photographs of two materials on the same film.

² The percentage composition of this gel computed to a water-free basis was: SiO_2 52.19, Al_2O_3 47.13, Na_2O 0.92.

V. GENERAL EXPERIMENTAL PROCEDURE

The 5 coprecipitated gels and the 6 mixtures of alumina and silica were inclosed in covered platinum or porcelain capsules (3 ml and 2 ml capacity, respectively) and treated with water in the bomb. Most of the experiments were carried out in one of three temperature ranges: 305 to 315, 340 to 355, or 380 to 395° C. The temperature variation during each experiment was within $\pm 5^\circ$ C. The temperatures given in column 3 of tables 2 and 3 are estimated average temperatures, and the pressures in column 4 are the water-vapor pressures corresponding to these temperatures. At temperatures above the critical point of water (374° C and 218 atmospheres) the pressures were taken from the isothermal curves of van Nieuwenburg and Blumendal (19), the mass of water in the bomb being estimated roughly (an error of 10 percent in the estimate corresponds to a difference of only 3 atmospheres at 390° C). The times of heating given in column 2 of tables 2 and 3 are somewhat arbitrary and were not based on any predetermined rate of reaction.

After the heating period was completed, the bomb was removed from the furnace, and cooled in air; the products were then removed and dried at 110° C.

While principal dependence for identification was placed in the X-ray patterns, examinations of the products were also made with a petrographic microscope. In most cases the product was a heterogeneous mixture of amorphous and birefringent material, which made accurate determination of optical properties difficult, but in some cases good crystals were obtained.

VI. SYNTHESIS OF KAOLINITE AND DICKITE

1. EXPERIMENTAL RESULTS

The results are summarized in table 2, from which it is evident that, in general, kaolinite resulted from treatment of coprecipitated Al_2O_3 - SiO_2 gels and admixtures of alumina and silica at 310° C, and dickite resulted from treatment of the coprecipitated gels at 345, 350, and 365° C.

X-ray patterns of the products of experiments 6 and 8 are reproduced in figure 1. The patterns of synthetic kaolinite and synthetic dickite show the same characteristic differences (indicated by arrows) as do the natural minerals.

TABLE 2.—*Synthesis of kaolinite and dickite*

| Experiment | Starting material | Time of treatment | Temperature | Pressure | X-ray pattern of product |
|------------|--|-------------------|-------------------------|----------|--------------------------|
| | | <i>Days</i> | $^\circ\text{C}$ | atm | |
| 1..... | Al_2O_3 - 2SiO_2 coprecipitated gel. | 300 | ^a Room temp. | 1 | Amorphous. |
| 2..... | do..... | 300 | Room temp. | 1 | Do. |
| 3..... | do..... | 100 | ^a 95 | 1 | Do. |
| 4..... | do..... | 100 | 95 | 1 | Do. |
| 5..... | do..... | 11 | 250 | 39 | Weak kaolinite. |
| 6..... | do..... | 7 | 310 | 97 | Kaolinite. |
| 7..... | do..... | 7 | 345 | 157 | Weak dickite. |
| 8..... | do..... | 11 | 345 | 157 | Dickite. |
| 9..... | do..... | 10 | 365 | 202 | Do. |
| 10..... | Al_2O_3 - 4SiO_2 coprecipitated gel. | 10 | 350 | 167 | Do. |
| 11..... | Al_2O_3 - SiO_2 coprecipitated gel. | 8 | 350 | 167 | Dickite and böhmite. |
| 12..... | $2\text{Al}_2\text{O}_3$ - SiO_2 coprecipitated gel. | 10 | 350 | 167 | Böhmite. |
| 13..... | Al_2O_3 gel + 2SiO_2 gel (mixed)..... | 10 | 310 | 97 | Kaolinite. |

^a Unpurified gel aged in contact with original supernatant liquid, following Schwarz and Brenner (1). In all other experiments purified (but not soda-free) gels were treated with pure water.

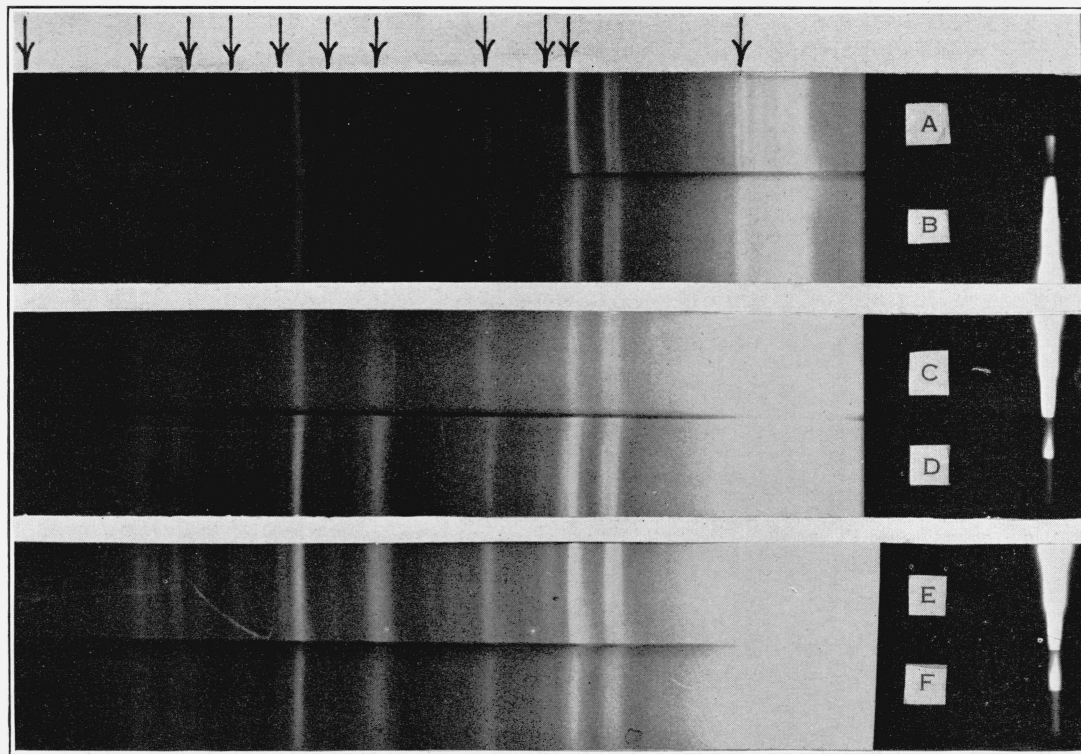


FIGURE 1.—X-ray patterns of natural and synthetic kaolinite and dickite.

A, Red Mountain dickite B, zettlitz kaolinite; C, synthetic dickite (experiment 6); D, zettlitz kaolinite; E, Red Mountain dickite; F, synthetic kaolinite (experiment 8).

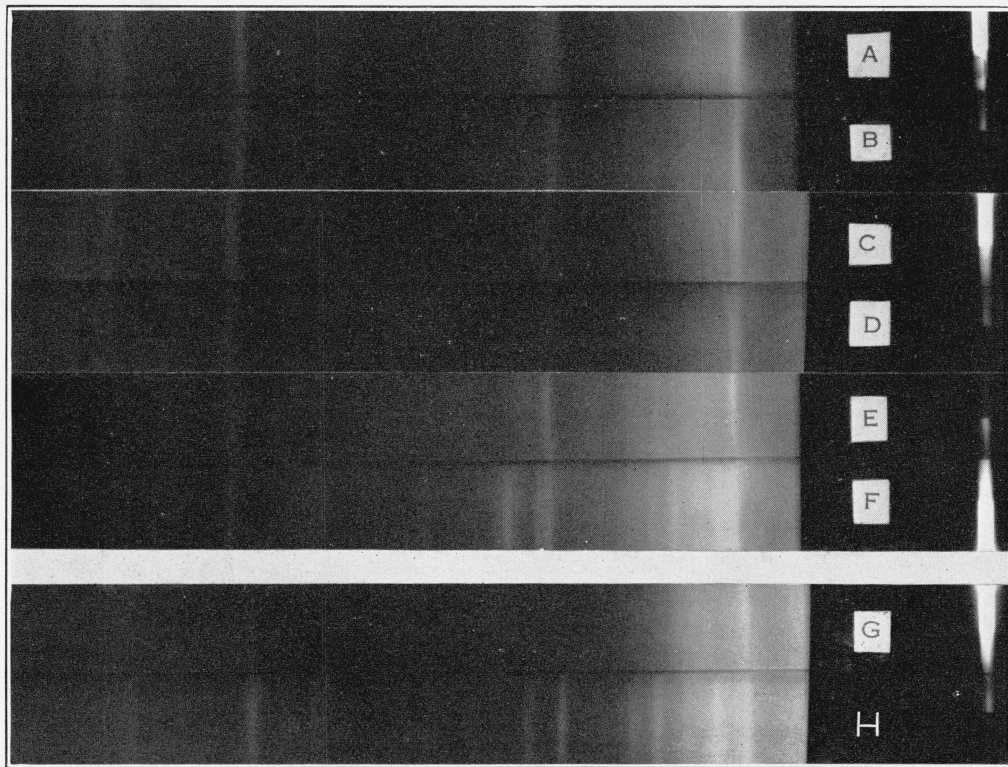


FIGURE 2.—X-ray patterns of natural and synthetic beidellite and nontronite.

A, Montmorillonite from Otay, Calif.; B, beidellite from Beidell, Colo.; C, "pink clay" from San Diego, Calif.; D, synthetic beidellite (experiment 14); E, beidellite from kaolinite (experiment 23); F, zettlitz kaolinite; G, nontronite from Sandy Ridge, N. C.; H, synthetic iron silicate product.

2. DISCUSSION OF RESULTS

Schwarz and Brenner (1) claimed that, while newly precipitated Al_2O_3 - SiO_2 gels were amorphous, after aging 21 days in contact with the original mother liquor, one gel developed a crystalline structure which was shown by X-rays to be "similar to or at least closely related to that of kaolin", but they gave no reproduction of their X-ray pattern or spacing data. Our experiments 1 and 2, aged at room temperature in water and in contact with the mother liquor, respectively, for periods greatly exceeding those used by Schwarz, fail to confirm his results. Furthermore, experiments 3 and 4, performed at 95°C , where any crystallization process would be expected to proceed more rapidly, failed to give any evidence of crystallinity. In addition, Schwarz states that all the alumina in his product was soluble in HCl and that the product lost most of its water below 260°C , both of which properties are unlike those of kaolinite.

Gels with a higher ratio of Al_2O_3 to SiO_2 than 1:2 may contain böhmite as is shown by experiments 11 and 12. Experiment 13 shows that kaolinite may also be formed from mixtures of the amorphous oxides although not in as close contact as in the coprecipitated gels (see other results with mixtures of the oxides in section VII).

3. MICROSCOPICAL EXAMINATION OF PRODUCTS

Microscopical examination of the synthetic kaolinite-dickite products showed them to be very heterogeneous and finely divided, and no accurate measurements of optical properties could be made. However, the following optical characters were observed—

Experiments 1, 2, 3, 4. Clear, isotropic grains, no perceptible birefringence.

Experiment 5. Very slight birefringence, mean index of refraction about 1.51.

Experiment 6. Somewhat more birefringent than 5, index of a few grains higher than 1.56 but most were lower than 1.56.

Experiments 7, 8, 9. Moderate birefringence, mean index about 1.56.

Experiment 10. About the same birefringence as 7, mean index about 1.52.

Experiment 12. High birefringence, mean index about 1.62.

The birefringence and mean index of the products of experiments 7, 8, and 9 agree with those of dickite. The low mean index of 10 is probably explained by the excess silica and the high birefringence and high mean index of 12 are due to the large amount of böhmite present.

VII. SYNTHESIS OF BEIDELLITE

1. EXPERIMENTAL RESULTS

In general beidellite was formed by treatment of mixtures of alumina and silica at 350 and 390°C , and of coprecipitated gels and of kaolinite at 390°C . The results are summarized in table 3. Experiments 24 to 28 are inserted to show how the individual component oxides used in experiments 14 to 21 behave when treated alone under the same conditions.

TABLE 3.—*Synthesis of beidellite*

| Experiment | Starting material | Time of treatment | Temperature | Pressure | X-ray pattern of product |
|------------|---|-------------------|-------------|----------|---------------------------|
| | | Days | °C | atm | |
| 14..... | Al ₂ O ₃ gel+2SiO ₂ gel..... | 12 | 350 | 167 | Beidellite. |
| 15..... | Al ₂ O ₃ gel+2SiO ₂ glass..... | 12 | 350 | 167 | Beidellite+faint böhmite. |
| 16..... | γ-Al ₂ O ₃ +2SiO ₂ gel..... | 18 | 350 | 167 | Beidellite. |
| 17..... | γ-Al ₂ O ₃ +2SiO ₂ glass..... | 18 | 350 | 167 | Do. |
| 18..... | Böhmite+3SiO ₂ gel..... | 9 | 350 | 167 | Böhmite+beidellite. |
| 19..... | Böhmite+3SiO ₂ glass..... | 9 | 350 | 167 | Do. |
| 20..... | Al ₂ O ₃ gel+2SiO ₂ gel..... | 10 | 390 | 260 | Beidellite. |
| 21..... | γ-Al ₂ O ₃ +2SiO ₂ gel..... | 10 | 390 | 260 | Do. |
| 22..... | Al ₂ O ₃ -2SiO ₂ coprecipitated gel..... | 14 | 390 | 260 | Do. |
| 23..... | Zettlitz kaolin..... | 14 | 390 | 260 | Do. |
| 24..... | Al ₂ O ₃ gel..... | 5 | 350 | 167 | Böhmite. |
| 25..... | γ-Al ₂ O ₃ | 5 | 350 | 167 | Do. |
| 26..... | Böhmite..... | 5 | 350 | 167 | No change. |
| 27..... | SiO ₂ gel..... | 5 | 350 | 167 | Cristobalite. |
| 28..... | SiO ₂ glass..... | 10 | 350 | 167 | No change. |

2. DISCUSSION OF RESULTS

Patterns of the products of experiments 14 and 23 are reproduced in figure 2. Patterns of 15, 16, 17, 20, and 21 were identical with that of 14, except for the presence of a few faint lines of böhmite in the pattern of 15. The differences between the patterns of beidellite and kaolinite are quite pronounced and leave no doubt as to the identity of these synthetic beidellite products.

The pattern of 23 is that of beidellite, except for the presence of 3 or 4 faint lines which are not present in the pattern of pure beidellite and which have not been accounted for, and is profoundly different from that of the Zettlitz kaolin, from which it was made. This change in crystal structure is also apparent microscopically, the birefringence having increased from 0.006 (value for kaolinite) to more than 0.030. The pattern of 22 was identical with that of 23.

As will be shown in section VIII, the products of experiments 18 and 19 would probably have gone completely to beidellite if given a longer time. Experiments 14 to 19 show no significant difference in the reactivity of SiO₂ gel and SiO₂ glass.

3. MICROSCOPICAL EXAMINATION OF PRODUCTS

The synthetic beidellite products were much better crystallized and their optical properties could be more accurately determined than in the case of the synthetic kaolin minerals. The indices of refraction of the products were all higher than those of natural beidellite (see table 1) and, furthermore, beidellites formed in different experiments at the same temperature varied in indices. These variations might be due to variations in water content or to variations in Al₂O₃:SiO₂ ratio. Examinations of partially dehydrated natural beidellite showed qualitatively that the indices do vary with water content. Larsen and Steiger (12) found that the indices of nontronite increased with loss of H₂O, and beidellite would be expected to behave similarly.

The synthetic beidellites consisted principally of platy material with low birefringence when viewed normal to the cleavage and moderately high birefringence (0.020 to 0.030) when viewed parallel to the cleavage. The plates sometimes occurred as spherulitic

aggregates. Extreme variations in indices of refraction were: $\alpha=1.51$ to 1.545 and $\gamma=1.53$ to 1.575 . When the plates stood on edge they gave the appearance of birefringent needles of parallel extinction and positive elongation, and provided the best means of determining the maximum and minimum indices.

Besides the platy materials, there were also aggregates of finely divided material presenting a mosaic appearance, partly crystalline (probably beidellite like the platy material) and partly amorphous. These particles usually had birefringent margins which were convenient for determining indices. The appearance of some of the products was strikingly like that of some natural beidellites, montmorillonites and bentonites.

The results of microscopical examination of products of some of the experiments were as follows:

Experiments 16 and 17. Principally imperfect spherulites and some plates with $\alpha=1.52$, $\gamma=1.54$.

Experiment 14. More heterogeneous than 16, many plates with $\alpha=1.51$, $\gamma=1.53$.

Experiment 15. Most like natural beidellite in appearance, many plates with $\alpha=1.53$, $\gamma=1.55$.

Experiment 23. Large masses of highly birefringent plates with $\alpha=1.545$, $\gamma=1.575$, quite different in appearance and index from the original kaolinite.

Experiment 22. Mosaic particles with mean index of 1.56 and moderate birefringence. There were no particles large enough to measure indices in different directions.

Since experiments 23 and 22 have identical X-ray patterns and their mean indices are consistent, they are probably the same material.

VIII. MECHANISM OF FORMATION OF BEIDELLITE

It will be noted from tables 2 and 3 that dickite was formed from coprecipitated gels, and beidellite from alumina-silica mixtures at the same temperature, namely, 345 to 350°C . This difference in resulting product is probably due to the greater intimacy of contact between the alumina and silica in the gels than in the mixtures. That there is sufficiently intimate contact between alumina and silica in coprecipitated gels to bring molecular forces into play has been indicated by recent work of the present authors (20). Since there is this close molecular contact in the gels, it is not difficult to imagine a mechanism of direct combination of alumina, silica, and water to form dickite and kaolinite.

However, since the alumina and silica could hardly have been in such close contact in the mixtures of experiments 14 to 21 in spite of the thorough grinding, it seemed interesting to try to discover the mechanism of beidellite formation in these experiments. Three possible mechanisms suggest themselves:

(a) Solution of SiO_2 and its transport through the liquid phase to the Al_2O_3 where the reaction takes place between SiO_2 in solution, and solid Al_2O_3 .

(b) Solution of Al_2O_3 and its transport through the liquid phase to the SiO_2 , where the reaction takes place between Al_2O_3 in solution and solid SiO_2 .

(c) Solution of both Al_2O_3 and SiO_2 and reaction in solution with precipitation of beidellite.

In order to test these hypotheses, six experiments were performed. In each experiment about $\frac{1}{2}$ g of either dried Al_2O_3 gel or SiO_2 gel was placed in the bottom of the bomb. A smaller amount (about $\frac{1}{20}$ g) of the other oxide was placed in a platinum capsule, which was then filled with water and covered with a platinum foil cap tightly wired on. The capsule was placed in the bomb on top of the first-mentioned oxide and water added to cover the capsule. The cover of the capsule was wired on so tightly that no convection currents could possibly carry the outside oxide into the capsule, and therefore any transport of either oxide would have to be made by means of diffusion of dissolved material. After each experiment, X-ray patterns were made of the material in the capsule. The results are summarized in table 4.

TABLE 4

| Experiment | Oxide in capsule | Oxide outside capsule | Time | Temperature | Pressure | X-ray pattern of material in capsule | X-ray pattern of material outside capsule |
|------------|----------------------------------|-------------------------------|-----------|-------------|-------------|--------------------------------------|---|
| 29..... | Al_2O_3 gel..... | SiO_2 gel... | 12 days.. | ° C 355 | atm. 178 | Beidellite... | Cristobalite. |
| 30..... | SiO_2 gel..... | Al_2O_3 gel.. | 10 days.. | 355 | 178 | (See next paragraph of text.) | Böhmite. |
| 31..... | do..... | None..... | 7 days... | 355 | 178 | do..... | None. |
| 32..... | Al_2O_3 gel..... | SiO_2 gel... | 12 days.. | 385 | 248 | Beidellite... | Cristobalite. |
| 33..... | do..... | do..... | 4 hours.. | • 385 | 248 | Böhmite..... | Do. |
| 34..... | Product of 33 (in capsule). | None..... | 10 days.. | 355 | 178 | do..... | None. |

* The bomb was removed when the temperature first reached 385°C , 4 hours after the beginning of heating.

X-ray patterns of the products inside the capsule from experiments 29 and 32 were identical with that of 14 shown in figure 2. In experiment 30 most of the SiO_2 (at least 75 percent) had disappeared from the capsule. The small amount that was left was yellow-brown in color, presumably due to iron. It gave an X-ray pattern different from patterns of both beidellite and cristobalite, and which did not correspond to any known form of silica, alumina, aluminum silicate, iron oxide, or iron silicate. Microscopical examination showed it to be a yellowish, crystalline material with an index (about 1.67) too high for a hydrated aluminum silicate. The same result was obtained in experiment 31 when there was no Al_2O_3 in the bomb.

The evidence of experiments 29, 30, and 31 shows that beidellite must have been formed in experiments 14 to 21 by transport of SiO_2 in solution, and not by transport of Al_2O_3 , and that therefore hypothesis (a) is the correct one.

Microscopical examination of the products inside the capsule from experiments 29 and 32 showed them to consist entirely of good spherulites of birefringent plates (fig. 3) with mean index of 1.53 and birefringence of at least 0.020. At the center of each spherulite there was a small core of a material with higher index. In the light of experiment 33, this core is undoubtedly böhmite (index about 1.65).

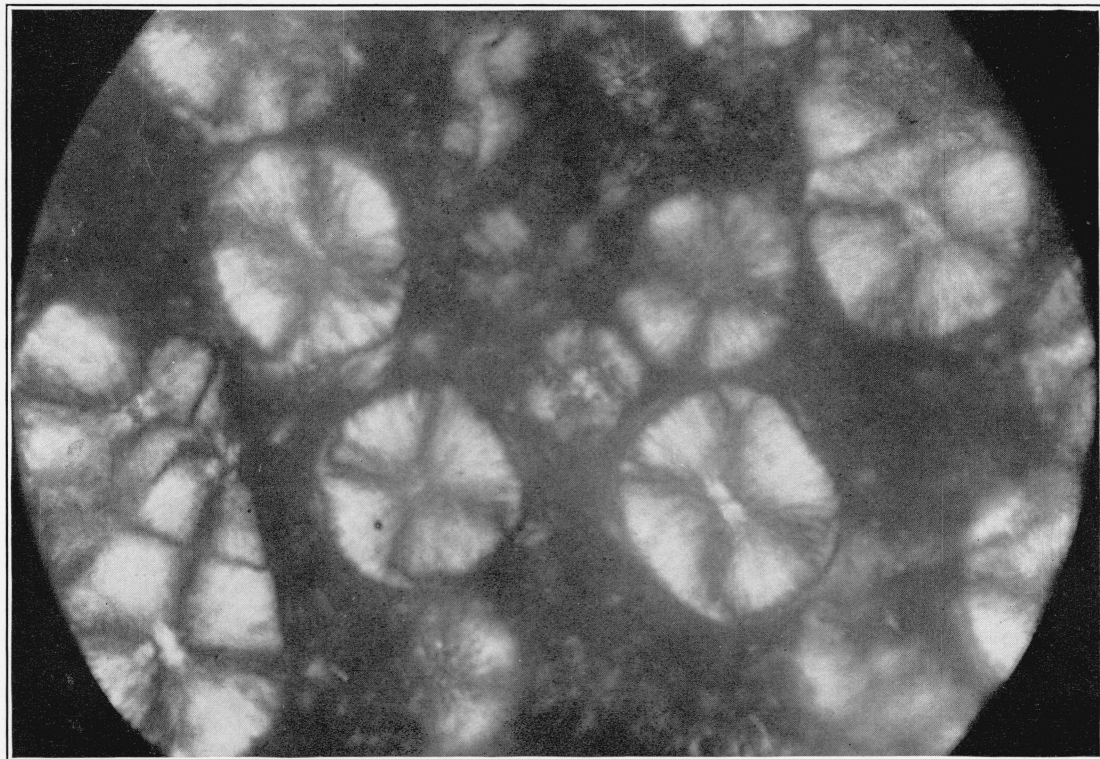


FIGURE 3.—*Spherulites of synthetic beidellite from experiment 29.*
Crossed nicols. Magnification 1,400 \times .

The absence of böhmite lines in the X-ray pattern is due to the small amount of böhmite (less than 2 percent) in the spherulites. Formation of böhmite in these experiments is evidently an intermediate step in the formation of beidellite, and is probably completed before the slower process of solution of the silica and its diffusion and reaction with the alumina has even reached a steady state.

The product of experiment 32 was identical with that of 29, although the former experiment was carried out above the critical temperature of water where there is no liquid phase (or rather, where the differences between the liquid and vapor phases become indeterminate). These two experiments indicate a transport of silica through the gaseous as well as the liquid phase. Van Nieuwenburg and Blumendal (21, 22, 23, 24) and Gillis (25) have given evidence that many silicates may be formed pneumatolytically by transport of silica through the compressed gaseous phase, while Morey (26) was unable to duplicate their results. Morey concluded that the transport of silica in their experiments must have taken place through the liquid phase in the heating interval before the temperature exceeded the critical point. Our experiments 33 and 34 were performed to test this conclusion. Experiment 33 shows that no beidellite was formed up to the time when the critical temperature was exceeded. The product of experiment 34 shows further that 33 did not contain any appreciable amount of silica which had been transported through the liquid phase but had not yet reacted with the alumina, since no beidellite was observed in 34. It may, therefore, be concluded that the beidellite in 32 was formed by transport of silica through the dense gaseous phase. One would hardly expect a discontinuity in the solubility of silica in water at the critical temperature, since the properties of water (which determine its solvent power) undergo no discontinuity at that temperature.

The presence of soda in the materials used, mentioned in section III, may have had some effect on these experiments. In order to test this, some new soda-free gels were prepared. A new silica gel was prepared by boiling a commercial silica gel in concentrated nitric acid; the product gave a residue of 0.05 percent nonvolatile with hydrofluoric acid. A new alumina gel was prepared by precipitating aluminum chloride with ammonia instead of sodium hydroxide; this gel was not completely amorphous as was the gel precipitated with sodium hydroxide in iced solution, but gave a faint diffuse X-ray pattern of böhmite. Both these preparations were indicated to be free from soda by testing with zinc uranyl acetate. When experiments 27, 29, and 32 were repeated using these gels, the results were not the same as given above. The silica gel did not change to cristobalite in any of the experiments; in 29 and 32 the material inside the capsule was böhmite instead of beidellite. These results show that soda was a necessary factor in the formation of beidellite in the experiments reported in this paper. Probably the soda accelerates the reaction by increasing the solubility of the silica (and possibly that of the alumina also). The presence of soda in the coprecipitated gels probably was a factor in the formation of kaolinite and dickite in experiments 1 to 13, but whether it was a necessary factor would be hard to prove since it would be difficult to prepare such a coprecipitated gel completely free of soda.

IX. SYNTHESIS OF NONTRONITE

The dried $\text{Fe}_2\text{O}_3\text{-}2\text{SiO}_2$ gel was treated in the bomb for six days at 340 to 350° C. The resulting product was a mixture of a red and a green material. When treated with hot 6*N* HCl the red material (hematite) quickly dissolved, leaving the bright green material. This was washed and dried at 110° C.

The X-ray pattern of the green material (fig. 2) showed lines corresponding to each line of natural nontronite, plus several extra lines which did not correspond to any known form of iron oxide or silica.

Chemical analysis of the green material dried at 110° C gave: Fe_2O_3 41.6, SiO_2 53.5, H_2O 4.9 percent, corresponding to a molar ratio of $\text{Fe}_2\text{O}_3\text{:}3.43 \text{SiO}_2\text{:}1.04 \text{H}_2\text{O}$.

Microscopical examination of the green material showed the presence of two intimately associated phases in about equal amounts:

1. Small needles (or plates on edge) with $\gamma=1.63$, $\alpha=1.60$, positive elongation, parallel extinction.

2. Large masses of weakly birefringent green material with no extinction position.

Substance 1 is probably nontronite since its optical properties are consistent with those of natural nontronite (Larsen and Steiger (12) give variations of the β index of nontronite as 1.585 for 13.06 percent of H_2O to 1.69 for 1.81 percent of H_2O), and the extra lines in the X-ray pattern must be ascribed to substance 2. The nature of substance 2 was not investigated further. It is probably a hydrated iron silicate, and from comparison of the above chemical analysis with the formula of pure nontronite ($\text{Fe}_2\text{O}_3\text{:SiO}_2 = 1\text{:}3$), substance 2 must have $\text{SiO}_2\text{:Fe}_2\text{O}_3$ greater than 3.5, possibly 4.

A ground mixture of Fe_2O_3 and SiO_2 gel was also treated in the bomb, but only hematite and cristobalite resulted.

X. HYDROTHERMAL TREATMENT OF OTHER ALUMINUM SILICATES

Andalusite, cyanite, sillimanite (all of formula $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), pyrophyllite ($\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$) and orthoclase ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$) were heated in the bomb for 10 days at 350° C. No change was observed in any case.

XI. DISCUSSION

The data in this paper pertain to the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Data such as these are difficult of accurate interpretation since amorphous solid phases are present in the final products and conditions are such that equilibrium may not have been reached. Furthermore there are surface forces in the coprecipitated gels which make the results of those experiments uncertain in their relation to true equilibrium. Thus it can be concluded from these data only that the stability ranges of kaolinite, dickite, and beidellite probably occur in that order with increasing temperature.

Ross and Kerr (4) have summarized the geological evidence pertaining to the formation of the kaolin minerals and conclude that kaolinite is the result of low-temperature weathering processes and that dickite and nacrite are formed by hydrothermal processes at

higher temperatures. This conclusion is consistent with the relative temperatures of formation of kaolinite and dickite given in this paper.

The conditions of formation of beidellite in nature are not well known, but at least some bentonites (a rock containing beidellite) seem to have been formed by low-temperature weathering of volcanic glass. This is seemingly in opposition to our data.

Nacrite and pyrophyllite were not observed in any of the products, so their regions of stability are either outside the range studied or occupy a narrow range which was overlooked.

XII. SUMMARY

Four clay minerals were synthesized by treating coprecipitated hydrogels and mixtures of oxides with water in a pressure bomb at high temperatures as follows:

1. Kaolinite from coprecipitated $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels and mixtures of Al_2O_3 and SiO_2 at 310°C .
2. Dickite from coprecipitated $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels at 350°C and 365°C .
3. Beidellite from mixtures of Al_2O_3 and SiO_2 at 350 and 390°C and coprecipitated gels and kaolinite at 390°C .
4. Nontronite from a coprecipitated $\text{Fe}_2\text{O}_3\text{-2SiO}_2$ gel at 350°C .

The products were identified by X-ray powder patterns. Their optical properties were also consistent with the natural minerals.

Beidellite was formed in these experiments in the presence of soda by transport of SiO_2 in solution to the Al_2O_3 and reaction with the Al_2O_3 in situ. This is true both below and above the critical temperature of water. In the absence of soda this reaction did not take place.

The stability ranges of kaolinite, dickite, and beidellite probably occur in the order named with increasing temperature. This relation between kaolinite and dickite is consistent with geological evidence pertaining to their formation in nature.

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