THE SYSTEM Al$_2$O$_3$-SiO$_2$-H$_2$O

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ABSTRACT

A fundamental approach has been attempted in the study of the temperatures of formation and limits of stability of certain clay minerals and metamorphic rock assemblages. This has been done by studying the phase equilibrium relationships in the system Al$_2$O$_3$-SiO$_2$-H$_2$O under conditions of independently controlled temperature and water-vapor pressure. The data from a large number of runs are presented in a series of compatibility triangles for various temperatures and pressures. The equilibrium decomposition temperature of the kaolinite minerals has been placed at 405° C. (at 10,000 psi water pressure) and that of pyrophyllite at 575° C. Two new clay-phases exist in the system and are described in detail, one a pure Al-Si montmorillonite and the other herein named hydralsite, one of the decomposition products of kaolinite. The application of the results to geological and ceramic problems is discussed.

I. INTRODUCTION

Minerals appearing as phases in the system alumina-silica-water (Fig. 2) have been recognized by mineralogists and geologists as being important keys in attempts to decipher the history of rocks. Fenner's study (1913) of the silica minerals, describing the stable and metastable ranges of existence of the various forms of silica, and the investigation of the system Al$_2$O$_3$-SiO$_2$ by Bowen and Greig (1924), which indicated that mullite, rather than andalusite, sillimanite, or kyanite, is the stable aluminosilicate at high temperatures and atmospheric pressure, were significant milestones in studies contributing to our knowledge of the ternary system. More recently, hydrothermal studies, summarized to 1937 by Morey and Ingerson (1937a), have added further data. Among the many later papers may be mentioned especially those by Noll (1944), Ewell and Insley (1935), and Gillingham (1948).

Conditions of temperature, pressure, and composition at which the hydrous aluminosilicates can be synthesized have been of especial interest in previous studies. Data are numerous and conflicting. In Table 1 an attempt is made to summarize the most reliable of these data on stability ranges of ternary compounds. Kaolinite has been synthesized

at temperatures as low as 250° C., and up to 400° C. and a montmoril-lonite probably of the composition near beidellite has been obtained within approximately the same range of temperature where alkali ions have been present. The stability range of kaolinite, particularly the upper temperature limit was not established. Similarly no previous data are at hand to indicate the temperature ranges of stability for pyrophillite and a pure alumina-silica montmorillonite if such a structure exists. The rela-tionship between endellite and halloysite provides another problem, and

TABLE 1. SUMMARY OF PREVIOUS DATA ON THE STABILITY RANGE OF ALUMINA-SILICA HYDRATES

Mineral	Workers	Minimum		Maximum		Time Days
		Temp. °C.	Press. psi.	Temp. °C.	Press. psi.	
Kaolinite	Ewell and Insley (1935)	250	600	310	1450	10
	Noll (1944)	250	600	400	4500	
Dickite	Ewell and Insley (1935)	345	2300	365	3000	10
Nacrite	Permyakov (1936)	335	4500			6
Beidellite	Ewell and Insley (1935)	350	2500	390	3900	10
Montmorillonite	Noll (1944)	Same range as kaolinite				
Pyrophyllite	Noll (1944)	400	4500	500	8000	

a definite series of dehydration temperatures of endellite to halloysite with varying pressure should exist.

The stability ranges of sillimanite and kyanite are unknown. Kyanite has not been synthesized, but possibly sillimanite has. Synthesis of sil-limanite has been reported by Morey (1942), Balconi (1941), and Michel-Levy (1950), but in no case was unequivocal evidence presented that the "sillimanite" was not mullite. Andalusite has been reproducibly synthe-sized by our colleague, D. M. Roy (1953). The suggested range of sta-bility at high water pressures is 450° to 650° C. or higher.

The present study is directed toward finding compatible phases under conditions of divariant equilibrium, and the phase equilibria are de-scribed by means of composition triangles, i.e., combinations of three phases which co-exist stably in a particular range of temperature and pressure. The results embody the data relating the starting material, temperature, pressure and time to the product as identified by optical and *x*-ray methods, for some 2,000 runs. The implications of the results in terms of natural mineral association are discussed.

II. Method of Investigation

A. Equipment

The hydrothermal equipment used consists of pumps in parallel supplying water under pressure through a system of pressure lines and valves to separate vessels. Each pressure vessel, or bomb, is heated to the desired temperature in an automaticallly controlled furnace, and maintained at a particular pressure independent of that in other bombs in the system. The motor driven pumps with a ball and cone seat are rated for 40,000 psi., but after a few weeks operation with distilled water need constant attention to reach pressures above 20,000 psi. A high-pressure pump (Roy and Osborn, 1952) consisting of a stainless steel chamber in which water is compressed with a stainless steel jack,⸱ was constructed, and pressures up to 50,000 psi. can be reached in a few seconds. Much higher pressures are attainable, but are limited by the system of valves and tubing. No leaking occurred in this pump in over one year's continuous and varied operation supplying 20 separate vessels.

The pressure vessels used include the closed type of bomb described by Morey and Ingerson (1937*b*); a modification of this bomb, wherein the plug was drilled and then this connected to the pressure line; and a smaller modification of the "Morey-type" bomb which proved very convenient (Roy and Osborn, 1952*a*). The type of pressure vessel used most extensively was the "test-tube" bomb (see Roy, Roy and Osborn, 1950), a thick-walled test tube of stainless steel or another high-temperature alloy, usually 8 inches long, $1''$ outer diameter, $\frac{1}{8}''$ inner diameter, closed at one end and the other attached to the pressure line. The sample is placed in the bottom and the bomb suspended vertically with a thermocouple well near the sample. The top of the bomb extends about two inches above the top of the furnace. For highest temperatures an apparatus similar to that described by Tuttle (1949) was used. In addition, for hastening reaction and decomposition, a "grinding" apparatus (Roy and Osborn, 1952) was used, consisting of rotating Morey type bombs containing several stainless steel rods. The sample is ground at high temperatures and pressures as the bomb rotates.

B. Starting Materials

Standard methods are not available for the preparation of mixtures, and reactivity of alumina-silica mixtures is extremely slow. Mechanical mixtures of the reactive substances, γ-Al₂O₃ (very finely divided, $<.02\mu$ size) and dried silica gel were tried, but even these fine-grained, metastable starting materials were not satisfactory from the standpoint of completely reacting to yield equilibrium phases. More suitable starting materials were co-precipitated alumina-silica gels. The gels were first

prepared according to the method described by Ewell and Insley (1935), which consisted of coprecipitating solutions of aluminum nitrate and sodium silicate, adjusting the pH to slightly basic with NH_4OH, and washing several times after filtering. The gels thus prepared contain sufficient Na_2O to yield sodium-containing minerals such as analcime, and are not suitable for accurate work in the system Al_2O_3-SiO_2-H_2O. Further purification was carried out by electrodialysis in an apparatus similar to that described by Roy (1949), for two to three days in order to remove the alkali. The maximum Na_2O content of the gels thus prepared was of the order of $\frac{1}{2}$ to $\frac{1}{4}$ of one per cent, or less. Mixtures were also prepared from ethylorthosilicate and aluminum nitrate by dissolving in absolute ethyl alcohol and evaporating and heating, thus avoiding Na_2O altogether.

Natural minerals, purified by various methods including electrodialysis and in some cases synthetic minerals prepared in the present study were used as starting materials, particularly for the determination of decomposition temperatures.

C. Procedure

The materials were contained in small platinum or gold envelopes, and in confirmatory runs these were surrounded by another envelope containing more of the same materials acting as a buffer. Temperatures were automatically regulated, and measured with chromel-alumel thermocouples made of calibrated wire, which rarely showed a variation of more than $\pm 1°$ C. when checked with standards. The bombs were brought up to temperature as rapidly as possible with the pressure turned on. An over-all precision of $\pm 3°$ C. was attainable under the best conditions, and reproducible with the same type of apparatus. Generally speaking the data presented are accurate to $\pm 10°$ C. and ± 3 per cent of the pressure.

The products were identified largely by x-ray diffraction techniques, in combination with petrographic methods and electron microscopy. Most of the products were extremely fine-grained, and the petrographic microscope was not very useful. Phases such as montmorillonite were further identified by expansion characteristics (observed in the x-ray diffraction pattern) and differential thermal analysis. X-ray data were obtained on North American Philips Geiger-counter spectrometer units. Cu-Kα radiation (filtered through Ni) was used in most cases. Such a unit is of great help especially in studying the endellite-halloysite relationship since no tedious experimental procedure is necessary. The sample is simply made into a paste with water and placed on the glass slide. Under ordinary room temperature conditions conversion of endellite to

halloysite does not take place in less than $\frac{1}{2}$ hour, and only 5 minutes are essential for identification.

III. DESCRIPTION OF MINERALS, THEIR SYNTHESIS AND DECOMPOSITION

A. *Compounds in the System Al₂O₃-SiO₂*

1. *Sillimanite, Andalusite and Kyanite*. Attempts were made to synthesize these three minerals of the composition $Al_2O_3 \cdot SiO_2$, using a great variety of starting materials. Hydrothermal runs (nearly 500) were made in the temperature range 110° to 930° C. at pressures of 1,000 to 30,000 psi., starting either with minerals or with gels with ratios of 2:1, 1:1 and 1:2 alumina:silica. In no case were we able to synthesize any of these minerals beyond doubt. Seeding with one of the minerals or all three simultaneously was also tried, but no growth was observed on any seeds. Attempts were made to repeat all previously reported syntheses of sillimanite, by following as closely as possible the described procedures such as those of Balconi (1941) and Michel-Levy (1950). In no case was a product formed which could unequivocally be distinguished from mullite. There has been much interest recently in distinguishing sillimanite from mullite by *x*-ray methods (McAtee and Milligan, 1950, and de Keyser, 1951). In the light of this work, the differences appear to be so small that we consider it impossible to identify positively the broadened patterns obtained from the fine-grained products, especially when admixed with other phases. Relying on optical and thermal evidence only, we were unable to find a single clear case of the formation of sillimanite. Attempts were made to duplicate the synthesis of andalusite as described by Baur (1911, 1912), but we were unable to identify any andalusite in the product. Hydrothermally treating the groundmass of a schist which contained andalusite phenocrysts did not result in certain growth of andalusite. The usual product included a micaceous phase and some needle-like crystals having approximately the correct refractive index for andalusite, but the needles existed in insufficient quantity to identify by *x*-ray difraction and were not large enough to determine the optical properties accurately. Since these experiments were carried out, Lacy (1951) has reported the synthesis of andalusite by a somewhat similar method, although again the identification based on optical properties of very small crystals is not certain.[1] As mentioned earlier, D. M. Roy has now reproducibly synthesized andalusite.

Several unidentified phases were encountered in these studies. Occasionally the *x*-ray diffraction pattern of a particular phase matched that of andalusite or kyanite fairly well. In the absence of definite duplicate

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[1] Lacy, E. D., Personal communication, 1952.

runs and optical evidence, however, synthesis of these minerals is questionable.

Decomposition through ordinary hydrothermal treatment was slight. Several runs giving long exposure at 700° to 900° C. to water at pressures in the range 2,000 to 10,000 psi. caused slight decomposition of kyanite, and possibly of sillimanite and andalusite as indicated under the light microscope. The products of decomposition were not detected in the x-ray diffraction patterns. In the higher temperature runs (800°–900° C.) corundum made an anomalous appearance as small hexagons in the decomposition product in several runs. Decomposition of the natural minerals by grinding at lower temperatures was more complete. Andalusite, sillimanite and kyanite were decomposed in the grinding apparatus at temperatures of 350° to 450° C. and water pressures in the range of 2,000 to 5,000 psi. The efficiency of the grinding apparatus (Roy and Osborn, 1952) may be illustrated by the fact that in static runs at 375° C. no evidence for kaolinite was obtained in the x-ray pattern after 60 or 90 days, whereas considerable kaolinite is formed in 3 days of grinding. Below 400° C. the decomposition products contained mainly kaolinite, and usually included a mica, suggesting the presence of alkali in the natural minerals. The mica may, however, have been present as an original undetected impurity.

2. *Mullite.* The aluminosilicate phase formed in most cases from high-alumina mixtures at temperatures above about 425° C. is mullite ($3Al_2O_3 \cdot 2SiO_2$). At lower temperatures the hydrates, diaspore, kaolinite, and aluminum montmorillonite, are stable in the presence of high pressure water. Mullite was identified in most cases by x-ray diffraction patterns since the crystals were too small to identify optically. The difficulty in distinguishing between the x-ray diffraction patterns of mullite and sillimanite makes it possible that in some cases the pattern ascribed to mullite was actually that of sillimanite.

Mullite was decomposed through long runs in the grinding apparatus at temperatures of 330° and 450° C. (water pressures 2,000 and 10,000 psi.), and the products included kaolinite, pyrophyllite, and possibly hydralsite. No recognizable decomposition was effected through ordinary hydrothermal treatment at higher temperatures up to 900° C. for two weeks.

B. *Compounds in the System Al_2O_3-H_2O*

The system Al_2O_3-H_2O has been described by Laubengayer and Weisz (1943) and by Ervin and Osborn (1951). A schematic representation of the relations among the compounds is shown in Fig. 1. The only crystalline phases stable under hydrothermal conditions are gibbsite, boehmite,
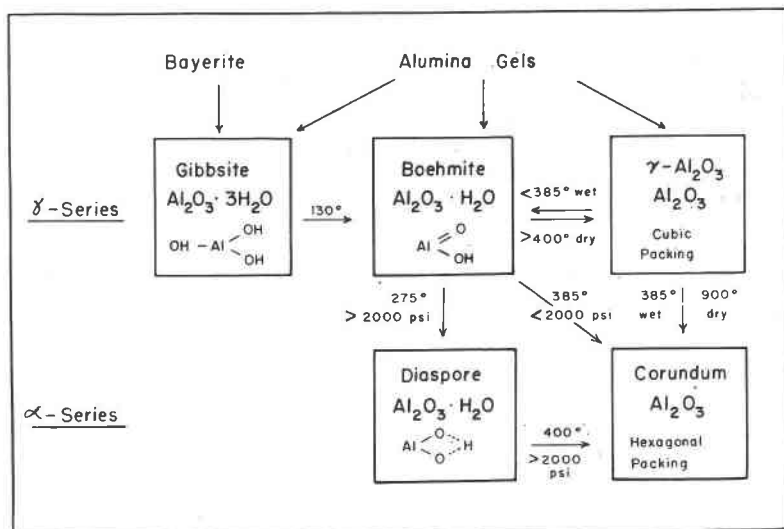
Fig. 1. Schematic representation of relationships among phases in the system
Al_2O_3-H_2O.

diaspore and corundum. Under such conditions gibbsite is formed stably
below 130° C. Boehmite[2] exists stably between 130° and 275° C. at pres-
sures greater than 2,000 psi., and up to 385° C. at lower pressures. Dia-
spore is apparently formed only under pressures greater than 2,000 psi.,
and at temperatures between 275° and 415° C.; in most cases "seeding"
is necessary for the growth of this crystalline phase. Otherwise boehmite
will be formed metastably. However, diaspore was synthesized under
very high water pressures by Ervin and Osborn (1951), and we have re-
cently synthesized crystals, without seeding, at pressures as low as
20,000 psi. Crystals 1 to 2 mm. in length have been obtained. Corundum
or α-Al_2O_3, is the stable phase above 410° C., and almost invariably
grows as euhedral hexagonal prisms.

C. Ternary Compounds

1. *Endellite and Halloysite.* The ternary phase of highest water content
(see Fig. 2) is endellite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$),[3] and this on partial dehydra-
tion yields halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Bates, Swineford and Hilde-

[2] A typographical error in the paper of Ervin and Osborn for the refractive indices of
synthetic boehmite has been noted. These should be: $\alpha = 1.649 \pm 0.001$, $\beta = 1.659 \pm 0.002$,
$\gamma = 1.665 \pm 0.002$.

[3] Throughout this paper the terms "endellite" and "halloysite" are used to designate
the phases of nominal composition $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ and $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, respectively.
Other workers (see for example Brindley, 1951) have chosen to refer to the first as "hal-
loysite" and to the second as "metahalloysite."

brand (1950) have demonstrated that endellite and halloysite have a tubular habit. Acceptance of this view leads to the deduction that halloysite cannot be formed except by dehydration of endellite. The tubes of endellite are believed to develop as a consequence of the "misfit" between the silica and gibbsite layers in the structure and because of the separation of the layers one from the other by a layer of water molecules. When this interlayer water is removed, halloysite is formed as the layers collapse and meet, setting up new bonds which apparently cannot be broken again to permit the re-entry of water. Thus, once endellite has been dehydrated
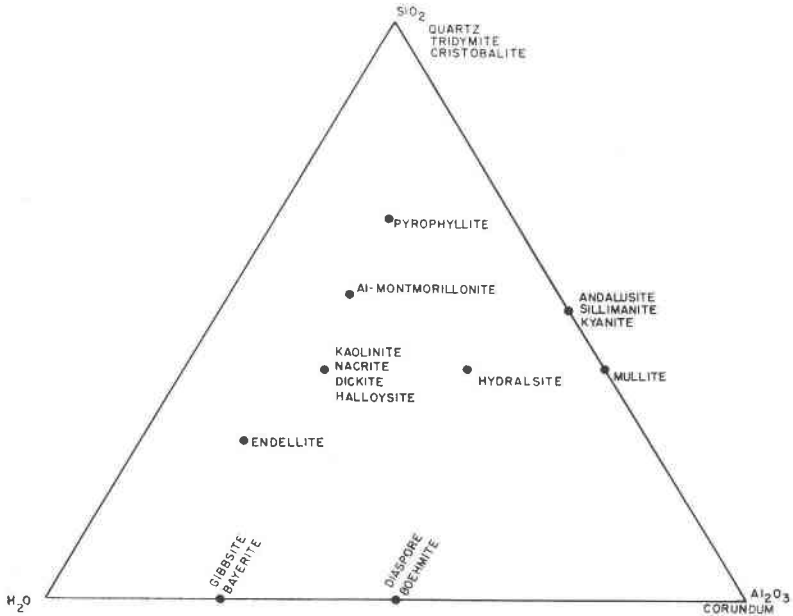

Fig. 2. Crystalline phases in the system Al_2O_3-SiO_2-H_2O.

to yield halloysite, rehydration back to endellite will not take place. This is borne out by all the experimental evidence to date. We have not yet synthesized endellite (and therefore halloysite). Runs of duration from one month to three months, and "grinding" runs have been made starting with gels, at temperatures from 100° upwards to 400° C. When any crystalline structure has appeared it has been that of kaolinite, but generally at the low temperatures virtually no reaction takes place. Halloysite and kaolinite from several localities were treated under various conditions, usually the same conditions as above, and the wet sample was examined for any sign of the formation of endellite. In no case has endellite appeared.

Brindley and Goodyear (1948) have stated that halloysite has an 001 spacing of 7.4 or 7.5kX. Such a spacing was encountered in several of our runs and it was at first considered feasible that the 7.4 Å reflection—characteristic of a hydrate with more than 2 H_2O—represented the true value for halloysite. This would have meant that halloysite and kaolinite are not polymorphs. However, a study of the spacings of halloysite dehydrated at temperatures from 100° C. to 450° C. shows that after the attainment of equilibrium the spacing is constant at 7.17 Å. Apparently in the work of Brindley (1951, p. 52) and also in our runs which yielded a structure with a 7.4 Å spacing, dehydration was not carried to equilibrium at the temperatures used. In hydrothermal runs at temperatures and pressures in the region near the equilibrium decomposition curve, endellite may dehydrate only partially to yield the 7.4 Å phase. However, we have found that the spacing of halloysite derived by decomposition of endellite under temperature and pressure conditions existing to the right of Curve II (Fig. 6) is invariably 7.17 Å. Moreover, halloysites dehydrated at 110° C., 300° C. and 400° C. would not rehydrate to the 7.4 Å phase, even under high water pressures at appropriate temperatures. While the above shows that halloysite is a true polymorph of kaolinite with a 7.17 Å spacing, it also does suggest that the interlayering proposed by Brindley and Goodyear has some unique stability, since no other intermediate spacings have been consistently found.

2. *Kaolinite, Nacrite and Dickite* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Kaolinite, or a mineral of the kaolin group was synthesized from coprecipitated Al_2O_3-SiO_2 gels between 150° and 405° C., under varying water pressures. Identification was made by x-ray diffraction, and in some cases the crystals were well enough formed to show distinctive shapes under the electron microscope. No distinction was made between kaolinite, nacrite or dickite in the products of reaction. These products are extremely fine-grained, yielding diffuse x-ray diffraction patterns from which a clear verdict with respect to which of the three phases is present cannot readily be obtained. For the same reason, members of the kaolin group (such as the fire clay minerals) (Brindley & Robinson, 1947) are not distinguished. The product therefore is referred to as kaolinite. In many runs, the pattern obtained was more similar to nacrite or dickite than to kaolinite, but no trends could be found indicating that certain temperature-pressure ranges favored formation of nacrite or dickite. From the natural occurrences it might be expected that nacrite and dickite would form at higher temperatures. However, even at 400° C. and 10,000 psi., only 5° C. below the stability limit of the three minerals as determined by decomposition studies, the x-ray diffraction pattern of the synthesized structure agrees more closely with that of kaolinite than

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TABLE 2. X-RAY AND ELECTRON DIFFRACTION DATA ON PHASES

HYDRALSITE				PYROPHYLLITE				
X-ray		Electron		Natural (API)		Synthetic (F-228)		
"d" (Å)	I/I_0	"d" (Å)	$hk0$*	"d" (Å)	I/I_0	hkl†	"d" (Å)	I/I_0
8.91	80			8.97	30	002	9.32	90
4.448	60	4.45	100			?	4.94	15
3.414	100	2.57	110	4.53	40	020, 004	{4.634	20
2.430	50	2.225	200				4.439	100
2.362	40	1.682	210	4.12	20	{111		
						11$\bar{2}$	{4.280	30
2.074	20	1.483	300			021	4.077	30
2.044	10	1.285	220	3.85	5	{11$\bar{3}$		
						022	3.786	5
1.845	20	1.234	310	3.34	25	113	3.420	15
1.810	10	1.113	400			?	3.186	5
1.768	20	1.021	320	3.037	80	006	3.084	90
1.471	5	.9706	410	2.524	20	200	2.571	40
1.450	10	.8902	500			13$\bar{2}$	2.543	60
1.405	10	.8565	330	2.400	30	204	2.424	70
						132		
1.3804	10	.8410	420	2.287	20	008	2.309	5
1.3360	5	.7988	510	2.142	15	20$\bar{6}$	2.166	20
						134		
1.2765	5	.7418	600	2.071	10	204	2.078	40
1.2343	20	.7316	430	2.044	10			
		.7126	520	1.881	5			
		.6787	610	1.828	30	0010	1.843	20
		.6424	440					
		$a_{\text{hex}} = 4.450$		$a_0 = 5.14$		$a_0 = 5.13$		
		$a_{\text{orth}} = 5.138$		$b_0 = 8.90$		$b_0 = 8.88$		
		$b_{\text{orth}} = 8.90$		$c_0 = 18.55$		$d_{001} = 18.50$		

* This is indexed on 120° hexagonal axes.

† *API* Indices common to natural and synthetic pyrophyllite.

of nacrite or dickite. Other factors than temperature appear to be responsible for the formation in nature of nacrite and dickite instead of kaolinite.

Decomposition runs were made on several natural minerals. Three different samples of kaolinite were studied to check on the variations within the same mineral species: Florida kaolinite, Langley kaolinite, and kaolinite from Banda, India. The last is an extremely pure kaolinite which under the electron microscope is seen to consist only of well-

formed hexagons. Halloysite samples used were from Eureka, Utah, and Bedford, Indiana. The dickite used was from Pottsville, Pa., and the nacrite from Brand, Saxony (obtained through the courtesy of Dr. C. Frondel). All these minerals were found to decompose at the same temperature, within experimental error, this being 405° C. at 10,000 psi. water pressure. Varying the pressure from 2500 to 25,000 psi. did not alter the decomposition temperature by more than 10° C. from this value. The main difference in decomposition behavior is the rate of decomposition, with the larger particles of dickite and nacrite requiring longer periods of time to effect significant decomposition (see Table 3). Differences in the thermodynamic constants among these four phases must be slight.

The first phase forming on hydrothermal decomposition of kaolinite, nacrite, dickite, and halloysite is so-called "hydralsite" which is described below. Mullite and pyrophyllite or mullite and cristobalite are formed at higher temperatures, usually not much below 500° C.[4]

3. *Hydralsite.* On the hydrothermal decomposition of kaolinite, nacrite, dickite and halloysite, or when $1:2$ $Al_2O_3:SiO_2$ gels are heated under water pressure at temperatures greater than 405° C., a hydrous aluminosilicate phase appears which does not occur as a mineral nor has it been encountered in other investigations. X-ray and electron diffraction data and an electron micrograph of this phase appear in Table 2 and Fig. 3a. In a previous publication (Roy and Osborn, 1952), we referred to this structure as "X-phase" for lack of a better name. Inasmuch as this is a term applicable to any unknown phase, whereas the approximate composition and many of the properties of this compound are known, some other designation is needed. The term "hydralsite," a contraction of hydro-aluminosilicate, is used herein for convenience for want of anything better. This term would be equally applicable to any of the ternary phases, but confusion should not result inasmuch as the others all have mineral names.

Hydralsite contains less H_2O and has a higher $Al_2O_3:SiO_2$ ratio than kaolinite. Its precise composition is not known, but evidence suggests a composition in the neighborhood of $2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ or conceivably $Al_2O_3 \cdot SiO_2 \cdot H_2O$. That this phase is a monohydrate is not established beyond question because of the inevitable uncertainty regarding purity of samples used in water loss determinations and because the $Al_2O_3:SiO_2$ ratio is not definitely known. The weight loss (at 1,000° C. for 50 hours) of hydralsite, prepared from kaolinite and dried to constant weight at 110° C., was 5.61 per cent. Another sample, prepared from a 1:1 Al_2O_3

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[4] Earlier workers have reported the formation of pyrophyllite at temperatures just above the stability limit of kaolinite. There is little doubt that hydralsite was here mistaken for pyrophyllite.
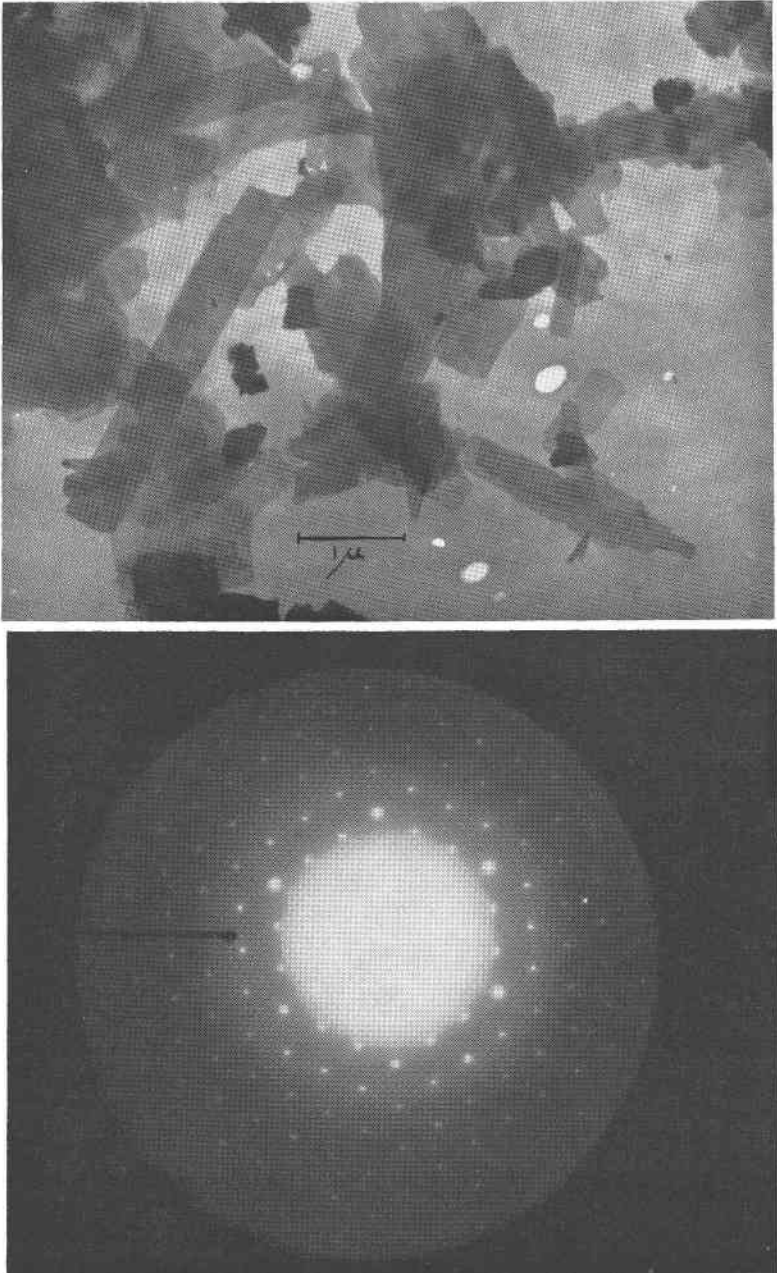
Fig. 3. Hydralsite prepared from 1:1 Al_2O_3:SiO_2 gel: (a) Electron micrograph.
(b) Single crystal electron diffraction pattern.

: SiO_2 nitrate-ethyl silicate mixture, showed a weight loss of 6.03 per cent. The weight loss corresponds approximately to the water content of $2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, which is 5.27%. The $Al_2O_3 : SiO_2$ ratio is considered to be higher than that in kaolinite on the basis of the following facts: (1) On the complete conversion of kaolinite, hydralsite is invariably accompanied by a small amount of pyrophyllite, no other phase being present in sufficient amounts to be identified (see Table 5). Were the $Al_2O_3 : SiO_2$ ratio in hydralsite and kaolinite the same, either hydralsite alone should be the decomposition product or a higher alumina phase such as mullite as well as pyrophyllite should be present (due to non-equilibrium conditions) with hydralsite in the mixture. Similarly, if the $Al_2O_3 : SiO_2$ ratio were lower than in kaolinite, some other higher alumina phase must be present. (2) Starting with a $1:1$ $Al_2O_3 : SiO_2$ gel or nitrate-ethyl-silicate mixture, the product contains no detectable pyrophyllite or other phase than hydralsite, and under the electron microscope appears more homogeneous and better crystallized. This does not necessarily prove, however, that the $Al_2O_3 : SiO_2$ ratio is $1:1$ because in our experience some Al_2O_3 or SiO_2 or both may remain in an apparently "amorphous" state and not be readily detected, at least at lower temperatures.

Hydralsite bears a resemblance to paragonite and pyrophyllite in its x-ray diffraction pattern, but as may be seen from Table 2, the basal spacing is distinctly different from that of pyrophyllite (8.91 Å for hydralsite as compared with 9.0 Å for pyrophyllite). Moreover, the strongest reflection for pyrophyllite, at 3.04 Å, is completely absent in the pattern for hydralsite. Single crystal electron diffraction patterns[5] (Fig. 3*b*) yield directly the *a* and *b* parameters: $a = 5.14$, $b = 8.90$. The pseudo-hexagonal nature of the *a-b* projection can be seen immediately from the photograph (Fig. 3*b*). Careful measurement shows that the cell is not triclinic like kaolinite, the *a* and *b* axes intersecting at 90° within the precision of measurement (one part in one thousand in favorable cases). The basal spacing (equal to $c \sin \beta$) as obtained from x-ray diffraction is 8.91 Å.

From the data available certain speculations can be made regarding the structure of hydralsite. A formula of $Al_2O_3 \cdot SiO_2 \cdot H_2O$ can be fitted into a structural scheme wherein a disilicic tetrahedral layer is formed by aluminum replacement, the charge being balanced by the introduction of more hydroxyl ions in place of oxygen (Fig. 4*a*). However, such a formula requires a weight loss on ignition of about 10% which is far

[5] These patterns were initially obtained through the assistance of Dr. A. F. Moodie (of the CSIRO, Melbourne, Australia), and we are also greatly indebted to Dr. Moodie for advice and guidance in obtaining and interpreting single crystal electron diffraction patterns. These patterns are similar in type to those published by Finch (1937), Cowley (1952, 1953), and Brown and Clark (1952).

greater than that found. The formula $2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$ would be in better accord with all the *compositional* data. A structure compatible with this may be obtained by replacement of more than $\frac{1}{4}$ of the tetrahedral Si by Al, and the balance of charge being made up by a possible filling of more than $\frac{2}{3}$rds of the octahedral positions by Al. Under such conditions any exact stoichiometric ratios for the hydralsite phase would be unlikely, as is seen in Fig. 4 (*b*) and (*c*).

POSSIBLE STRUCTURES FOR HYDRALSITE

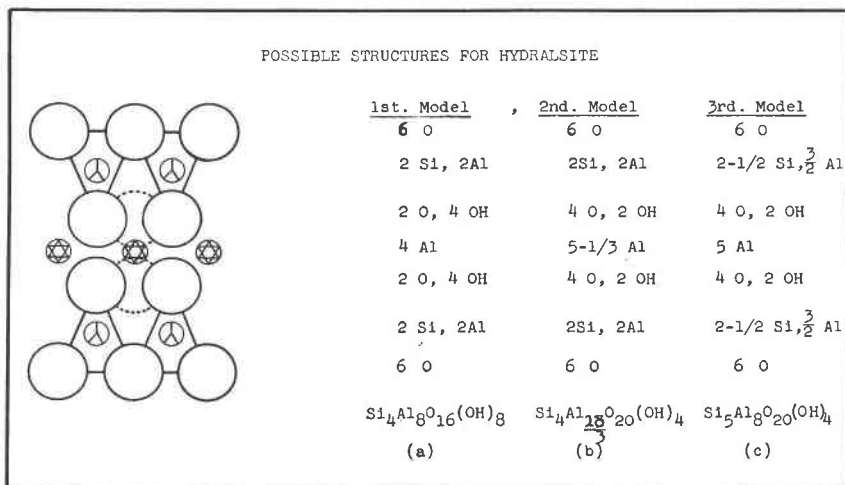|	1st. Model	, 2nd. Model	3rd. Model
	6 0	6 0	6 0
	2 Si, 2Al	2Si, 2Al	2-1/2 Si, $\frac{3}{2}$ Al
	2 0, 4 OH	4 0, 2 OH	4 0, 2 OH
	4 Al	5-1/3 Al	5 Al
	2 0, 4 OH	4 0, 2 OH	4 0, 2 OH
	2 Si, 2Al	2Si, 2Al	2-1/2 Si, $\frac{3}{2}$ Al
	6 0	6 0	6 0
	$Si_4Al_8O_{16}(OH)_8$	$Si_4Al_{\frac{28}{3}}O_{20}(OH)_4$	$Si_5Al_8O_{20}(OH)_4$
	(a)	(b)	(c)

Fig. 4. Schematic representation of possible structures for hydralsite based on a mica-type arrangement, with complete "internal" balance as suggested by low base exchange capacity.

The index of refraction of hydralsite is not distinctly different from that of pyrophyllite, being of the order of 1.600. The differential thermal analysis pattern of hydralsite resembles that of mica or pyrophyllite rather than that of a clay mineral. A broad endothermic peak, which may be accentuated by increasing the rate of temperature rise to 12° C. per minute, occurs with the maximum at 550° C. (see Fig. 5*a*). The infrared absorption for hydralsite is indicated in Fig. 5*b*.

The hydralsite structure persists to high temperatures when heated in air. A recognizable *x*-ray diffraction powder pattern is still obtained after heating hydralsite for 30 hours at 900° C.

The surface area of a sample made from other minerals as starting materials was about 57 m^2/g. The base exchange capacity is quite low, also indicative of a "balanced" structure. A value of only 1 m.eq./100 gms. was obtained on the same sample.[6]

Hydralsite is formed invariably under the conditions given, but no consistent maximum stability limit or temperature of decomposition could be obtained. Pyrophyllite and mullite are the products of its decomposition, as determined in these studies, and in addition andalusite as found by D. M. Roy (1953). Once formed it has never been converted
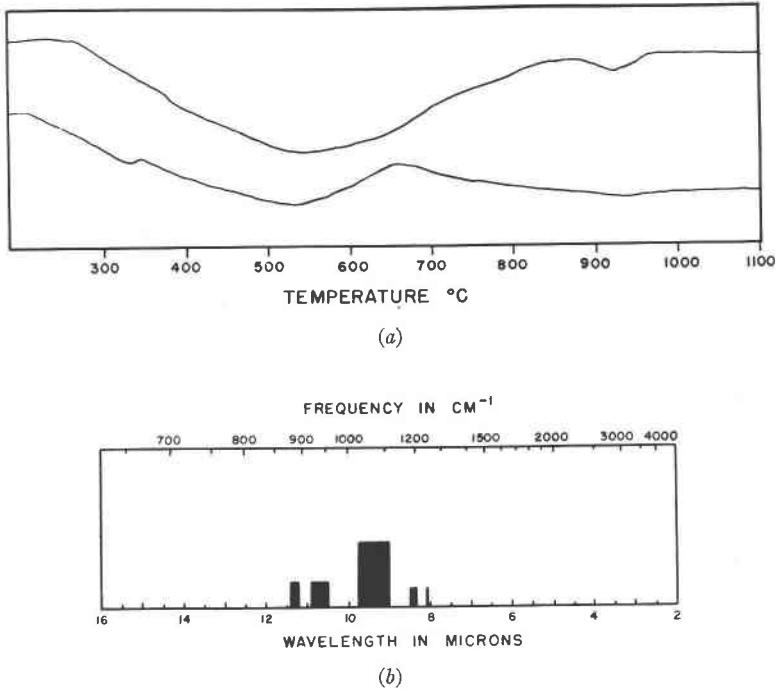

TEMPERATURE °C

(*a*)

FREQUENCY IN CM⁻¹

WAVELENGTH IN MICRONS

(*b*)

FIG. 5. (*a*) Two differential thermal analysis curves of hydralsite. The material used for the upper curve was prepared from a 1:1 Al_2O_3-SiO_2 gel; that for the lower curve from kaolinite. Heating rate used: 12° C./min. (*b*) Infra-red absorption spectrum for hydralsite shown as a block diagram.

to kaolinite or montmorillonite. An interesting observation in connection with studies in the system MgO-Al_2O_3-SiO_2-H_2O (Roy and Roy, 1952) is that hydralsite is still formed in the presence of Mg^{2+}, at temperatures between the upper stability temperature of Mg-montmorillonite and the lower temperature of formation of pyrophyllite.

While the double layer structures (kaolinite, etc.) are not stable above 405° C., the triple layer structures, pyrophyllite and montmorillonite,

[6] We are indebted to Mr. T. D. Oulton of the Filtrol Corp., Los Angeles, for the measurements of surface area and base exchange capacity.

persist as stable phases to higher temperatures. Therefore, the former (double layer structures) must decompose to yield the latter (triple layer structures) when heated under equilibrium conditions. This involves a major rearrangement of atoms, including the complete removal of one gibbsite sheet. In this process an intermediate, metastable phase might be expected to form. Hydralsite may be such a phase, appearing invariably on the decomposition of double layer structures. Our inability to obtain consistent decomposition temperatures for hydralsite is also suggestive of metastability. The non-occurrence of hydralsite in nature may possibly be explained both on the basis of this probable metastability and on the fact that the ubiquitous alkali ions would facilitate the transformation to micas and montmorillonites.

4. *Aluminum montmorillonite.* This phase is obtained from 1:4 $Al_2O_3:SiO_2$ gels (which have been carefully electrodialyzed to remove any impurity ions) between the lowest temperature used, 200°, and 420° C., under varying H_2O pressure. This structure represents a pure aluminum end member[7] of the montmorillonites (beidellites). The *x*-ray diffraction pattern (Table 3) corresponds closely to that of natural montmorillonite, and the structure swells to a basal spacing of 14 Å with ethylene glycol. This diminished "expansibility" is noteworthy; no explanation has been found for it.

The question of the possible existence of such a phase, namely a pure hydrated aluminum silicate with the montmorillonite structure, has previously attracted the attention of mineralogists. Ross and Hendricks (1945) suggest the possibility of such an end member of the beidellite series, where the exchangeable base may be $Al(OH)_2^+$. Hoffman, Endell, and Wilm (1933) in their earliest work had also suggested a typical formula, where only Al and Si cations were present. The formula of Ross and Hendricks (1945) gives a composition ratio of very nearly $Al_2O_3:2SiO_2$. Substitution in the tetrahedral layer of Al^{3+} for Si^{4+} was assumed to be extensive $(Al_{.83}Si_{3.17})$ in order to reach the formula $(Al_2O_3:2SiO_2)$. This was probably done to accommodate the experimental results of Ewell and Insley. However, the latter authors had at least 2 to 3 per cent soda in their mixtures, which would occupy the base exchange position. Thus we have found that with nonelectrodialyzed gels

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[7] Chemical and spectroscopic analyses of mixtures used in synthesis of aluminum montmorillonite and of the phase itself showed the presence of no other oxides than Al_2O_3 and SiO_2 in quantities greater than a few tenths of one per cent, total impurities not exceeding 0.5 per cent. Whether or not even the one or two tenths of a per cent of alkali actually are essential to the structure cannot easily be proved. However, the amounts of alkali present cannot alone balance the excess charge caused by substitution in the tetrahedral layer and the basic picture is therefore unchanged.

TABLE 3. X-RAY DATA ON AL-MONTMORILLONITE

(Run #5454, 390° C., 25,000 psi)

2θ	d (Å)	I/I_0	hkl
8.00	11.05	100	001
16.40	5.405	3	002
19.90	4.462	2.5	110, 020
28.15	3.170	37	
45.55	1.991	1.5	
49.05	1.857	1	006 (?)
	Expanded With Ethylene Glycol		
6.57	13.43	100	001
	Dried at 110° C.		
8.9	9.94	100	001

prepared in the manner described by Ewell and Insley, when the composition is 1:4 Al_2O_3:SiO_2, analcime is obtained in a wide composition range, and only at lower silica concentrations do the clay phases form, since there are no sodium minerals with such compositions.

We may ascribe to the mineral an ideal formula such as $(Al(OH)_2)_{.33}$ $Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2$ where the $(Al(OH)_2)^+$ is the exchangeable base. The ideal composition then approaches an alumina:silica ratio of 1:3. It is more than likely, however, that the structure can exist over a range of compositions. This structure does not form above about 420° C., where pyrophyllite is the stable phase. No lower decomposition temperature has been found, and this phase is presumably stable down to atmospheric temperature and pressure. Its natural analogue is of course the high alumina beidellite with mainly Na^+ ions in the base exchange positions.

5. *Pyrophyllite* $(Al_2O_3 \cdot 4SiO_2 \cdot H_2O)$. Pyrophyllite is a stable phase above 420° C. under varying water pressures, in all alumina-silica mixtures high in silica. Pyrophyllite is obtained as the only crystalline phase from 1:4 Al_2O_3:SiO_2 gels at equilibrium. The substance forms with considerable difficulty in our experience and is invariably fine-grained. It was identified by its x-ray diffraction pattern which is essentially identical with that of natural pyrophyllite. The close correspondence is illustrated for a typical sample in Table 2.

The difficulty in synthesizing pyrophyllite may be ascribed to the fact that in the co-precipitated gels the alumina and silica are intimately mixed, and on heating, the Al^{3+} ions tend to go into fourfold coordination in the silica network, this being especially true for the high silica gels from

which pyrophyllite forms. Pyrophyllite has Al^{3+} only in sixfold coordination. There is a great resistance to this required rearrangement, so much so that several anhydrous aluminosilicate minerals having aluminum in octahedral coordination have never been synthesized, e.g., kyanite, jadeite, and pyrope. Kaolinite, which also has aluminum in octahedral coordination, forms with relative ease as compared to pyrophyllite. This difference in rate of growth of kaolinite and pyrophyllite may be ascribed to the lower temperature range of stability of kaolinite where six-fold coordination of aluminum is favored and to the fact that kaolinite is synthesized in a general higher alumina compositional range. The additional hydroxyl ions in kaolinite would also be a factor in promoting octahedral coordination for aluminum.

IV. Phase Relations

A. Binary Systems. The three bounding binary systems have been previously investigated. The system Al_2O-H_2O was studied by Ervin and Osborn (1951) over a wide range of temperature and water pressure. An interesting feature of their proposed equilibrium diagram for the system is the pressure "bottom" for the stability region of diaspore. This phase is believed to be stable only at water pressures greater than 2,000 psi and in the temperature range of 275° to 415° C. Repeated runs at water pressure below 2,000 psi failed to produce diaspore[8] whereas at higher pressures diaspore grows readily. Since this work was published, we have made longer runs to obtain additional information of diaspore stability. Both alumina gel and gamma alumina were used as starting materials, both seeded with diaspore crystals. Data obtained on representative runs are listed in Table 4. These data on two-week runs along with evidence obtained in connection with a study of the system $Al_2O_3-Ga_2O_3-H_2O$ (Hill, Roy, and Osborn, 1952) support the conclusion that diaspore is stable only above 2,000 psi. water pressure and 275° C.

[8] Laubengayer and Weisz (1943) report the growth of diaspore at 305° C. with "about 0.7" degree of filling of the bomb (their run 17a), and it is implied that under these conditions the pressure would be that of the saturated vapor pressure of water, about 1,325 psi. Actually, 0.7 degree of filling at room temperature is very critical with respect to complete filling with liquid water at 305° C., as shown by data of Kennedy (1950) and by extrapolation of curves of van Niewenburg and Blumendahl (1932). With precisely 0.7 degree of filling, the pressure at 305° C. is approximately 2,100 psi. A few tenths of a milliliter in excess of that required for 0.7 degree of filling in bomb used by Laubengayer and Weisz would cause a sharp increase in this pressure. Moreover, a temperature increase of a few degrees over 305° C., to be expected with normal variations in temperature under their experimental conditions, would produce a similar marked increase in pressure over the nominal 2,100 psi. The data of Laubengayer and Weisz are thus consistent with those of Ervin and Osborn (1951), rather than being at variance with them.

Table 4. Representative Runs of Alumina Gel and Gamma Alumina,
Seeded with Diaspore

Temperature ° C.	Water pressure psi.	Time, days	Result
270	32,000	15	Boehmite
295	32,000	14	Large amount of diaspore plus boehmite
302	1,280	14	Boehmite

In the system SiO_2-H_2O, no binary compounds were found or are known
to exist. The form of SiO_2 most commonly present in the product of a
hydrothermal run where gels are starting materials is cristobalite, and
only prolonged heating, especially at higher temperatures will produce
the stable modification, quartz, This of course indicates a degree of meta-
stability in such runs; but inasmuch as we have been able to crystallize
quartz under similar conditions without affecting the over-all equilibria,
it is considered that the equilibria must be essentially identical with
quartz substituting for cristobalite.

No additional work has been done in the "dry" system Al_2O_3-SiO_2, and
our present concept of the system is that presented by Bowen and Greig
(1924), with the eutectic temperature modification as proposed by
Schairer.[9] In addition to information on the compound mullite, which
occurs in the condensed system Al_2O_3-SiO_2, it was hoped that the present
study would reveal some further information on the problem of the
stability of compounds andalusite, sillimanite and kyanite. This has
been discussed in connection with the individual minerals and their
synthesis.

B. The Ternary System

1. *General Statement.* A summary of significant phase equilibrium data
for the system Al_2O_3-SiO_2-H_2O is given in Table 5. These are representa-
tive runs selected from more than two thousand, chosen to illustrate the
type of data actually obtained for each run. Our interpretation of the
phase equilibrium relations in the system Al_2O_3-SiO_2-H_2O is represented
by a series of composition triangles (Fig. 6), showing the phases in equi-
librium for a given composition within certain temperature and water
pressure limits. The triangles drawn here apply for a pressure of about

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[9] A later temperature figure of 1,585° C. for the eutectic was suggested by Schairer
'See Osborn, 1952) as probably being more nearly correct.

TABLE 5. REPRESENTATIVE RUNS FOR THE SYSTEM Al_2O_3-SiO_2-H_2O

Run No.	Starting Material	Temp. (° C.)	Water Pres. psi.	Time (days)	Products*
		CURVE II			
3277	Endellite	125	34	22	end.
3174	Endellite	132	250	13	end.+l. hall.
3249	Endellite N. C.	143	200	2	l. end.+hall.
3270	Endellite	145	100	2.5	l. end.+hall.
3247	Endellite	150	150	2	hall.+l. end.
3237	Endellite	160	250	1	hall.
3274	Endellite	150	75	2	hall.+int.
3307	Endellite	155	78	11	hall.+end.
3335	Endellite N. C.	165	100	8	hall.
3336	Endellite Ind.	165	100	8	hall.+end.
3212	Endellite	160	10,000	3	end.
3531	Endellite	172	100	1	hall.
3215	Endellite	170	10,000	2	end.
3357	Endellite Ind.	175	5,000	2	hall.+int.+l. end.
3380	Endellite Ind.	180	10,000	2	end.+l. hall.
3382	Endellite Ind.	184	10,000	3	end.+l. hall.
3391	Endellite N. C.	190	10,000	6	end.+hall.
3521	Endellite N. C.	190	182	4	hall.
3404	Endellite	195	15,000	3	hall.+some end.
3418	Endellite	200	10,000	4	hall.
3423	Endellite	205	10,000	2	hall.+possibly v. l. end.
3495	Endellite	210	4,000	1	hall.+l. end.
3485	Endellite	225	400	2	hall.
3517	Endellite (suspension)	250	5,000	1	hall.
3500	Endellite	288	3,500	1	hall.
3507	Endellite Utah	274	6,000	1	hall.
3503	Endellite N. C.	310	3,500	1	hall.
		CURVE IV			
3286	kaolinite	395	5,000	2	kaolinite
3160	kaolinite	400	250	14	kaolinite−v.l. decomp.
3152	kaolinite	403	1,000	2	kaolinite−v. l. decomp.
1713	kaolinite	405	20,000	3	kaolinite−slight change
3306	kaolinite	411	5,000	4	kaolinite+l. hyd.
3189	kaolinite	408	15,000	2	kaolinite+v. l. decomp.
3463	kaolinite	415	10,000	28	hyd.+l. kaol.
3101	Banda kaol.	400	8,000	6	kaolinite, possibly
3102	Langley kaol.	400	8,000	6	trace of decomposition
3103	Florida kaol.	400	8,000	6	no detectable hyd.

* Abbreviations used: and.=andalusite; crist.=cristobalite; cor.=corundum; end. =endellite; hall.=halloysite; hyd.=hydralsite; kaol.=kaolinite; ky.=kyanite; mont. =montmorillonite; mull.=mullite; pyroph.=pyrophyllite; sill.=sillimanite; N. C.=North Carolina; Ind.=Indiana; l.=little; v.=very; int.=intermediate.

Run No.	Starting Material	Temp. (° C.)	Water Pres. psi.	Time (days)	Products*
3128	Banda kaol.	404	10,000	6	clearly observable
3129	Langley kaol.	404	10,000	6	decomposition
3130	Florida kaol.	404	10,000	6	kaol.+hyd.
3107	Banda kaol.	407	8,000	8	hyd.+kaol.
3108	Langley kaol.	407	8,000	8	hyd.
3109	Florida kaol.	407	8,000	8	hyd.+l. kaol.
3166	nacrite	408	250	9	nacrite
3186	nacrite	408	15,000	2	nacrite
3305	nacrite	411	5,000	4	nacrite, slight decomp.,
3203	nacrite	410	10,000	3	optical only.
3318	nacrite	420	5,000	9	nacrite-decomp.; anomalous *x*-ray
3464	nacrite	415	10,000	28	mostly hyd.
3072	dickite	397	5,000	5	dickite—intensity change
3047	dickite	400	15,000	12	dickite—v. l. change
3202	dickite	410	10,000	3	dickite—mottling visible
3465	dickite	415	10,000	28	hydralsite+dickite
3071	halloysite	397	5,000	5	halloysite, v. l. decomp.
3188	halloysite	408	15,000	2	halloysite
3208	halloysite	414	10,000	2	halloysite+l.hyd.+l.monty
3017	halloysite	428	9,000	6	pyroph(?)+hyd.
3309	1:2 n.e.d. gel	155	80	11	kaolinite
3177	1:2 e.d. gel	195	250	69	kaolinite
3190	1:2 e.d. gel	408	15,000	2	kaolinite
3201	1:2 e.d. gel	410	10,000	3	kaolinite
3209	1:2 e.d. gel	414	10,000	2	hydralsite
3018	1:2 e.d. gel	428	9,000	6	hydralsite
5453	1:2 e.d. gel	417	25,000	9	monty+hydralsite
5443	1:2 organic-nit.	390	30,000	7	kaolinite
5452	1:2 organic-nit.	417	25,000	9	hydralsite+pyroph.

CURVE VI

3110	1:4 e.d. gel	407	8,000	9	mont.
3098	1:4 e.d. gel	417	10,000	5	mont.
3121	1:4 e.d. gel	423	10,000	9	mont.+pyroph
1734	1:4 e.d. gel	430	5,000	7	pyroph (broadened peaks)
3170	1:4 e.d. gel	440	10,000	30	pyroph

CURVE VII

3018	1:2 e.d. gel	428	9,000	6	hydralsite
1757	1:2 e.d. gel	448	8,000	10	prophy+hyd.
3171	1:2 e.d. gel	440	10,000	30	hydralsite+cor. ?
3516	1:2 e.d. gel	475	10,000	6	pyroph+hyd.
1581	1:2 e.d. gel	485	8,000	12	pyroph+mullite
1799	1:2 e.d. gel	515	8,000	7	pyroph+mullite
F-284	1:1 organic-nit. mixt.	435	5,000	8	hydralsite
F-267	2:3 organic-nit. mixt.	445	6,000	13	hyd.+l. pyroph
F-239	1:2 organic-nit. mixt.	440	10,000	17	hyd.+pyroph
F-242	1:3 organic-nit. mixt.	440	10,000	16	hyd.+pyroph

Run No.	Starting Material	Temp. (° C.)	Water Pres. psi.	Time (days)	Products*
3172	1:1 e.d. gel	440	10,000	30	hydralsite
3138	1:1 gel	481	12,000	8	hydralsite
3025	kaolinite e.d.	435	10,000	7	hydralsite
3515	kaolinite e.d.	475	10,000	6	hyd.+pyroph+cor. ?
3522	kaolinite e.d.	495	10,000	13	mainly hydralsite
3449	kaolinite e.d.	530	5,000	30	mull.+l. hyd.
3514	hydralsite	475	10,000	6	hydralsite+pyroph.
3523	hydralsite	495	10,000	13	hydralsite+l. pyroph +quartz (?)
3450	hydralsite	530	5,000	30	mull.+pyroph.+hydralsite

CURVE VIII

3095	pyroph.	555	10,000	1½	pyroph.
3104	pyroph.	562	10,000	4	pyroph.
3125	pyroph.	567	1,000	2	mottled (pyroph. x-ray)
3224	pyroph.	568	250	4	pyroph. good
3115	pyroph.	567	10,000	3	attack (pyroph. x-ray)
3134	pyroph.	573	1,000	4	mottling, needles seen (pyroph. x-ray)
3149	pyroph.	578	1,000	4	mottled pyroph.
3140	pyroph.	578	10,000	3	pyroph.+qtz.+mull.
3253	pyroph.	581	250	6	qtz.+pyroph.
5188	1:4 e.d. gel	525	20,000	7	pyroph.
3282	1:4 e.d. gel	555	5,000	17	pyroph.
5176	1:4 e.d. gel	555	15,000	10	pyroph+? ?
1707	1:4 e.d. gel	565	4,000	4	crist. mostly
1774	1:4 e.d. gel	582	8,000	3	crist.+mullite
3325	kaolinite	530	6,000	25	mullite+cor.+pyroph.
3329	kaolinite	565	5,000	20	mullite+crist.
3327	1:2 e.d. gel	530	6,000	25	pyroph.+mull.+cor. ?
3330	1:2 e.d. gel	565	5,000	20	mullite+crist.

DECOMPOSITION BY GRINDING

G 666	sillimanite	340	3,000	8	sill.+kaol.+mica
G 674	mull.	330	2,400	35	kaol.+?
G 675	mull.	450	3,700	35	kaol.+pyroph.+hyd. ?
G 669	andalusite	360	3,000	6	and.+kaol.+mica
G 665	kyanite	347	5,000	4	kaol.+ky.
G 662	kyanite	375	5,000	26	ky.+and.+kaol.
G 678	kyanite	425	4,500	32	kaol. or nacrite
G 667	kyanite	438	10,000	6	kaol. ?+ky.+mica
G 670	kyanite	510	13,500	3	amorphous+mica
G 672	kyanite	515	14,000	11	ky.+mica

MISCELLANEOUS

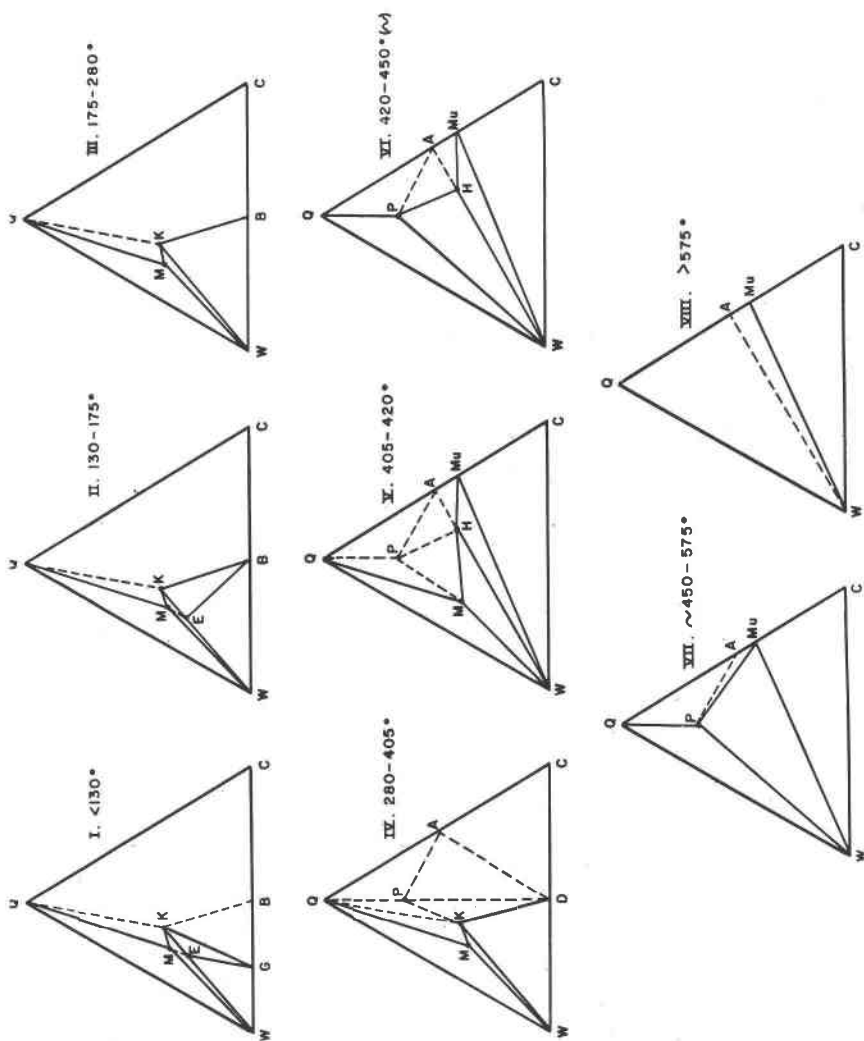|					
1719	1 kaol.+1 diaspore	415	20,000	3	diaspore+hyd.
3119	pyroph.	195	250	69	pyroph.+kaol.
3033	pyroph.	225	200	18	definite attack (mic.) no kaol. in x-ray.

Fig. 6. Triangles showing compatible phases in the system Al_2O_3-SiO_2-H_2O for various temperature ranges, illustrated for a pressure of about 10,000 psi. Triangles bounded by solid lines have been experimentally determined. Dashed lines indicate probable relationships. A = andalusite, B = boehmite, C = corundum, D = diaspore, E = endellite, G = gibbsite, H = hydralsite, K = kaolinite, nacrite, dickite, or halloysite, M = Al-montmorillonite, Mu = mullite, P = pyrophyllite, Q = quartz, W = water.

10,000 psi, and except for the transition, endellite = halloysite + H_2O, increase in pressure (up to 20,000) or decrease down to about 2,000 psi would produce only a very small change in the equilibria. The equilibria determined in the present study apply only to triangles having H_2O as an apex, $i.e.$, where an aqueous phase exists. Various attempts were made to study phase equilibrium relations in composition having too little H_2O to give a water solution as one phase at equilibrium. Sealed platinum tubes, for example, were used, with the mixture inside and water pressure applied outside. With such small amounts of water present, reaction is extremely slow, and no useful data were obtained. The equilibria which have been definitely established are therefore those involving water as one of the three phases.

The equilibrium data may also be expressed by a series of pressure-temperature curves, as shown in Fig. 7. The curves represent conditions of univariant equilibrium, and the areas between the curves represent divariant equilibria, with three phases coexisting over a range of pressure and temperature for ternary mixtures. The triangles of Fig. 6 describe
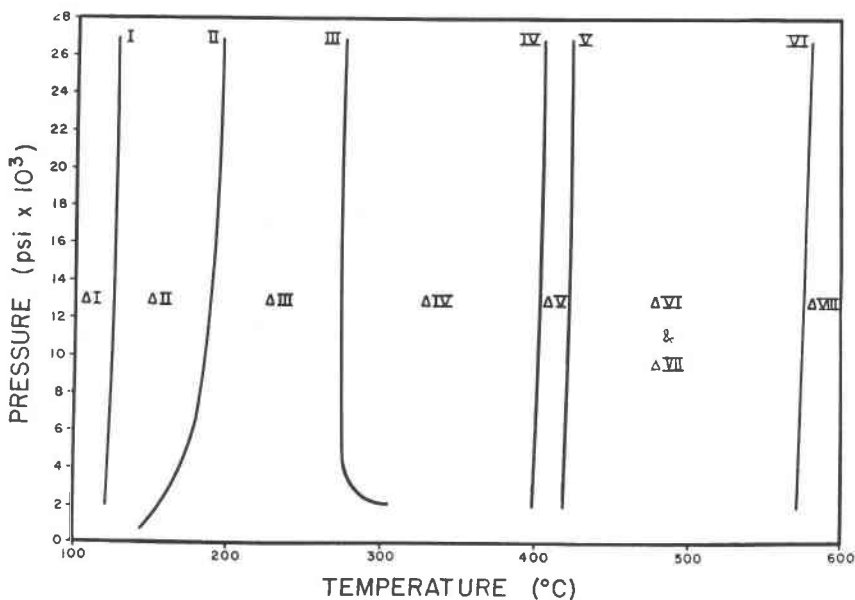
FIG. 7. Univariant curves for the system Al_2O_3-SiO_2-H_2O. The triangle numbers in areas between curves refer to triangles in Fig. 6. Reactions taking place along the curves are as follows: I, Gibbsite⇌boehmite+H_2O; II, Endellite→halloysite+H_2O; III, boehmite⇌diaspore; IV, diaspore⇌corundum+H_2O, and kaolinite⇌hydralsite+pyrophyllite +montmorillonite; V, montmorillonite⇌pyrophyllite+hydralsite+H_2O; VI, pyrophyllite⇌mullite (or andalusite)+quartz+H_2O.

the latter equilibria. Univariant curves are almost vertical at pressures between 5,000 and 25,000 psi in this system, and in view of the error limits no attempt has been made to show "true" slopes.

2. *Discussion of Triangles.* Triangle I (Fig. 6) applies to temperatures below 130° C., the estimated decomposition temperature of gibbsite (Ervin and Osborn, 1951). Stable structures in equilibrium with the water phase in this temperature range are: quartz, montmorillonite, gibbsite, and either kaolinite or endellite. Whether tubular endellite or platy kaolinite will form depends on factors incompletely understood, except that endellite should not form if water pressures are lower than those at which endellite dehydrates to form halloysite. At the lower water vapor pressures, therefore, kaolinite is the stable phase, but it is not clear at present which of the two structures has the lower free energy at higher pressures. Hence, in Triangle I (Fig. 6), both endellite and kaolinite are shown as possible phases in equilibrium with a water phase, and a dashed line is shown joining montmorillonite and endellite. The pairs of crystalline phases coexisting in equilibrium with the aqueous phase at temperatures below 130° C., are therefore: quartz+montmorillonite, montmorillonite+endellite or kaolinite, and gibbsite+endellite or kaolinite. If insufficient water is present for the existence of an aqueous phase, other stable assemblages as indicated by the dashed lines are: quartz+montmorillonite+kaolinite and gibbsite+kaolinite+boehmite.

Halloysite is not shown as a stable phase inasmuch as it forms only through the dehydration of endellite. Various workers have concerned themselves with the decomposition of endellite, among them MacEwan (1946, 1948), Brindley and Goodyear (1948), and Sand (1952). Brindley and Goodyear presented data which would indicate that endellite, halloysite, and an aqueous phase coexist with two degrees of freedom. Assuming that the system halloysite-water is binary, with endellite being an intermediate compound in the system, this is not possible if equilibrium is presumed. Sand (1952) showed that endellite was stable up to 100° C. in the presence of water vapor pressures greater than the saturated vapor pressure. We extended these studies to 400° C. and 30,000 psi. water pressure. The experimental data indicate that endellite is stable up to about 175° C. at the saturated vapor pressure, but above this temperature, pressure has very little effect and endellite is not stable even at the highest pressures used (30,000 psi.). This was not the expected result, for it was thought that endellite would be stable as long as liquid water were present, *i.e.*, below the critical temperature and at pressures greater than the saturated vapor pressures. One criterion only, however, was used to judge the progress of the reaction. The sample after reaction was extracted wet, and immediately made up into a slide for examination by

x-ray diffraction, the elapsed time being 5 to 10 minutes. If the pattern showed the presence of endellite, it was concluded that endellite does not dehydrate under those conditions, even though halloysite was also found to be present. If the sample contained largely halloysite mixed with minor amounts of endellite, the run was repeated. In these experiments two different samples of endellite were run simultaneously, one from Eureka, Utah, and the other from Bedford, Indiana. It is not easy to understand the fact that in most of the runs the product contained halloysite. There are, of course, several operations during which part of the sample may dehydrate, e.g., in the removal from the bottle and partial drying to introduce the sample into the very small platinum envelopes, during the introduction into the long test-tube type bombs which are initially dry, and in the process of removing the sample and obtaining its x-ray pattern. Furthermore, small pockets of air may form in the envelope, permitting dehydration of endellite crystals near the air pockets before attainment of equilibrium. To discount this possibility the runs were repeated using a finely dispersed sample of endellite in the Morey type vessels. No different results were noted. If one considers that there is an exchange between the liquid and vapor water molecules, especially prior to the establishment of equilibrium, then should any of these exchanging water molecules originate from between the layers of the alumina-silica sheets in endellite, we can picture a possible irreversible collapse of the structure. The water layer in endellite may be considered essentially "solid" or "liquid," and not structureless, like vapor. That the water between the layers in endellite is essentially the same as unbound water is borne out experimentally by both our data and those of Sand (1950) inasmuch as the decomposition curve of endellite follows so closely, if not coincides with the vaporization curve of water.

The fact that endellite once formed, persists up to at least 175° C., would indicate that other factors besides composition must play a deciding role in its formation; for kaolinite also forms at these temperatures and in the presence of an abundance of water. The influence of pH, presence of other ions, and especially "structural control" depending on the parent mineral are all possibly important factors in determining whether kaolinite or endellite forms. Sand (1952) has shown that there is evidence for at least the last named factor. If during the formation of the clay minerals the system is saturated with water, either endellite or kaolinite may form (below at least 175° C.), but it is not clear which is the more stable. If the system is not saturated with water, endellite is unstable and should not form. Halloysite, as mentioned in an earlier section, forms only as a dehydration product of endellite.

Triangle II (Fig. 6), representing equilibrium relations between 130°

and 175° C. differs from Triangle I in the substitution of boehmite for gibbsite as the stable alumina hydrate.

Triangle III describes the relations in the range of about 175° C. to 280° C.[10] The assemblages kaolinite+boehmite+water, kaolinite+montmorillonite+water, and montmorillonite+quartz+water are stable. We have been able to synthesize kaolinite throughout this temperature range. Halloysite will also form, presumably as a metastable phase, if endellite is used as a starting material. Triangle III is applicable for water pressures in the range of 2,000 to at least 30,000 psi. If, however, pressures are less than 2,000 psi., then the relations shown in this triangle prevail up to about 385° C.[10]

Above 280° C.[11] and 2,000 psi water pressure, diaspore replaces boehmite as the stable alumina hydrate as shown in Triangle IV. The assemblages, diaspore+kaolinite+water, kaolinite+montmorillonite +water, and montmorillonite+quartz+water are stable. We still have no positive data for the equilibria in which an aqueous solution is not one of the three phases. However, natural associations of diaspore with pyrophyllite and with andalusite suggest the joins shown as dashed lines.

With increasing temperature, kaolinite and diaspore are no longer stable,[11] and relations between 405° and 420° C. are shown in Triangle V. The crystalline material which we here designate as "hydralsite" replaces kaolinite in the phase assemblages appearing in the system, and diaspore is replaced by corundum. Mullite is formed from high-alumina mixtures, and therefore the join, mullite-water is presumed to exist under stable equilibrium conditions. Joins involving hydralsite, however, may be metastable, although they appear reproducibly just above the decomposition temperature of kaolinite.

Above 420° C. aluminum montmorillonite is no longer stable, and relations are as described in Triangle VI. Pyrophyllite forms in high-silica mixtures, and hydralsite from compositions lower in silica. The upper

[10] The boehmite-diaspore transformation temperature varies from 275° C. at 20,000 psi. to 300° C. at 2,500 psi. water pressure (Ervin and Osborn 1951). Other reaction temperatures, such as diaspore⇌corundum+water, boehmite⇌corundum+water, and pyrophyllite⇌mullite+quartz+water, are also a function of pressure, although at higher pressures the effect of pressure on temperature of reaction is usually small. A single temperature is given in order to simplify the discussion.

[11] The decomposition temperature of kaolinite is 405° C. at 10,000 psi. and is not greatly affected by pressure; the decomposition temperature of diaspore increases from 385° C. at 2,000 psi. of 415° C. at 20,000 psi. Therefore, at lower water pressures diaspore disappears as a stable phase at a lower temperature than kaolinite, and the reverse is true at higher pressures. For the sake of brevity, triangles are not shown for these two cases. At 10,000 psi., kaolinite and diaspore cease to be stable at approximately the same temperature.

limit of stability of hydralsite is not well-established, as has been previously discussed, but it persists to 450° C. or higher.

Triangle VII indicates the relations where hydralsite is no longer obtained, and the assemblage pyrophyllite+mullite+water appears. The join shown as a dashed line connecting pyrophyllite with andalusite, sillimanite, or kyanite is probable, although we have no direct evidence for the stability of these three minerals in the temperature range indicated.[12]

Triangle VIII represents the relations above 575° C., where pyrophyllite is no longer stable, and the triangles mullite+corundum+water and mullite+quartz+water are stable. A dashed line indicating a possible join between sillimanite, andalusite or kyanite and water is drawn. As suggested previously, the difficulty in distinguishing sillimanite from mullite makes it possible that some of the equilibria we have shown as involving mullite may actually involve sillimanite.

V. Discussion and Conclusions

1. The dehydration of endellite, which approximately follows the vapor pressure curve of H_2O at lowest temperatures (below 100° C.) and increases to about 175° C. at 5,000 psi., suggests a temperature limit for the formation of this phase in nature. Recently it has been recognized that many of the clays previously described as "kaolin" contain significant amounts of endellite or halloysite, whereas others are nearly all kaolinite. We were unable to synthesize endellite in the present study, which may be partly a result of extremely slow reaction at such temperatures. The phase which was synthesized at higher temperatures, however, was a kaolinite, having characteristic hexagonal platy structure recognizable under the electron microscope, but never the tubular crystals of halloysite (or endellite).

Whereas we have not been able to synthesize the minerals endellite and halloysite, an upper stability temperature of about 175° C. has been indicated for endellite, at water pressures which would be attained near the surface in nature. Kaolinite would alternatively be formed within the same temperature range when the vapor pressure of water is insufficient to form endellite. The structural relationship between endellite and halloysite suggests that halloysite is only formed as a dehydration product of endellite and therefore endellite must always be formed first.

In nature, endellite and kaolinite may both form under apparently similar temperature and water vapor pressure conditions. In such instances it is not clear which is the more stable. Where the water vapor pressure is sufficiently high for endellite to form, the free energies of the

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[12] D. M. Roy (1953) has since shown that andalusite forms between 450° and 650° C.

two structures are probably very similar, and a factor such as arrangement of atoms in a previous structure becomes controlling. Sand (1952) has shown that in the North Carolina pegmatite area endellite is formed from the rapid weathering of feldspars, whereas the product always formed by weathering of primary or secondary micas is kaolinite. But within such environmental limitations endellite could only be formed when there is sufficient H_2O present, within the pressure and temperature range indicated above.

2. An upper stability temperature of about 405° C. has been established for kaolinite, halloysite, nacrite and dickite, and this may be applied to natural occurrences. Much kaolinite is formed through weathering at low temperatures, but the upper temperature limit may also be applied to kaolinite formed by hydrothermal action and to nacrite and dickite, which commonly have a hydrothermal origin. Their presence or transformation may provide a fairly reliable temperature index in a metamorphic sequence. These temperatures would apply for burial of 1–5 miles.

3. The significance of the upper stability temperature for aluminum montmorillonite (420° C.) is less clear, since widespread solid solution occurs among the various natural montmorillonite minerals. For relatively pure "beidellites," i.e., montmorillonites consisting largely of alumina and silica, the upper temperature limit may be applied approximately. Systematic addition of other components is necessary to determine stability relations for a number of montmorillonites, and the results of the present study provide a framework for such additional work. The addition of MgO, for example has been shown (Roy and Roy, 1952) to increase the upper stability temperature of montmorillonite.

4. The absence of a phase corresponding to hydralsite in natural deposits may be a result of the presence of numerous cations which could enter the structure and convert it to various types of mica, which could form stably in the corresponding temperature range.

5. Pyrophyllite would be expected to crystallize only in the temperature range of 420° to 575° C. when excess H_2O is present, i.e., sufficient water present for assemblages shown in the triangles (Fig. 6) to form. It is no doubt a stable phase, however, at much lower temperature (see Triangle IV) and will form if insufficient water is present to convert the mixture to higher hydrates. Whereas pyrophyllite is not a very common mineral—and the range 420° to 575° may be sufficient to include most of its associations—the occurrence of diaspore with pyrophyllite in some natural deposits suggests a temperature of formation of these deposits in the range of 275° to 405° C.

6. The failure to synthesize sillimanite, andalusite and kyanite has

been discussed in some detail. Sillimanite may have been synthesized in this study but the very fine-grained material could not be distinguished from mullite, and thus the relations are expressed in terms of equilibria involving mullite. Andalusite, sillimanite and kyanite have been decomposed hydrothermally at temperatures below 450° C., which indicates that they are not stable below this temperature in the presence of excess water. This is to be expected from the equilibrium relations established, wherein alumina-silica hydrates are stable. Andalusite, sillimanite and kyanite may be stable in this temperature range, but only where there is a deficiency of water with respect to that required to form the stable hydrates. In Fig. 6 it is seen that the composition $Al_2O_3 \cdot SiO_2$ (andalusite sillimanite and kyanite) is located behind the joins which describe equilibria involving H_2O as one component. It is therefore possible that these phases may be stable with a deficiency of H_2O at temperatures up to 575° C. Such a proposed relationship is indicated by dashed lines in Triangles IV to VII.

7. The problem of the mullitization of kaolinite is of fundamental importance to ceramists, and has been studied very extensively. The results of the present work provide an answer to the *equilibrium* progress of the mullitization of kaolinite. Kaolinite decomposes finally at 405° C. (and obviously very much lower at the very low partial pressures of water obtaining under ordinary conditions of firing) and if sufficient water is present to cause recrystallization forms a little pyrophyllite along with hydralsite. On heating to about 500° C. pyrophyllite and mullite are formed, and above 575° C. kaolinite is completely "mullitized" to mullite and cristobalite. This therefore indicates the possibility of actually "firing" a ceramic body hydrothermally at less than 600° C. and obtaining the same phase assemblage as is obtained by firing dry at very much higher temperatures.

Data obtained under equilibrium conditions will usually not correspond to those obtained by various other methods. In the study of clays and hydrous oxides both differential thermal analysis and "dehydration isobars" are used. While these methods, especially the former, can serve as excellent tools for the characterization of a wide variety of phases, they can lead to quite erroneous results if used for other purposes such as the detection of other phases in a system and the determination of either the equilibrium constant or certain other thermodynamic parameters of a phase or reaction. Thus, it is well-known that by the use of dehydration isobars of several trihydrates of group III oxides no evidence is found for the existence of "monohydrates" which have been well-established. Differential thermal analysis would similarly indicate no other "peaks" or stepwise decomposition in these trihydrates. These methods are dynamic non-equilibrium methods in most cases, as may

also be inferred from the frequent circumstance that the product of de-hydration is "amorphous." And while they can provide a great deal of useful data on a particular process under specified conditions, these data will only in rare cases correspond to equilibrium, reproducible data. A relevant example in the recent literature is the study by Stone (1952) of the decomposition of the kaolinite group minerals. It is claimed that the reaction studied is

(1) $$Al_2Si_2O_5(OH)_4 = Al_2O_3 + 2SiO_2 + 2H_2O.$$
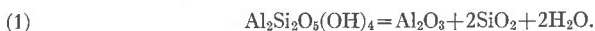
Such a reaction could probably never be made to take place under any conditions whatsoever, and certainly no evidence is presented for as-suming that the reaction is other than

(2)   Kaolinite = dehydrated kaolinite (not heated above 1,000° C.) + water.

Several erroneous conclusions are reached such as "in the steam (15 psi.) atmosphere it (kaolinite) will not decompose until about 475° C." We have shown that at even 1,000 atmospheres of steam the decomposition temperature is about 410° C. A decomposition temperature (under very low partial pressures of water vapor) of 465° C. is arrived at for diaspore (formula incorrectly given as $Al(OH)_3$ p. 94) whereas it has been shown not to exceed 400° C. at 10,000 psi. water pressures. A significantly (100° C.) higher decomposition temperature was assigned to dickite as com-pared to kaolinite, whereas we have shown that at equilibrium there is no significant difference in the equilibrium decomposition temperatures. These examples serve to illustrate the differences which may be obtained between equilibrium and non-equilibrium conditions. While from the former it is possible to predict something about the latter, the opposite is not always as sure a process. Thus the data from the present study would indicate that *DTA* curves of dickite would approach more and more closely those of kaolinite as the particle shape and size were made more and more equal. They also indicate that kaolinite may be decom-posed below 400° C. under very low partial pressures of water. Under equilibrium conditions we also know that the first products of decom-position of kaolinite are hydralsite and pyrophyllite.

8. The data obtained herein suggest that mullite should not be as rare a mineral as has been supposed. While we have very little positive data on the stability of andalusite, sillimanite and kyanite, the data suggest that mullite should be formed whenever a relatively pure alumina rich aluminosilicate rock is heated above 575° C. at relatively low pres-sures. Such conditions prevail at the contacts of lava flows (or near-sur-face extrusive rocks), and certain clays and it is not inconceivable that mullite should occur in such localities. The phase called hydralsite herein, may also possibly be found in localities where relatively pure alumino-

silicate rocks have been metamorphosed. In this connection, it is interesting to note that the mineral zunyite has a composition quite similar to that proposed for hydralsite, and occurs in such an assemblage as mentioned above. The essential Cl^- ion present in zunyite however, precludes a similarity in structure.

Acknowledgments

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