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A NEW POLYMORPH OF Al_2SiO_5 AND FURTHER STUDIES IN THE SYSTEM Al_2O_3-SiO_2-H_2O[1]

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ABSTRACT

A re-examination of the system Al_2O_3-SiO_2-H_2O up to 900° C. and 6000 bars in sealed noble metal systems has been carried out. Two new phases are described: one, AS(H)-II, is probably a new polymorph of Al_2SiO_5 previously mistaken for andalusite. Single crystal and powder *x*-ray, and optical data are presented for this phase. The other, AS(H)-I appears to be a very high-alumina phase. P-t curves for the dehydration of kaolinite and pyrophyllite in the range 2000–5000 bars fit well with earlier data of Roy and Osborn. The remarkable influence of silica in inhibiting diaspore formation is noted. A p-t curve for the decomposition of AS(H)-II to mullite+quartz is presented.

No useful data on the interrelationships among sillimanite, andalusite, kyanite and AS(H)-II could be obtained. The experimental data continue to point in the direction of *some* possible stability field for the quartz+corundum assemblage. Crystal chemical and structural arguments likewise favor the examination of this possibility, and the corresponding *possibility* of the metastability of the anhydrous aluminosilicates under the conditions of their formation.

Precise measurements on lattice parameters of two dozen mullites and sillimanites show the absence of any continuity between these two families of phases, at least as prepared below 5000 bars. Order-disorder within the mullite phase is demonstrated.

INTRODUCTION

In 1948–49 Roy and Osborn (1954) studied the system Al_2O_3-SiO_2-H_2O to 800° and approximately 2000 bars, the limits of their apparatus. They determined the stability limits of kaolinite and pyrophyllite and the existence of the new phase hydralsite. They were unable to synthesize andalusite, sillimanite or kyanite, although shortly thereafter D. Roy (1954) reported the synthesis of andalusite. Soon afterwards L. Coes (1953) communicated his dramatic success in the first synthesis of all: the previously unsynthesized "dense" minerals. Most of this work had been done in 1948, and among the phases synthesized were excellent specimens 2–3 mm long of kyanite and sillimanite. Although Coes had synthesized all these phases he made no attempt to determine stability p-t limits for them. In the case of the alumino-silicates recent workers have reported data on particular reactions: Kennedy (1955) studied the reaction "from pyrophyllite to mullite" (sic) in the range to 20,000 bars and the supposed solid solution between mullite and sillimanite. Griggs and Kennedy (1956) include a curve but no details on the equilibrium reaction pyro-

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phyllite⇌sillimanite+quartz+water. Clark *et al.* (1957) have studied the sillimanite-kyanite reaction at high pressures (~20,000 bars) and high temperatures. The present work conducted over the period 1957–1959 included a re-examination of the system Al_2O_3-SiO_2 (Aramaki and Roy, 1958, 1959a, 1959b, 1962) and an extension of the previous study in the Al_2O_3-SiO_2-H_2O system with the newer experimental tools available.

Experimental

Starting materials: The prejudice, introduced by the structure of the starting material, is always important in phase equilibrium studies; in this system at low temperatures it is so important as to dwarf all other considerations in the attainment of equilibrium. The development of a method for making homogeneous gels in almost any part of a silicate system in the earliest hydrothermal work in this laboratory added one of the most important types of new "structures" which could be used as starting materials in systems such as the present one where glasses cannot be made.[1]

Most gels were prepared from aluminum nitrate and ethyl orthosilicate or the ammonium stabilized silica sol (170 Å particles) sold under the name "Ludox."

Composition of the mixtures was checked in two ways: 1) by following the weights of the starting materials and products of heating and 2) by analysis. The latter was done both by systematic *x*-ray fluorescence analysis for both Al and Si on the dehydrated samples and by wet analysis of the same. The results of the former show excellent self-consistency. Indeed the preparation of gels for *x*-ray fluorescence standards can be highly recommended, as it circumvents dissolving in $LiBO_2$ glass. The powder of well-formed single crystals of an arc-fused mullite was also analyzed and plotted on the same diagram. Its chemical analysis, excluding a 3% corundum impurity (Aramaki and Roy, 1962), gives a composition of 67.5 mol % Al_2O_3, 32.5 mol % SiO_2. The *x*-ray fluorescence analysis gave the composition as 76 wt % Al_2O_3 and 26 wt % SiO_2 (=67:33 mol ratio). Impurities in the samples are extremely low in those made from gels, the chief impurity being alkali. Near the mullite composition this amounts to about 0.1% as Na_2O. The Al_2O_3:SiO_2 ratio is probably within $\pm\frac{1}{2}$%. Wet analysis results would indicate a spread of ± 1%, but this is a check both across different laboratories and dif-

[1] In our parallel study on the 'dry' system Al_2O_3-SiO_2, true glasses were prepared in the system up to 60 mole per cent Al_2O_3, probably for the first time. However, the alumina-rich ones could be made only in very small quantities (~1 mgm) and they devitrify to mullite, etc. very easily at room temperature, making their use as starting materials quite inadequate.

ferent methods and it is felt that the reliability of analyses is the weakest link here.

Other starting materials included:

1. Silica glass of high purity and C.P. α-Al_2O_3 (Baker's analyzed, Lot No. 122149) were used for the high-temperature dry runs. After weighing and grinding together under alcohol for 30 minutes the mixtures were heated at 1100° C. for eight to ten hours.
2. Mixtures of the vapor-formed silica, sold under the trade name "Cab-O-Sil," with alumina supplied as gibbsite (A.R. grade) provided starting materials for other runs.

Natural minerals:

1) *Kaolinite* electrodialyzed, Langley, S. C. Same specimen used by Roy and Osborn (1954).

2) *Andalusite* from Bull Mountain, Patric Co., Virginia. This specimen was used in the earlier part of the present work but later was found to contain too many impurities (mostly mica), thus giving misleading results for the decomposition points.

3) *Gem Andalusite* from Teofilo Otoni, Minas Gerais, Brazil. A transparent single crystal was crushed and purified with HF. The powder contained no optically detectable impurities. Precise measurement of the unit cell dimensions and optical properties are given in Table I.

4) *Kyanite* from Stony Point, Alexander Co., North Carolina. After purification powder was completely free from impurities.

5) *Sillimanite* (*fibrous*) from Brandywine, Delaware Co., Pa. The powder was also free from impurities. Its chemical composition is given in Table II, which shows only 0.13 wt % Fe_2O_3 as a major impurity. Precise x-ray powder data and optical properties are given in Tables I & III.

6) *Glass* from a partly fused sediment ejected from the Asama Volcano. With the use of the Franz isodynamic separator and heavy liquids a portion rich in glass was separated from the rock. In contained sillimanite and cordierite in moderate quantities together with glass.

Experiments: The hydrothermal experimental procedures used are now well known. Small amounts (~30 mgm) of the sample were sealed into gold tubes (Pt tubes were used at temperatures above 900° C.) with a small amount of water. The sealing was checked by weighing the tubes before and after each run. The samples were run in test tube cold-seal vessels at the desired "p" and "t" for periods from 30 minutes to two months. Most runs were held for a week. After quenching, the samples were examined petrographically and by x-ray diffraction on a wide-range diffractometer. Some 20 runs were made with opposed anvil apparatus up to 50,000 bars and up to 600° C. On some specimens precise x-ray spacings were obtained by the usual methods of slow scanning with an internal silicon standard. *All* the spacings actually reported in this paper were so determined. A detailed report of the method is given elsewhere (Aramaki and Roy, 1962). Infra-red absorption patterns were obtained in KBr pellets with a Perkin Elmer 21 instrument.

Accuracy of the temperatures recorded is given in general terms from previous experience at $\pm 5°$ C., and of the pressures as $\pm 3\%$ below 1400 bars and $\pm 5\%$ to 7000 bars but an overall accuracy, including fluctuations during the run is $\pm 10°$ C. and $\pm 5\%$ of pressures unless otherwise specified.

Results

A total of some 600 runs were made in the hydrothermal range. The results are presented partially in tabular form and partially in diagrams, especially Fig. 1.

The p-t stability of the hydrates: The stability of kaolinite and pyrophyllite at pressures between 2000 and 4000 bars was checked. The curve obtained by Roy and Osborn (1954) was quite steep in the region between 2000 and 200 bars, requiring a very large heat of reaction. Moreover, kaolinite was found to decompose to a phase not found in nature, which was named hydralsite. It was suggested at the time that hydralsite could in all likelihood be a metastable step in the reorganization of the 1:1 layer lattice to the 2:1 lattice of pyrophyllite plus boehmite. This suggestion has been confirmed very well. At low pressures of 1–2000 bars hydralsite was obtained from gels heated above 400° C., whereas at 4000 bars pyrophyllite and boehmite were formed from the same gels at the same temperature. Clearly the hydralsite is metastable as otherwise a pressure minimum for the pyrophyllite-boehmite assemblage would be required. Moreover, the decomposition temperature for the reaction kaolinite→pyrophyllite+boehmite+H_2O is still seen to be nearly the same as that obtained by Roy and Osborn in the 1000–2000 bars range, viz. $405 \pm 10°$ C. where hydralsite+pyrophyllite were obtained. The density of the solids and of water at 4000 atm. near 400° C. is such that the ΔV term in the Clapeyron equation is very small indeed. The presumptive stable phases here should be diaspore rather than boehmite but in every case, even in the presence of diaspore seeds, only boehmite was encountered. In several runs boehmite was found at temperatures which must be regarded as being well above the maximum stability of any alumina hydrate. The presence of silica in the environment must result in some silicon atoms entering the lattice and not being removed. This has two effects: it prevents the transition to diaspore and it raises the "stability" of the boehmite. In some runs below 5000 bars boehmite was obtained as high as 500° C. Attempts to determine whether or not this should be regarded only as "metastable solid solubility" or whether it actually represented an equilibrium solid solution of SiO_2 in boehmite were inconclusive. At 4000 bars the dehydration temperature for diaspore in the pure Al_2O_3 system has recently been restudied by Erickson and

TABLE 1. X-RAY DATA ON PHASES

AS(H)-I		AS(H)-II[1]				
I/Io	2θ(CuKα)	I[2]p/Io	I[3]osc	hkl	$2\theta_{obs}$(CuKα)	$2\theta_{calc}$
30	20.3	100	vs	110	15.85±.04	15.89
40	27.6	10	m	020	21.43±.04	21.48
5	32.2	50	s	111	22.36±.04	22.38
30	35.95	5	m	200	23.53±.04	23.56
5	37.3	50	d	021	26.65±.04	26.69
60	38.25	5	—	002	31.59±.03	31.61
30	38.6	100	vs	220	32.06±.01	32.07
100	42.75	3	w	130	34.56±.03	34.60
30	48.9	15	ms	112	35.55±.02	35.54
		7	m	022	38.51±.03	38.51
10	54.4	3	m	202	39.77±.03	39.77
(5	56.0)	25	m	122	40.42±.02	40.39
			m	230		40.47
15	56.7		mw	311[4]	40.70~40.80	40.68
15	59.8	12	ms	212	41.30±.02	41.30
5	61.5	3	mw	140	45.40±.03	45.43
		3	—	013	49.50~49.63	49.51
			m	312		49.66
		5	ms	331	51.70±.03	51.70
		7	m	241	52.96±.03	52.96
		5	w	420	53.33±.07	53.28
			—	023		53.33
		12	ms	332	59.44±.03	59.43
			mw	242[4]	60.63±.03	60.58
			—	133		60.67
		3	w	511	64.83±.03	64.81
		4		004	65.95±.03	65.97

[1] Sample No. 90203, at 567±5° C., 5350 bars. Trace of mullite present.
[2] Powder pattern intensity.
[3] Oscillation photo intensity (No. 71104).
[4] Overlapped with mullite peaks.

Roy (1958) and is placed at 440±10° C. Attempts to check this temperature in the silica-saturated system were complicated by the appearance of a new phase (vide infra). But the very interesting effect of silica in inhibiting the formation of diaspore may bear directly on the petrology of the "nodular" diaspore deposits of the Clearfield, Pennsylvania basin. The correlation noted by Erickson and Roy of high silica content with the presence of boehmite (absence of diaspore) is an obvious parallel to our experiments.

The maximum temperature at which pyrophyllite forms or persists at 4000 bars is approximately 565°±10° C. which may be compared to Roy

TABLE I (*continued*)

Natural andalusite				Natural sillimanite (fibrolite)		
I	hkl	$2\theta_{obs}$	$2\theta_{calc}$	hkl	$2\theta_{obs}$	$2\theta_{calc}$
90	110	15.95±0.03	15.97	110	16.52±0.03	16.55
100	{011, 101}	19.56±0.03	{19.55, 19.63}	200	23.76±0.03	23.79
50	111	22.62±0.03	22.66	120	26.08	26.10
45	120	25.26	25.28	210	26.49	26.51
40	210	25.43	25.48	002	30.98	30.98
80	220	32.23	32.25	220	33.44	33.43
22	221	36.14	36.16	112	35.32	35.32
22	310	36.35	36.36	130	37.13	37.12
5	031	37.78	37.79	202	39.43	39.42
4	301	38.19	38.21	122	40.94	40.93
25	{131, 022}	39.60±0.03	{39.58, 39.66}	230	42.85	42.80
				400	48.65	48.64
20	311	39.94	39.93	312	49.73	49.73
40	122	41.35±0.04	41.38	330	51.13	51.12
45	212	41.51	41.51	240	53.67	53.66
3	040	45.93	45.92	420	54.55	54.54
30	400	46.57	46.55	042	57.68	57.67
3	410	48.05	48.04	402	58.80	58.80
3	132	49.06±0.04	49.06	332	61.00	60.98
3	141	50.38±0.04	50.38	422	64.06	64.06
5		50.56±0.03		004	64.58	64.58
5	411	50.92±0.03	50.94	250	65.72	65.72
6	113	52.05±0.03	52.06	520	67.11	67.09
7	402	57.74	57.75	440	70.24	70.24
10	223	60.03	60.05	152	70.61	70.60
3	151	62.21±0.03	62.20			
40	242	62.38	62.38			
7	{313, 422}	62.73±3	{62.70, 62.77}			

and Osborn's value (1954) of 575° C. and ~650° C. (intrapolated) reported by Kennedy. The Roy and Osborn value was assigned mainly on runs starting with pyrophyllite, which normally tends to give higher values. Comparison of such data on a quantitative basis is meaningless, since it is virtually impossible to demonstrate reversible equilibrium for a particular reaction for which an ideal equation can be written. In this case for instance, Roy and Osborn show as the equilibrium dissociation products quartz+mullite+H_2O. However, in many runs cristobalite was actually obtained. In every run, our present knowledge would require that the term "mullite" be defined much more closely, since mullite is not an unequivocal description of a phase. In practice, more-

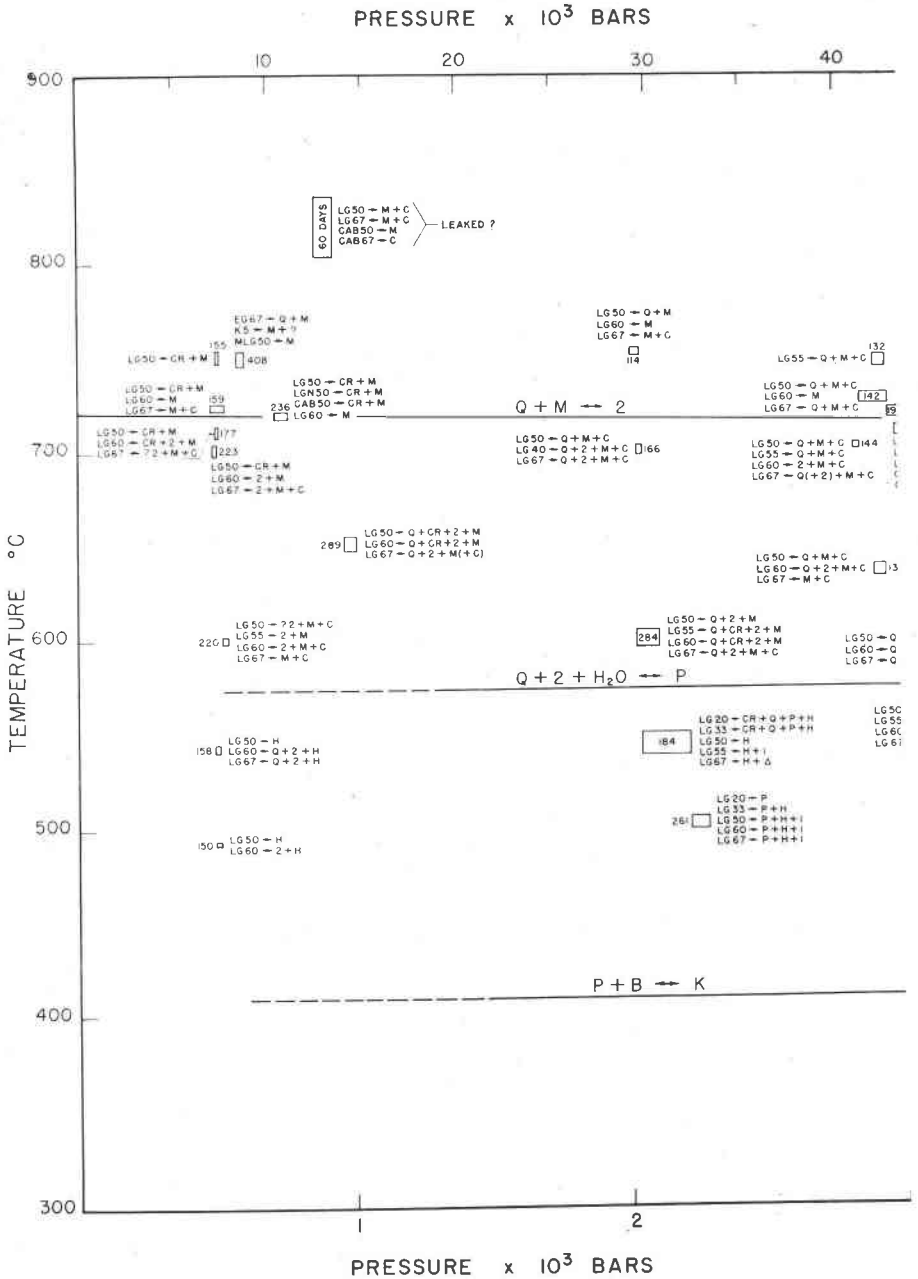
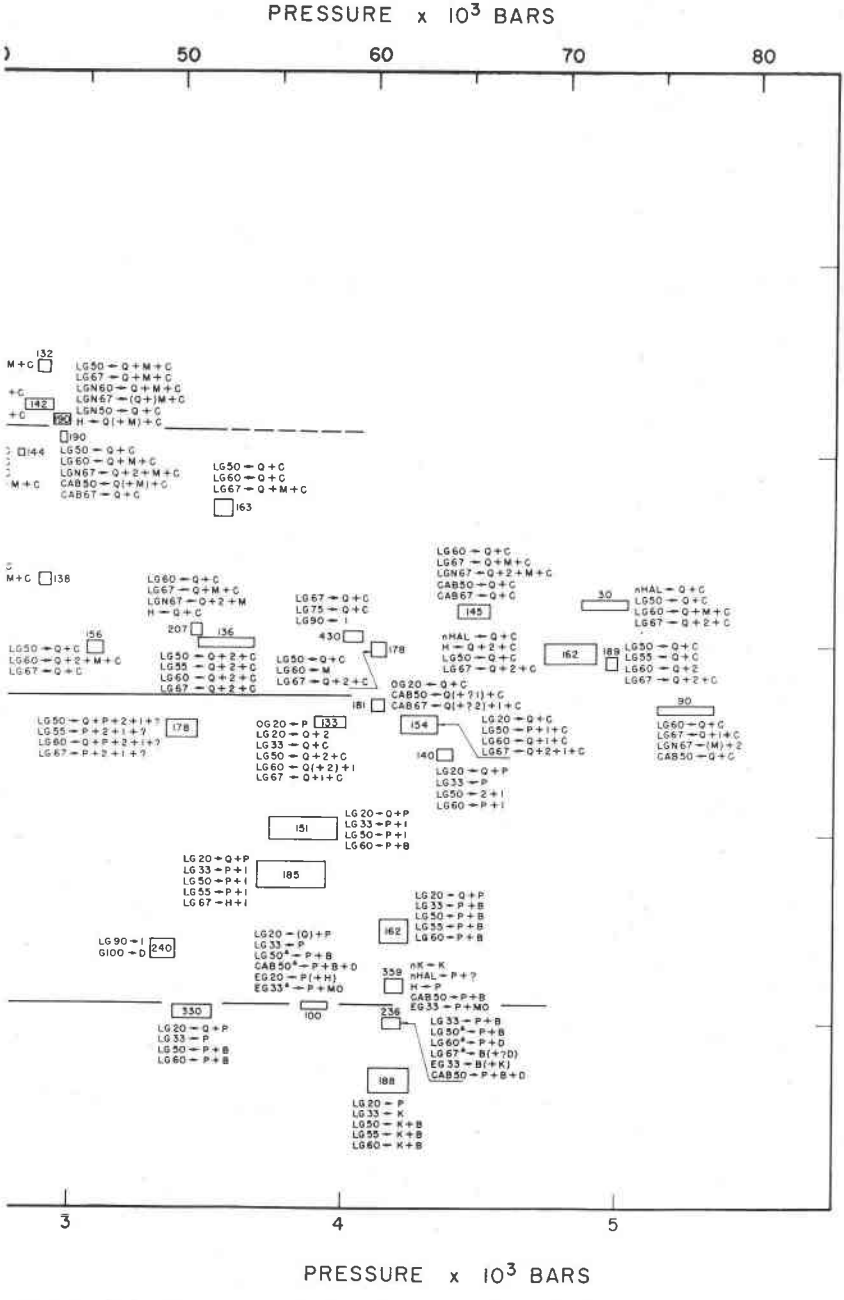


FIG. 1. Pt. 2. Diagrammatic summary of selected data obtained on stability of various phases. LG = mixture made from Ludox Gel; Cab = mixture made with CabOsil, EG = electrodialyzed gel; Q = quartz; M = mullite; 1 = AS(H)-I; 2 = AS(H)-II; Cr = cristobalite; C = corundum; H = hydralsite; B = boehmite; D = diaspore; P = pyrophyllite; K = kaolinite;



Hal = halloysite. The rectangles indicate the measured spread of temperature and pressure of the run; the number beside the rectangle indicates the length of the run in hours (unless specified), the number following the letters indicates the mole fraction of Al_2O_3 in the starting mixture.

TABLE II. CHEMICAL ANALYSIS OF NATURAL SILLIMANITE

	wt. %		mol. no.	mol. %
SiO_2	35.84	SiO_2	5967	49.0
TiO_2	trace			
Al_2O_3	63.36	Al_2O_3	6214	51.0
Fe_2O_3	0.13			
FeO	trace			
MnO	<0.02			
MgO	<0.1			
CaO	<0.1			
Na_2O	0.20			
K_2O	0.02			
$H_2O^{(+)}$	0.43			
$H_2O^{(-)}$	0.00			
	100.20			

Analysts: H. Haramura and T. Katsura.

over, at the higher pressure we actually obtained quartz+corundum, or quartz+new phases. Relations among these phases can therefore only be given on an approximate basis, although the differences in free energy among the various anhydrous assemblages must be very small and will not affect the maximum stability of pyrophyllite very markedly.

Two synthetic new phases:

1) *AS(H)-I.* It has already been mentioned that in the high pressure region the decomposition of the hydrates led to new phases. The most

TABLE III. UNIT CELL AND OPTICAL DATA ON THE ALUMINOSILICATES

$Al_2O_3:SiO_2$ Ratio	Kyanite	Sillimanite[2]	Mullites[2]		Andalusite	AS(H)-II[2]
	1:1	1:1	3:2	2:1	1:1	1:1(?)
Space Group	$P\bar{1}$[1]	*Pbnm*	*Pmmm*	?	*Pnnm*	*Pbam*
a (Å)	7.09 (α=90°)	7.481±.002	7.55	7.5	7.797±.002	7.553±.004
b	7.72 (β=101°)	7.672±.002	7.69	7.69	7.898±.002	8.273±.004
c	5.56 (γ=106°)	5.769±.002	5.77	5.77(×½)	5.551±.002	5.660±.004
Vol (Å)³	294	331	335	337	341.8	353.7
ρ (meas.)		3.255±.015		3.16±.015		
α	1.713	1.658	1.642	1.640	1.630	1.625
γ	1.728	1.678	1.654	1.651	1.641	1.641
$\gamma-\alpha$	.015	.020	.012	.011	0.011	0.016
2V	−83	+25	+45 to 50	+61	−83 to 86	
	$a=x$	$a=x$			$a=Z$	
	$c\wedge Z=30°$	$b=y$	$c=Z$		$b=Y$	$c=Z$
		$c=z$			$c=X$	

[1] Naray-Szabo, Taylor and Jackson (1929).
[2] *X*-ray and optical properties (except 2V) from this study.

important of these is herein called AS(H)-I and has no counterpart among natural minerals that are known today. This nomenclature follows the practice in this laboratory of naming a phase, which is not known to have a mineral counterpart, by the most euphonious combination of the first letters in the formula of its component oxides.

Under the microscope AS(H)-I is very fine-grained and massive, and individual grains cannot be resolved. Its average refractive index is about 1.71 and the aggregate shows a high birefringence. This phase occurs in association with quartz, pyrophyllite, hydralsite, and AS(H)-II, which will be described later. In no case was it clearly determined that AS(H)-I occurred with boehmite ($\pm$other phases). In a few cases it occurred with corundum ($\pm$other phases). Therefore, the order of appearance boehmite→AS(H)-I→(with an overlap)→corundum with respect to the rising temperature is clearly demonstrated (Fig. 1). AS(H)-I is formed more abundantly in Al_2O_3-rich mixtures, though it may be prepared from a gel as rich in SiO_2 as 67 mole % SiO_2. The lowest temperature of appearance is 440° C. at 3200 bars from a fresh gel of 90 mole % Al_2O_3 where it shows rather broad peaks in the *x*-ray patterns. The highest temperatures at which the phase appears are 570° C. at 4100 bars from mixtures of "Cab-O-Sil" and gibbsite and 567° C. at 5200 bars from "Ludox" gels.

Its most useful characteristic property is its powder diffraction pattern listed in Table I. The composition of the phase is not established since it was never obtained completely pure, but from the pattern of results it is estimated that the Al_2O_3:SiO_2 ratio would be approximately 4:1 or 5:1 or even higher. It cannot easily be proved whether or not AS(H)-I contains water. Its infra-red pattern shows only a rather broad absorption in the 2.75–2.9 μ region with no sharp OH band.

Hence, this may be another anhydrous aluminosilicate rather than a hydrous phase. For this reason its pseudonym has the "H" in parenthesis. No crystals large enough for detailed single crystal *x*-ray work were available.

2) *AS(H)-II*. In 1954 D. M. Roy reported the synthesis of what she called andalusite. This was a phase which had optical properties very similar to andalusite; it gave an *x*-ray powder pattern with the strongest three peaks closely matching the peaks of natural andalusite. However, its optical elongation is positive rather than negative. The same phase can be prepared quite consistently in several systems. Roy and Roy (1955) obtained it in the MgO-Al_2O_3-SiO_2-H_2O system. Several authors have prepared what is very probably this phase, both in our laboratory and others (*e.g.*, Warshaw, 1960; Hemley, 1959; Yoder, 1952; Winkler, 1957,) and all refer to it as andalusite. In the early part of the present

study this phase was encountered very reproducibly in the moderate temperature region and was in general taken as andalusite. Fyfe *et al.* (1958) imply on the basis of the optic elongation that this phase could be mullite rather than andalusite, although the *x*-ray and the refractive index data unambiguously distinguished this phase from mullite.

As more samples of the phase were obtained in the present study better optical properties could be measured and these showed that there exist small but measurable differences between the synthetic phase and natural andalusite. This led to more detailed studies on *x*-ray powder diffraction patterns and some single crystal work. Finally it became apparent that the two phases belong to different space groups and are, therefore, different mineral species. This new phase was called AS(H)-II with the "H" in parentheses indicating that the absence of H_2O in the crystal structure is not certain. A sample consisting largely of AS(H)-II was used to obtain the powder data in Table I. Single crystal *x*-ray work and the crystal structure are discussed in the next section.

Under the microscope AS(H)-II crystals are isolated needles, prisms or bundles of prisms up to 60×10 μ in size. The largest crystals ever observed occurred in mixtures in the system K_2O-Al_2O_3-SiO_2-H_2O close to kaolinite composition. AS(H)-II is orthorhombic and its unit cell dimensions (Table III) are rather remarkably different from those of andalusite though the spacings d(110), d(111) and d(220) are very similar, which led previous investigators to its misidentification as andalusite (Table I). It has also been prepared from "Cab-O-Sil"+gibbsite, hydralsite, or ethylorthosilicate gels.

As already reported by D. M. Roy (1954) the mean refractive index of AS(H)-II is about the same as natural andalusite but the double refraction is one and a half times larger than natural andalusite (Table III). It was found that crystals of AS(H)-II made in different runs sometimes showed slight variations in refractive indices. Some of the measurements are listed below:

Run No.	71104[1]	80127	90203
Starting Material	LG 67	LG 50	LG 67
Average size of crystal	10μ	50μ	50μ
α	1.622 ± 2	1.625 ± 2	1.625 ± 2
γ	1.637 ± 2	1.640 ± 2	1.641 ± 2
γ-α	0.015	0.015	0.016

[1] A single crystal for oscillation photos was taken from this sample.

The crystal is elongated parallel to the *c*-axis and lacks sharp terminal faces. The *z*-axis is parallel to the *c*-axis and this character is also different from the natural andalusite.

AS(H)-II could be prepared in rather good yields from gels of the compositions 20, 50, 55, 60 and 67 mole % Al_2O_3 at 500–720° C. and 500–5000 bars. Mixtures of a composition more aluminous than a 1:1 ratio usually gave more abundant AS(H)-II together with quartz and corundum and in some cases mullite, cristobalite, AS(H)-I and pyrophyllite.

It occurred frequently with quartz and corundum (especially around 600° C. and 4000 bars) and less often with mullite, AS(H)-I, cristobalite and pyrophyllite. Mixtures of the composition more Al-rich than a 1:1 ratio usually gave more abundant AS(H)-II. When Al-nitrate solution was added to 67 mole %, Al_2O_3 gel better developed AS(H)-II was often obtained. A favorable effect of higher pressures on crystallinity was generally well demonstrated; at the highest pressure (5350 bars) the best crystallized sample was obtained. This was used for an accurate cell dimension measurement (Table III). The composition of AS(H)-II is probably Al_2SiO_5 but could be somewhat more aluminous as is the case with mullite. The general p–t area for its formation is shown in Fig. 1. The upper stability limit of this phase was determined precisely and was found to be remarkably sharp and consistent.

In the early work using the ordinary andalusite a good correspondence in decomposition temperatures was noticed tending to confirm the identity of AS(H)-II and andalusite. After the differences between andalusite and AS(H)-II were found, the decomposition of gem quality andalusite was studied and found to be quite different.

Single crystal x-ray diffraction data and the crystal structure of AS(H)-II: A single grain of elongated AS(H)-II crystal (30 μ long) was selected for the single crystal *x*-ray work from batch No. 71104 which was run at 603° C. and 3500 bars (Fig. 1). The grain was mounted on a glass fiber with the axis of elongation parallel to the axis of rotation, and a series of oscillation photographs were taken with a 57 mm Unicam camera.

The obtained *c*-spacing coincided with that from the powder pattern and the reflections were indexed graphically using *a*- and *b*-spacings obtained from the powder data. It was found during the process that the mounted grain was not a single crystal, but actually consisted of two individuals twinned with the twinning axis perpendicular to (110). This fact was noticed by the presence of closely spaced pairs of (hkl) and (khl) reflections for stronger spots, one of the paired reflections having an impossible index for that particular orientation of the oscillation photo-

graph. It was possible in most cases to assign appropriate indices to such reflections without ambiguity. One individual of the twinned crystals was found to give far weaker spots than the other for the same reflection and the former individual gave spots for only the strongest reflections. Therefore, it was possible to distinguish the reflections of one of the twinned individuals from the other. Figure 2 represents relative intensities of reflections of an untwinned single crystal thus identified. In

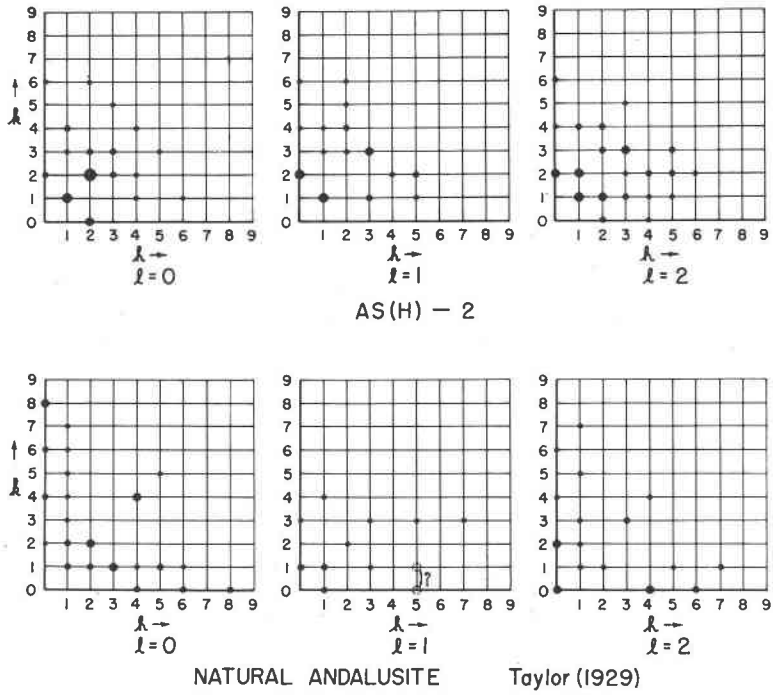


FIG. 2. Comparison of intensities of single-crystal x-ray diffraction spots (size of black circle is proportional to intensity) for AS(H)-2 and andalusite. The distinctiveness of these two phases is self-evident.

Fig. 2 relative intensities of the reflections of natural andalusite given by Taylor (1929) are also given for comparison. Although spots of AS(H)-II obtained on films are very weak and diffuse, it is apparent from Fig. 2 that AS(H)-II and natural andalusite give quite different intensities. The deduced space group is *Pbam* with some ambiguity. However, the space group *Pnnm* to which natural andalusite belongs is apparently impossible for the reflections of AS(H)-II *Pbnm* (for sillimanite) and *Pmmm* (for mullite) do not apply either. Therefore, it is apparent that AS(H)-II has a space group different from those of the orthorhombic aluminum silicates which are already known in nature.

It would appear worthwhile to consider the possible similarities between the structure of AS(H)-II and those of the other aluminum silicates. If we assume that AS(H)-II is an anhydrous aluminum silicate which has the composition Al_2SiO_5 and has a structure similar to those of already known Al_2SiO_5 polymorphs, *i.e.*, composed of Al-O octahedral chains parallel to the *c*-axis linked together by Al and Si, it appears possible that AS(H)-II is another polymorph of Al_2SiO_5.

The presence of *a*- and *b*-glides instead of diagonal glides makes it necessary for Si and Al ions, which are not contained in Al-O chains, to be distributed in the way indicated in Fig. 3. The arrangements of cor-

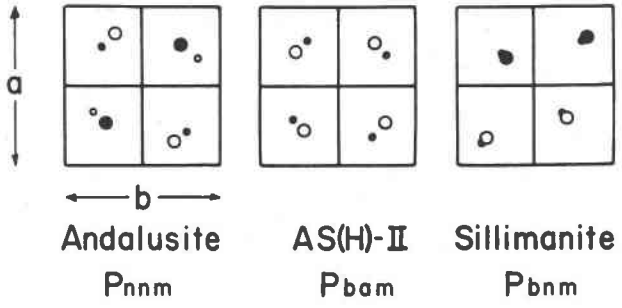


FIG. 3. A possible scheme to represent distribution of Al-Si ions in these aluminum silicates.

responding Si and Al ions in andalusite and sillimanite unit cells are also shown for comparison. If Si and Al are distributed in the AS(H)-II structure as shown in Fig. 3, it seems necessary for Al ions to have a four-fold not five-fold coordination with respect to oxygen ions. This will be clearly seen from the geometrical relation of O^{2-} ions in the unit cell and the resulting arrangement of O^{2-} ions will closely resemble that of sillimanite.

However, there is an indication that AS(H)-II may have a ratio of $Al_2O_3:SiO_2$ different from 1:1. It was found that among various batches of AS(H)-II produced under different p-t conditions the refractive indices fluctuated within a small but appreciable range. For example, in most cases the refractive indices are $\alpha=1.625\pm0.002$ and $\gamma=1.640\pm0.002$ (Table III) while the sample studied by the single crystal *x*-ray work shows $\alpha=1.622\pm0.002$ and $\gamma=1.637\pm0.002$. This fact might suggest that AS(H)-II is not strictly an Al_2SiO_5 composition but has a variable composition slightly deviating from the ideal composition, possibly with ratios of $Al_2O_3:SiO_2$ higher than unity and OH^- ions replacing some of the O^{2-} ions. It can be assumed that AS(H)-II with a supposed composition of Al_2SiO_5 and other aluminum silicates of the composition Al_2SiO_5 obey closely the law of molecular refractivity, *e.g.*, that represented by the Lorenz-Lorenz equation.

Mullites: The problem of the relation of various mullites to each other and to sillimanite has recently been reviewed thoroughly by Agrell and Smith (1960). They also made detailed measurements on about a dozen samples collected from various laboratories. Similar measurements were made on some 30 synthetic samples of our own where the composition and heat treatment, etc. were carefully controlled and performed under identical or comparable conditions. The accuracy of these actual measurements is better than $\pm .01°$ 2θ in the best cases, comparable with that claimed by Agrell and Smith; however, since many of our samples were relatively poorly crystallized and there is some error present due to inhomogeneities in the values of the lattice parameters calculated from various sets of reflections, our overall accuracy is perhaps one-half that claimed by Agrell and Smith. Details of our methods and some results on this phase of the work are described elsewhere (Aramaki and Roy, 1962).

The unit cell volumes obtained are plotted vs. the "*c*" parameter in Fig. 4 (following Smith and Agrell), a different presentation of the data having been given in Fig. 4 of the Aramaki and Roy paper (1962). This type of plot shows up the distinction between the sillimanites and mullites unambiguously. Our two new analyzed sillimanites (metamorphic) plot very close to those of Smith and Agrell, and all our mullites plot clearly together in a separate group with cell parameters definitely indicating that they are *all* mullites. Two anomalous phases were found both presumably sillimanites from formation and optical properties. These are the high temperature specimens from the Asama volcano and a sillimanite prepared in opposed anvil apparatus at 650° C. and 20 kb in two days. These represent in our view disordered sillimanites and it can be seen that one does *not* progress from sillimanite to mullite on disordering the former.

The important new analogous finding is that the lattice parameters of mullite of any given composition can be changed as a function of heat treatment, and that the magnitude of these changes compares favorably with the magnitude of the change brought about by introduction of the maximum amount of Al_2O_3 into the lattice (for details see Aramaki and Roy, 1962). However, following Smith and Agrell the distinction between sillimanite and mullite should be made on the basis of careful *x*-ray measurements which may also be used to characterize the "sillimanite" further. Inspection of a powder pattern is not enough to give a refined solution to the problem. The data obtained from our study are given below.

Single crystal *x*-ray work has also shown clearly the subtle differences between several mullites which may at first sight appear similar. In our

parallel study a new mullite with the simplest lattice so far reported was found with sharp spots and no intermediate ordering reflections.

Stability Relations of the Aluminosilicates: Clark, *et al.* (1957) have presented data on one p-t curve involved in the system that relates to the polymorphic reaction kyanite$\rightleftharpoons$sillimanite. The curve was obtained at temperatures from 1000 to 1300° C. and pressures of 18–21,000 bars. The data are not precise enough to allow extrapolation with any degree of confidence, but their "straight line extrapolation leads to the value of about 10–12,000 atm. at 400–500° C. for the transformation of sillimanite to kyanite." Petrologic evidence *appears* to demand a lower value for the formation pressures of kyanite. Clark *et al.* (1957) have indicated that a more reasonable p-t curve in the lower temperature region could be assumed on the basis of some tentative thermochemical considerations. Hence, it was considered a worthwhile attempt to study directly the phase relations in the range 400–1000° C. at moderate pressures.

A wide variety of techniques was tried with varying degrees of success. Since additional components which do not enter the solid phases cannot affect the polymorphic equilibria several different "mineralizers" were added inside the sealed gold tubes. These included H_3BO_4, Na_2WO_4, NaCl, LiCl, KF, HF, Al-nitrate, etc. It was hoped that if the mineralizers actually effected synthesis of the two polymorphs, the question of solid solubility could be tackled later. These hydrothermal runs were made up to pressures of over 5000 bars. In addition runs were made in Bridgman opposed anvil devices in which rather good precision had been attained in determining transitions by the use of long runs (Dachille and Roy, 1959, 1960).

In the entire range of experiments kyanite was never synthesized. What can be called sillimanite was obtained only in opposed anvil runs at 600° C. and above 20,000 atm. The sillimanite is compared to natural sillimanites in Fig. 4, and is seen to be measurably different from the several natural sillimanites and from all the mullites.

The question as to whether the phase being produced was mullite or sillimanite is crucial. Roy and Osborn claimed to have found only mullite in their runs at pressures below 2000 bars, while Kennedy (1955) claimed that there was complete solid solution between these phases at 2000 bars at 550–600° C. Griggs and Kennedy (1956) on the other hand show only the presence of sillimanite as the decomposition product of pyrophyllite at pressures as low as 1000 bars. In the range from 500 bars to 5000 bars literally hundreds of "mullites" were synthesized by us. From a study of the powder patterns (see below also) these were clearly determined to be of the mullite-family but in many cases they

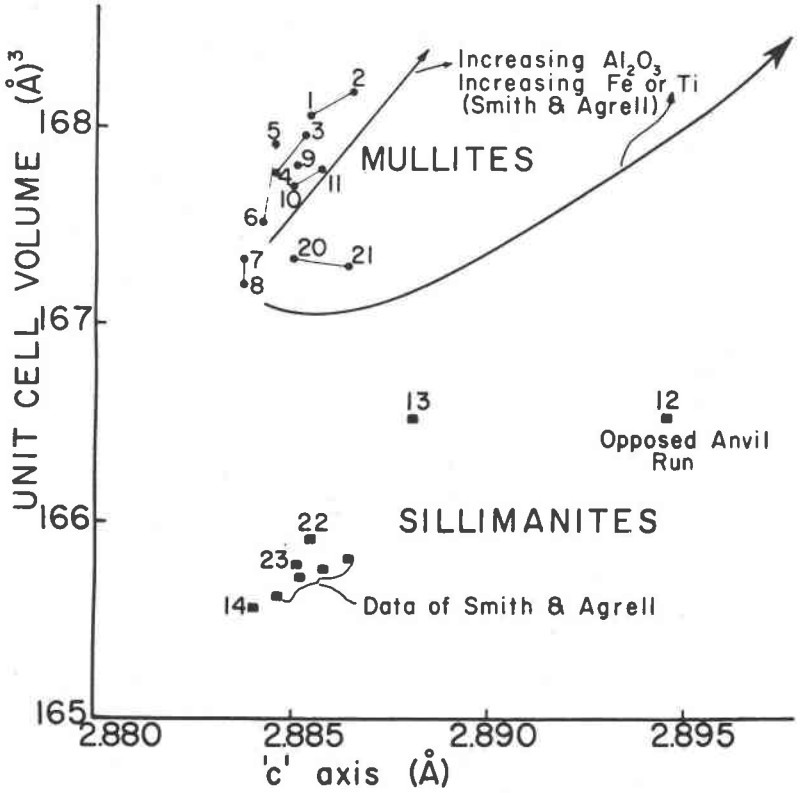


FIG. 4. Plot of unit cell volume of mullites and sillimanites versus "c" axis dimension. Note clearcut distinction between sillimanites and all mullites. All mullites, including those made at 4 and 5 kbars plot near the mullites. Moreover, the cell dimensions of the mullites vary with heat treatment rendering the suggested change (Smith and Agrell) due to composition less useful if valid. Note that synthetic sillimanite (typified by No. 12) does not become identical with natural material, except for the high temperature xenolith material shown at No. 13.

were not well enough crystallized for precise measurements; in others they were contaminated with other phases. Selected examples, however, were checked to verify in detail the important question of the extent of possible solubility between sillimanite and mullite. We have already demonstrated elsewhere (Aramaki and Roy, 1959a, 1962) that there is no evidence for any (certainly <1–2 mole per cent) solid solution from mullite toward sillimanite at solidus temperatures. At about 1000° C. there is excellent phase evidence which shows that mullite+tridymite (in large enough quantity to give a good x-ray pattern) is obtained in 50, 55 and 58 mole % mixtures while only a mullite phase is obtained at 60

mole %. In a mixture at 63 mole % a very small amount of fine-grained corundum was detected by a microscope. It is unlikely that the equilibrium solubility of silica in mullite will increase with decreasing temperature and there was no phase evidence to suggest this. Similarly higher pressure would not *in general* increase the solid solubility among two phases, although this is the kind of case which may be an exception. However, the precision measurements were carried out on mullites prepared at 4900 bars and at 623° C. and 3000 bars at 727° C., since it was argued that if these products were not sillimanite, and if they showed no solubility towards silica, it would be unlikely that lower pressure phases would be likely to. In neither case was there any suggestion that these phases were anything other than mullite; points 20 and 21 plot clearly in in the mullite field (Fig. 4). Thus there is no evidence either for structural (Agrell and Smith, 1960) or compositional gradation of sillimanite to mullite at these pressures (<5000 bars). There is positive evidence (Aramaki and Roy, 1959a, 1962) that mullites themselves may disorder without any compositional change, and perhaps sillimanites themselves may show order-disorder phenomena, presumably of Al and Si. Whether such changes in sillimanite and mullite are true second order transitions with a prescribed degree of order at equilibrium at any temperature, or whether a specific temperature exists for the low⇌high transformations are questions which are not likely to be resolved in the near future. Of course these considerations of disordered phases bear more generally on the entire p-t stability problem. To which phases do the thermochemical parameters apply? What of the experimentally determined p-t curves; would they change measurably if the phase were ordered or disordered? Here we may be safe in assuming that the natural minerals are "low," ordered forms, but what of the synthetic mullite? When such exceedingly small differences in heat content and entropy are involved, as in this series, the differences between an ordered and a disordered phase may reverse the ΔF term. Along these lines, the question of the identity of Clark, *et al.*'s "sillimanite" should be raised; was it low sillimanite or an intermediate member? Were all the "sillimanites" obtained in different runs identical? It is obvious that without detailed and careful, time-consuming work further data on this system will serve only to confuse the picture. Clark *et al.* mentioned that their sillimanite has refractive indices slightly lower than natural sillimanite. But the latter contains iron, so no standard value for the properties of any of the pure phases in a "standard state" are as yet available. A similar situation exists in the synthetic mica field (Crowley and Roy, 1959).

Thus, it is seen that the present study failed to reveal any new information on the kyanite-sillimanite curve; it has helped, however, to

point out that mullite is not and "sillimanite" *may* not be "sufficient" characterization of a sample to allow extrapolation of relations from a region where high-phases may be stable to regions where low-phases may exist. Neither is it possible to use with confidence thermochemical data obtained on phases which may not be precisely the same as the ones actually encountered in synthetic experiments, especially when the thermochemical differences are so subtle.

Of the other curves which must exist on the phase diagram, in the early part of this work we obtained and presented (1958) a precise, reproducible curve for the reaction "andalusite⇌mullite and quartz." Actually the reaction being studied was AS(H)-II⇌mullite (3:2, low temperature)+quartz. For this reaction a p-t curve with possibly a slight negative slope was found as shown in Fig. 5 on which a few of the runs made are also shown. The first sample of natural andalusite used appeared to confirm this curve, since microscopic evidence of attack appeared along the same p-t line. However, a sample of gem quality

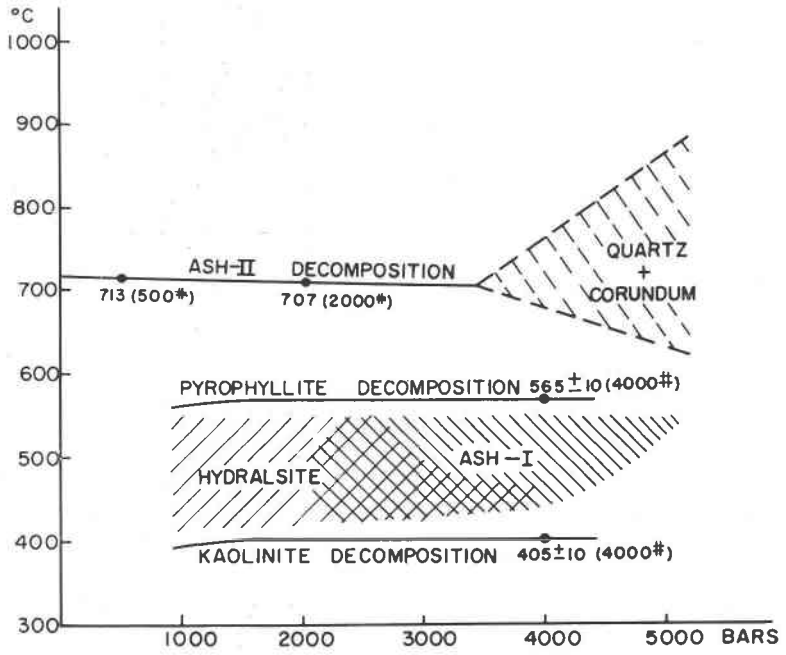


FIG. 5. Summary of important p-t relations involving minerals in the system Al_2O_3-SiO_2. The field for quartz and corundum is shown in the area where this assemblage forms from, and is therefore *more* stable than most other assemblages (see text) although thermodynamically *stable* equilibrium existence has not been rigorously established for this assemblage.

andalusite failed to dissociate 50° C. above the same line. Re-examination of the first sample showed the presence of microscopic amounts of some impurity (probably mica) which may have caused the apparent breakdown of the andalusite.

In spite of the failure to synthesize kyanite and true andalusite, a considerable amount of information can be obtained from the extensive data on syntheses from gels and other starting materials as well as from the "breakdown reactions." A glance at the summary of the data in Fig. 5 will show that in a certain p-t region the assemblage quartz+corundum was obtained again and again from a wide variety of starting materials. Clark, *et al.* also obtained essentially only this assemblage in half their runs as well as in all their runs below about 18,000 atm. and 1000° C. Roy and Osborn had not obtained this assemblage at all in their work below 2000 atm. In the present work, whereas mullite was formed at low pressures (<1000 atm.), in runs at the same temperature (600° C.) but considerably higher pressure the same starting materials yield quartz+corundum.

The data we have obtained to date do *not* yet establish that quartz and corundum are the stable phases in a particular p-t region. On the other hand, the mass of data accumulated require that this possibility be considered with an open mind. Indeed, the only strong argument against the tentative adoption of the Q+C assemblage as stable *in a certain part of the p-t diagram* is the fact that this assemblage is not found in nature. Were it not for this fact, the laboratory investigator would be compelled by logic to find room, on the basis of the data to date, for the stable existence of this assemblage. A wide variety of starting materials was used in the attempt to make sure that the structural prejudice of a particular material did not influence the final product. Thus, the range of materials included the Ludox gel with the Si and Al atoms interspersed in an oxygen network on a very nearly atomic scale, with a very probable prejudice towards 4 coordination. In the low temperature electrodialyzed gels the network included a much larger percentage of OH ions and probably much Al in 6 coordination. Clay minerals were used in which the Al ions were definitely in 6 coordination and separated from the silicon atoms by only one layer of oxygens not unlike the situation in the aluminosilicate structures themselves. Finally, simple mechanical mixtures of $Al(OH)_3$ and amorphous SiO_2 were used which certainly should be prejudiced toward the formation of two separate oxide phases. In many cases, a particular "oxide" as mineralizer was added in order to "solubilize" the Al_2O_3 which is supposedly the cause of the non-reactivity of the quartz+corundum assemblage: K_2O, KF, HF, Na_2O and MgF_2 were used.

The data are set forth schematically in Table IV (and Fig. 5). In the p-t region centering on the point at 600° C. and 4000 bars, a statistical listing of the products tabulated in Table IV shows that Q+C only was formed in 23/76 of the runs, while Q+C+some other phase was formed in 67/76 runs. Moreover, it was established at least for the case of the Q+M+C assemblage that mullite formed first and then decomposed to Q+C. This was done by making a run only long enough to have the bomb come up and "settle down" to the 'p' and 't' conditions of the run before quenching it. The total time from the insertion of the bomb in the furnace to the quenching was less than 30 minutes. The 1:1 gel yielded *mainly* mullite (+some Q+AS(H)-II) under these conditions. Under essentially identical conditions in a one-week run it gave mainly quartz and corundum. Clearly the direction of equilibrium is toward quartz and corundum. Thus, it has been shown that the appearance of quartz and corundum is *not* due to metastable formation and subsequent persistence. The fact that gibbsite+silica will react at low pressures to give mullite first is evidence along the same line. On the other hand a run for 32 days at 691° C. and 3900 bars showed no reaction of very fine quartz +corundum and only quartz+corundum forming from silica-glass +corundum.

It can easily be seen from the data that no structural prejudice is involved in the formation of Q+C. Indeed, this is the strongest argument (in the absence of data) for the thermodynamic stability of this assemblage. Hydralsite converts to Q+C; the various gels convert to Q+C; mullite converts to Q+C; AS(H)-II converts to Q+C; Q+C form together with muscovite or paragonite when alkali is present. Clark *et al.* (1957) have converted kaolinite and andalusite to Q+C. There is no structural feature in common for these materials. On the contrary, one would certainly assert that to consider that it is structurally reasonable for gibbsite and silica to combine to form mullite and then for mullite to dissociate into its component oxides as steps on the way to the formation of sillimanite is rather special pleading. Likewise, one destroys the convenient lattice of the clay minerals with their 6 coordinated Al^{3+} ions rather than rearranging it to give sillimanite or kyanite. This does not happen on the formation of mullite at atmospheric pressure and provides another example of special pleading in the case against the stability of quartz and corundum. In this connection it should be pointed out that Clark *et al.* (1957) make a common error in their paper (p. 634) in seeking to explain the formation of quartz and corundum from kaolinite. In spite of several dozen papers on the subject of the dehydration of kaolinite to the contrary, they assert "it is well known that when kaolinite is dehydrated at low pressure, this assemblage

TABLE IV.—SCHEMATIC SUMMARY OF THE NUMBER OF RUNS YIELDING QUARTZ+CORUNDUM ASSEMBLAGE

Starting Material	Mole %		Product										
	Al_2O_3	SiO_2	Q+C	Q+2+C	Q+M+C	Q+2+M+C	Q+M	M+C	M	Q+2	2+M	Q+2+M	Q+1+C	1
Ludox 'AS' gel	20	80		1										
	33	67	2											
	50	50	8	1	1									
	60	40	4	1	4	1			1	1				
	67	33	2	6	2									
	75	25						2						
	90	10												2
Ludox gel 67:33+Al-nitrate sq.			1	1		1					1			
Cabosil	50	50	3		1							2		
gibbsite	67	33	1		1								2	
synthetic hydralsite			3	1										
natural halloysite			2											
Electrodialysed orthosilicate	20	80	1			1								
gel	60	33				2								
Ludox gel 55:45+KF			1[1]											
Oudox gel 55:45+MgF_2			2[2]		2[2]									
Gel (1:1+small amount of K_2O)			6[1]											
Gel (1:2+small amount of Na_2O)			2[1]											

[1] Plus mica.
[2] Plus unidentified.
Abbreviations used: Q=quartz, C=corundum, M=mullite, 1=AS(H)-I, 2=AS(H)-II.

(quartz+corundum) appears as an intermediate stage in the reaction which eventually produces the stable assemblage mullite+quartz." Although a reference is given to Eitel (1954, p. 1104–6), reference to the latter book reveals that Eitel makes no such assertion. This error may result from equating the terms "Al_2O_3" or "alumina" with corundum and the term "silica" or "amorphous oxide" with quartz. A similar error in the work of Stone (1952) was already referred to in the previous paper by Roy and Osborn. The structural progress of dehydration of kaolinite is fairly generally agreed upon (for recent work see Glass, 1954; Roy *et al.*, 1955; Brindley and Nakahira, 1959) and at no stage involves the formation of either quartz or corundum. The lattice goes through a metakaolin stage and a "γ-Al_2O_3" or "silicon-spinel" phase on its way to the formation of mullite. Whether or not mullite is the stable phase even at one atmosphere at low temperatures, i.e., below about 1100° C., is not established. Certainly the possibility that the quartz +corundum assemblage is the stable one in the Al_2O_3-SiO_2 system below 1000° C. at 1 atm. has not been rigorously excluded. Indeed, although the authors agree with Clark *et al.*'s best interpretation of their own data, it must be admitted that none of the experiments show that either kyanite or sillimanite is more stable than quartz and corundum in the p-t regions where they were found. This could be established by a series of runs of increasing length, in which the longest ones should give kyanite. On the other hand kyanite and sillimanite *could* have formed as metastable phases just as mullite forms at 5000 bars in other runs.

In the opposed anvil runs, which gave sillimanite shown as point 12 in Fig. 4. there was no evidence for the formation of quartz and corundum as an intermediate step. Thus, the structural considerations are completely against the probability of the breakup of aluminosilicate lattices such as kaolinite, hydralsite, andalusite, mullite and AS(H)-II as a step in the formation of kyanite and sillimanite. Indeed, the converse is much more likely. There is one consideration which, ignoring the structural concepts, does speak for the possibility of the Q+C assemblage being an intermediate step. This is the molar volume. Next to kyanite, the quartz +corundum assemblage has the smallest molar volume of any other phase or phase assemblage.

In our studies of the decomposition of the aluminosilicates in the presence of water, runs were made only above the pyrophyllite maximum stability temperature. Roy and Osborn having previously decomposed the anhydrous phases to the hydrates. In nearly all cases there was evidence for the formation of corundum from andalusite, sillimanite and kyanite. Only in a few cases did both corundum and quartz or cristobalite appear. Where there was a leak in the tube, abundant corundum was

found indicating that these minerals can very easily be desilicated in open stems. However, the explanation for the formation of corundum in weight-checked sealed tubes with a very small volume of water is much more difficult. One has to assume not only very incongruent solubility for these phases in water at 4000 atm. and 600° C., but also that the amount of solubility is high enough to remove enough silica from the solid to cause precipitation of large enough amounts of corundum to be detected even in a diffractometer pattern. Since data on the solubility of SiO_2 in water at 4000 atm. and 600° C. was not known it was suspected that this may attain a very high value. A simple and rough check was made on this by determining the solubility of quartz (Brazil, clear crystal) under these conditions by weight loss measurements in a sealed gold tube. The solubility recorded was about 1.4 gms/100 ml which appears to be insufficient to explain the formation of corundum. However, supersaturation with respect to silica should not be difficult, and may account for a much larger amount of silica being leached out. The alternative to this suggestion is of course the possibility that in this p-t range corundum +quartz is more stable than kyanite and/or sillimanite and/or andalusite. A speculative diagram for the polymorphic relations of the Al_2SiO_5 composition may be presented, but this is avoided here to prevent further confusion in the literature. Instead, in Fig. 5 is presented a composite metastable equilibrium diagram for the system, showing assemblages and p–t curves which are actually observed, and not-impossible relations among them.

Conclusions

A re-examination of the Al_2O_3-SiO_2-H_2O system has revealed:

1. The existence of two "new" phases, one of them a polymorph of Al_2SiO_5 which occurs commonly in laboratory work.

2. The decomposition curves for kaolinite and pyrophyllite are extremely steep in the region 2000–6000 bars, setting 410° C. and 570° C. essentially as the upper stability temperature of these phases in observable natural occurrences. SiO_2 inhibits the formation of diaspore and *appears* to raise the decomposition temperature of boehmite.

3. Experimental results from several laboratories yield quartz and corundum consistently from many completely different starting materials. Structural and crystal chemical evidence is adduced to show that the metastable formation of this assemblage under these conditions would be a highly improbable event. The possibility of metastable formation of kyanite and sillimanite *in the laboratory* experiments to date must be considered seriously.

4. Considerable evidence is presented against the idea of solid solution

between mullite and sillimanite at 2000 bars as also against reports of sillimanite synthesis at low pressures (<5 kb). Order-disorder in mullite and probably in sillimanite is demonstrated.

Acknowledgments

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