

AN EXPERIMENTAL INVESTIGATION OF THE RELATIONSHIP OF MULLITE TO SILLIMANITE¹

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ABSTRACT

We have synthesized solid phases in the system $\text{Al}_2\text{O}_3\text{-SiO}_2$. The X-ray powder diffraction patterns of the run products range continuously from the pattern of mullite to the pattern of sillimanite depending on the run P - T conditions. Cell edges and volume have been measured and found to grade continuously from those of mullite to those of sillimanite. Low pressure phases, with mullite-like patterns, can be made to change continuously in cell dimensions to those of sillimanite by increase of pressure at temperatures high enough to produce suitable reaction rates. These cell parameter changes are consistent with two different interpretations; one interpretation would attribute the cell changes to a variable degree of Si-Al tetrahedral ordering between sillimanite (ordered) and mullite (disordered). The second interpretation which seems to better fit our observations, is that of a continuous isomorphous solid solution relationship between sillimanite and mullite.

INTRODUCTION

The system $\text{Al}_2\text{O}_3\text{-SiO}_2$ has been of primary interest to both petrographers and experimentalists because of the possibility that phases in the system may be both geologic thermometers and/or barometers. This binary system contains four naturally occurring compounds, three of which: kyanite, sillimanite and andalusite, have the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and are commonly found in metamorphic rocks. The fourth compound, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - 2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, mullite, occurs rarely in natural rocks but it is of importance as a principal component of some porcelains and related ceramic products. The problem of the pressure-temperature field of the phases in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system has attracted a good deal of experimental investigation during the past ten years. Griggs and Kennedy (1956) published the first curve of the kyanite-sillimanite boundary. Clark, *et al.* (1957) and Clark (1961) redetermined the kyanite-sillimanite PT equilibrium boundary with results quite similar to those earlier reported by Griggs and Kennedy. The first attempt to determine the position of the triple point involving the phases kyanite, sillimanite and andalusite was published in 1963 by Bell and by Khitarov *et al.* These earlier investigations were marked by substantial errors owing to failures to obtain equilibrium and owing to uncertain pressure distribution and reaction rates in the piston-anvil apparatus. More accurate and recent experimental studies in the system have been published by Newton

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(1966), Matsushima *et al.* (1966), Althaus (1967) and by Richardson *et al.* (1967).

Some calculations of the phase boundaries in the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ have been made from thermodynamic data. These calculations were initially based on heat of solution as measured by Neumann (1925) and Klever (1929). Their HF solution calorimetric data were almost certainly substantially in error and they have been criticized by Flood and Knapp (1957) on the basis of the ternary phase diagrams of Al_2O_3 and SiO_2 with CaO , MgO and FeO . Weill (1966) obtained new data on the free energies of formation of andalusite, kyanite, sillimanite and mullite by measuring their solubility in a cryolite melt. They also calculated the triple point of the three phases from their measurements coupled with the data of Pankratz and Kelley (1964) and Skinner *et al.* (1961). Fyfe and Turner (1966) calculated a triple point near that of Weill. Holm and Kleppa (1966) redetermined some of the thermodynamic parameters of the aluminum silicates by oxide melt solution calorimetry and their data have been amended in a recent paper by Anderson and Kleppa (1969). More recent experimental investigations (see Newton, 1966a, b; Matsushima *et al.* 1966; Althaus, 1967; Richardson *et al.* 1968; and Richardson *et al.* 1969) all agree on the position and slope of the sillimanite-kyanite boundary.

In spite of extensive attention to the phase relations among andalusite, kyanite and sillimanite, little attention has been paid to the stability field of mullite and, in particular, to its relationship to sillimanite. Kennedy (1961) suggested on the basis of some X-ray and experimental studies that a solid solution relationship exists between mullite and sillimanite and that a continuous gradation of composition exists. This suggestion was made in spite of the observation that most naturally occurring sillimanites which have been studied by X-ray techniques appear to be at one end of the spectrum. Aramaki and Roy (1962) report the preparation of "mullites" that grade in volume of unit cell from 168.2 to 167.3 \AA^3 and "sillimanites" with cell volumes ranging from 166.6 to 165.6 \AA^3 . They propose, however, that these variations are due to order-disorder changes and that the silica-rich limit of mullite solid solution occurs at 60 ± 1 mole percent.

The relative stability fields of sillimanite and mullite were computed by Holm and Kleppa (1966) from thermodynamic data assuming that no gradation in composition between the two phases exists. Thus, they showed the equilibrium curves for the reactions $\text{sillimanite} = \frac{1}{3} (\text{mullite} + \text{tridymite})$ and $\frac{1}{3} \text{mullite} = \frac{2}{3} \text{sillimanite} + \frac{1}{3} \text{corundum}$. The various computed and experimentally determined phase boundaries given by the various authors are shown in Fig. 1.

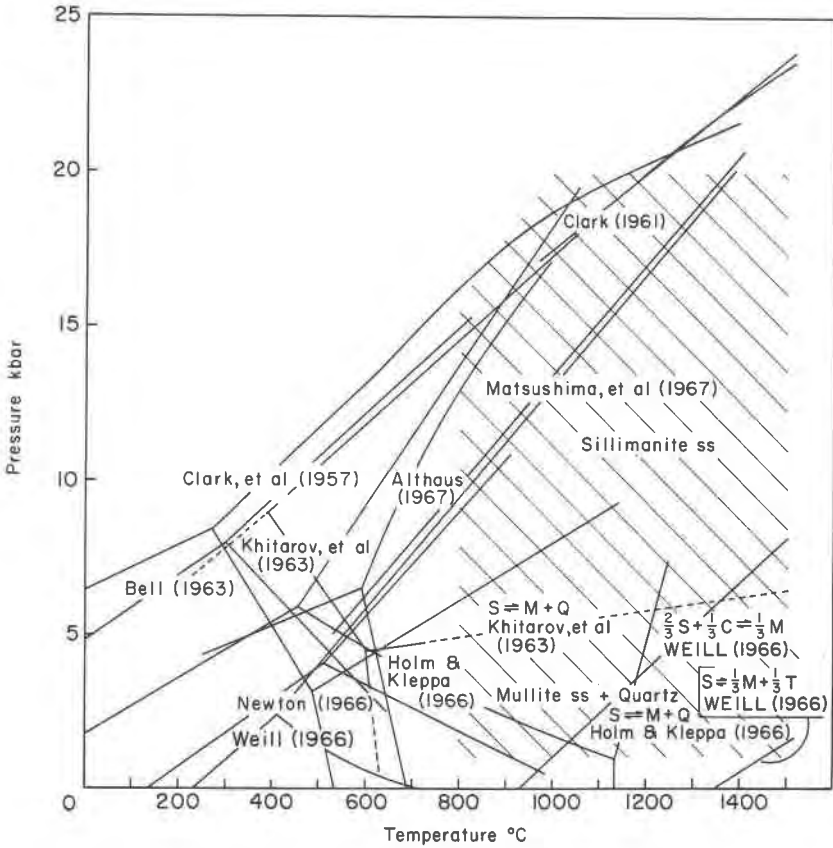


FIG. 1. Phase boundaries in the system Al_2O_3 , as given by various authors (the shaded portion of the diagram is the experimental area of this study).

Agrell and Smith (1960) showed that the composition of mullites ranges from $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. However, they excluded the possibility of an isomorphous series between sillimanite and mullite because "they have different crystal structures". Comparison, however, of the crystal structures of a 1.92:1 mullite (Burnham, 1963a) and a 1.71:1 mullite (Durovic, 1962), with the structure of sillimanite (Burnham, 1963b) shows the remarkable similarity of these structures. Only a few atoms need be slightly shifted (or removed) to create one compound from the other. An additional and complicating factor, however, is that whereas sillimanite is apparently ordered in nature, the distribution of Si and Al atoms among the tetrahedral sites of mullite is unknown and probably variable. No experimental results have been published relating the stability of mullite in the Al_2O_3 - SiO_2 system.

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

All the presently reported experiments were carried out in piston cylinder apparatus of 1/2 in. bore and 2 in. length. The pressure transmitting medium was molten pyrex glass, and the design of the pressure cell was similar to that figured by Hariya and Kennedy (1968). A hysteresis loop, relating piston displacement to ram thrust, on compression and decompression cycles was determined at a number of temperatures. The assumption that friction is symmetrical has been made. The results are plotted in Figure 2 showing the friction correction employed as both a function of pressure and temperature. Because of the decreased viscosity of the molten glass pressure transmitting medium, the correction to the

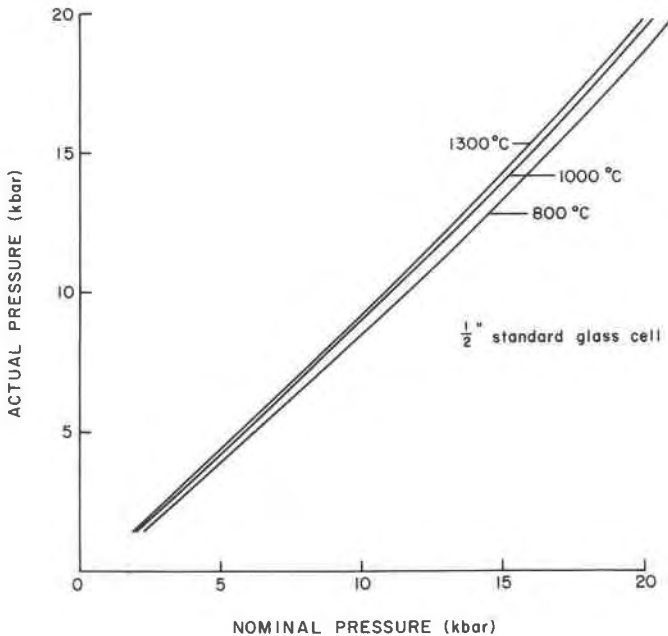


FIG. 2. Friction correction for various temperatures and pressures

nominal pressure, or pressure computed from ram thrust, decreases as temperature is increased. The double value of friction ranged from 1.2 to 3 kbar and the friction correction applied, as a function of both temperature and pressure, is shown in Table 1.

Temperatures were measured with Pt-Pt10Rh thermocouples which were in contact with the platinum sample capsules. Corrections were made for the effect of pressure on the e.m.f. of thermocouples according to the recent data of Getting and Kennedy. Unfortunately, temperature fluctuations of as much as $\pm 15^\circ$ took place in overnight runs and for shorter runs fluctuations of temperature of up to $\pm 8^\circ$ were encountered.

Starting material. Several different starting materials were used in various phases of this investigation. Much of the synthetic mullite used was prepared by heating natural kaolin obtained from the Southern Clay Company for 48 hours at 1450°C . According to the results of Brindley and Nakahira (1958) this should have produced a mullite of the approxi-

mate chemistry $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. They reported results of firing kaolin at various temperatures to be as follows:

$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	500°C	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$
		meta-kaolin
$2(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$	925°C	$2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{SiO}_2$
		silicon spinel
$2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	1100°C	$2(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2) + \text{SiO}_2$
		1:1 mullite-type phase
$3(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$	above 1500°C	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2$
		3:2 mullite

A powdered synthetic mullite purchased from the Tem-Pre Research Inc. of Pennsylvania was also used as a starting material. According to the manufacturer, this sample, prepared

TABLE 1. CORRECTION APPLIED FOR FRICTION AT VARIOUS TEMPERATURES^a

Temperature (°C)	Pressure(kbar)	Single value of friction
800	5	1.17
	10	1.80
	15	1.58
	20	1.55
1000	5	0.80
	10	.86
	15	.93
	20	.87
1300	5	.73
	10	.69
	15	.72
	20	.62

^a $\frac{1}{2}$ " chamber glass pressure cell

from Baker analyzed silicic acid and aluminum hydroxide, has a purity of greater than 99% with a stoichiometry of $60\% \pm 0.1$ mole percent Al_2O_3 -40 mole percent SiO_2 . The unit cell dimensions of these two mullites as well as data on other mullites extracted from the results of Agrell and Smith and Aramaki and Roy are shown in Table 2. In addition we record in Table 2 the unit cell dimensions of various natural sillimanites available to us as well as the various literature data on unit cell dimensions of natural sillimanites.

Phase identification and calculations of lattice constants. The phase produced in the experiments were identified by X-ray powder diffraction patterns. X-ray diffraction patterns were made with the samples mixed with approximately 15 percent of silicon metal which served as an internal standard. The 2θ values were recorded using $\text{CuK}\alpha$ radiation with a

TABLE 2. UNIT CELL DIMENSIONS OF MULLITES AND SILLIMANITES

	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
Mullites				
1. Vitrofax mullite	7.5788(25)	7.6939(17)	2.8895(6)	168.49(5)
2. Synthetic large single crystal mullite	7.5665(12)	7.6955(7)	2.8905(4)	168.31(3)
3. Synthetic mullite with composition 22.0 SiO ₂ and 77.6 Al ₂ O ₃ (wt %) (from data of Agrell & Smith)	7.5686	7.6865	2.8858	167.89
4. Synthetic mullite with composition 28.0 SiO ₂ and 71.6 Al ₂ O ₃ (wt %) (from data of Agrell and Smith)	7.5563	7.6874	2.8842	167.54
5. Synthetic mullite with composition 3Al ₂ O ₃ ·2SiO ₂ (no Fe or Ti) (from data of Agrell and Smith)	7.5582	7.6878	2.8843	167.60
6. Forster arc-fusion mullite (from data of Agrell & Smith)	7.5875	7.6801	2.8876	168.28
7. Synthetic mullite 33SiO ₂ and 67Al ₂ O ₃ (mole %) 1755°±15°C, 125 min. (from data of Aramaki and Roy)	7.572(2)	7.688(2)	2.8845(5)	167.92
8. Synthetic mullite 50SiO ₂ and 50Al ₂ O ₃ (mole %) 1755°±15°C, 125 min (from data of Aramaki and Roy)	7.555(2)	7.688(2)	2.8842(8)	167.52
9. Arc-fusion mullite composition 2Al ₂ O ₃ SiO ₂ (from data of Aramaki and Roy)	7.583(2)	7.681(2)	2.8854(5)	168.06
10. Fired kaolinite 1450°C 48 hr; starting material of this study	7.5467(1)	7.6944(1)	2.8844(5)	167.49(3)
11. Synthetic mullite; 99% single phase with stoichiometry 60 wt/mole %Al ₂ O ₃ (Tem-Pres Research Inc.)	7.5504(2)	7.6895(2)	2.8838(8)	167.43(6)
12. Natural mullite from fused Jurassic shale, Mull, Scotland (from data of Agrell and Smith)	7.5277	7.6913	2.8871	167.16
13. Natural mullite, from mullite-cordierite hornfels from carboniferous shale Northern Ireland (from data of Agrell and Smith)	7.5309	7.6877	2.8882	167.18
14. Natural mullite from Tievebulliagh, County Antrim, N. Ireland (from data of Agrell and Smith)	7.5442	7.7053	2.8952	168.34
15. Natural mullite from Tievebulliagh, County Antrim, N. Ireland (from data of Agrell and Smith)	7.5463	7.7064	2.8944	168.33
16. Natural mullite from Tievebulliagh, County Antrim, N. Ireland (from data of Agrell and Smith)	7.5397	7.6986	2.8927	167.91
Sillimanites				
	$a(\text{\AA})$	$b(\text{\AA})$	$c/2(\text{\AA})$	$V/2(\text{\AA}^3)$
17. Sardinia sillimanite	7.4907(8)	7.6780(7)	2.8882(3)	166.11(2)
18. Norwich Conn. sillimanite I	7.4871(15)	7.6799(8)	2.8887(4)	166.10(3)
19. South Dakota sillimanite I	7.4872(6)	7.6749(6)	2.8873(3)	165.92(2)
20. South Dakota sillimanite II	7.4846(13)	7.6734(12)	2.8854(4)	165.71(3)

TABLE 2-(continued)

	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
21. Lisenz Alps sillimanite	7.4856(13)	7.6731(13)	2.8876(6)	165.85(4)
22. Ceylon sillimanite	7.4818(13)	7.6708(10)	2.8861(5)	165.63(4)
23. Berne, South Dakota (UCLA collection #MS 3419B)	7.4889(21)	7.6757(17)	2.8852(8)	165.85(8)
24. Robertson Township, Quebec, sillimanite	7.4842(9)	7.6753(10)	2.8842(4)	165.67(3)
25. Natural sillimanite from volcanic xenolith of Asama volcano, Japan (from data of Aramaki and Roy)	7.498(2)	7.690(2)	2.8883(5)	166.53
26. Natural sillimanite from metamorphic rock, Brandywine, Delaware County, Pa. (from data of Aramaki and Roy '62)	7.481(2)	7.672(2)	2.8845(5)	165.55
27. Xenocryst of sillimanite in granite prophyry (from data of Aramaki and Roy, 1962)	7.486(4)	7.675(4)	2.8853(8)	165.78
28. Natural sillimanite (from data of Gelsdorf <i>et al.</i> , 1958)	7.486(4)	7.672(4)	2.883(2)	165.57
29. Natural sillimanite (from data of Agrell and Smith, 1960)	7.4864	7.6727	2.8858	165.76
30. Natural sillimanite (from data of Agrell and Smith, 1960)	7.4839	7.6758	2.8864	165.81
31. Natural sillimanite (from data of Agrell and Smith, 1960)	7.4876	7.6718	2.8852	165.73
32. Natural sillimanite (from data of Agrell and Smith, 1960)	7.4839	7.6718	2.8846	165.62
33. K-LH-558G ^a	7.4963(10)	7.6731(10)	2.8874(4)	166.08(4)

^a Natural sillimanite from sillimanite-quartz-plagioclase-garnet-biotite-chlorite rock, Kwoiek area, British Columbia, Canada.

monochromator and a scanning speed of $0.25^\circ 2\theta$ per minute. The cell parameters and their estimated standard deviations were calculated from the set of 2θ measurements using a least-squares computer program. The number of reflections employed varied from six for the fine grained run products (002, 041, 401, 250, 520, and 331) to as many as 34 for the coarser grained mullites and natural sillimanites.

EXPERIMENTAL RESULTS

Both mullite and sillimanite are extremely stable phases and reactions even at high temperatures are very sluggish. The direct determination of the mullite-sillimanite relationships at lower temperatures, the region of greatest geological interest, is experimentally difficult, if not impossible. As a consequence all of our present experiments were undertaken at temperatures ranging from 800 to 1500°C . The results of our experimental runs are shown in Tables 3, 4, 5 and 6 and cell dimensions of the run product are plotted in Figures 4, 5, 6, 7, and 8.

TABLE 3. RUNS AT 1500°C
Starting material: fired kaolin

Pres- sure (kbar)	Time (hr)	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$
Starting material: fired kaolin					
3.5	4.5	7.5401(15)	7.6907(16)	2.88600(7)	167.35(5)
7.5	6	7.5244(19)	7.6943(13)	2.8860(8)	167.09(6)
13	6	7.5121(17)	7.6938(15)	2.8864(9)	166.82(6)
Starting material: fired kaolin+1 mol excess quartz					
3.5	5	7.5304(13)	7.6880(13)	2.8865(5)	167.11(4)
5	5	7.5227(21)	7.6832(22)	2.8867(8)	166.84(6)
7.5	5	7.5181(15)	7.6848(16)	2.8836(6)	166.60(5)
10	5	7.5172(15)	7.6909(16)	2.8844(6)	166.76(5)
12.5	5	7.5103 (9)	7.6852 (9)	2.8843(4)	166.48(3)
15	5	7.4984(15)	7.6825(16)	2.8852(6)	166.21(5)
20	3.5	7.4908(17)	7.6745(15)	2.8864(6)	166.04(5)
Starting material: Tem-Pres mullite+1 mol excess quartz					
3.5	6	7.5404(31)	7.6917(32)	2.8823(12)	167.17(9)
5	6	7.5433(22)	7.6892(23)	2.8836(9)	167.25(9)
7.5	6	7.5316(22)	7.6892(24)	2.8832(9)	166.98(7)
8.5	8	7.5272(19)	7.6917(20)	2.8820(9)	166.86(8)
10	6	7.5244(17)	7.6879(18)	2.8835(7)	166.80(5)
15	6	7.5210(15)	7.6818(16)	2.8839(6)	166.62(5)
20	6	7.4996(17)	7.6838(18)	2.8847(7)	166.23(5)

Some X-ray powder patterns of the run products are shown in Figure 3. Mullite formed by firing kaolin at 1 atmosphere is shown as well as the pattern of natural sillimanite. A continuous gradation from the pattern of mullite to that of sillimanite as a function of pressure can be seen. Reflections such as (421) and (520) clearly show a regular change to higher angles of 2θ in the progression from mullite to sillimanite. Cell edge c , as seen from the (002) reflection of mullite and the (004) reflection of sillimanite, shows almost no change.

Experiments at 1500°C. Five different starting materials were used in a series of runs at 1500°C. These were fired kaolin, fired kaolin+1 mole percent quartz, Tem-Pres synthetic mullite, Tem-Pres synthetic mullite +1 mole percent quartz and Tem-Pres synthetic mullite+2 mole percent quartz. These runs are listed in Table 3, and in Figure 4 we have plotted the variation of the cell volume with the cell edge a of the various

TABLE 4. RUNS AT 1300°C
Starting material: fired kaolin

Pressure (kbar)	Time (hr)	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$
5	6	7.5347(15)	7.6872(16)	2.8844(6)	167.06(4)
7.5	6.5	7.5258(17)	7.6884(15)	2.8864(5)	167.01(5)
10	6	7.5253(18)	7.6847(15)	2.8852(6)	166.85(6)
15	6	7.5108(13)	7.6799(15)	2.8860(5)	166.47(4)
20	6	7.5021(15)	7.6831(16)	2.8878(6)	166.45(4)
Starting material: Tem-Pres mullite					
3.5	7	7.5430(13)	7.6842(13)	2.8816(5)	167.03(4)
5	7	7.5443(10)	7.6832(11)	2.8814(4)	167.02(3)
7.5	6.5	7.5426(17)	7.6831(18)	2.8811(7)	166.96(5)
10	5	7.5492(13)	7.6826(13)	2.8827(6)	167.19(4)
15	7	7.5416(9)	7.6814(16)	2.8844(4)	167.09(4)
Starting material: Tem-Pres mullite+1 mol excess quartz					
3.5	20	7.5371(38)	7.6925(40)	2.8834(15)	167.18(11)
5	20	7.5426(20)	7.6886(21)	2.8839(8)	167.24(6)
7.5	20	7.5395(22)	7.6902(23)	2.8840(8)	167.22(7)
10	15.5	7.5308(18)	7.6859(19)	2.8844(7)	166.95(6)
15	16.4	7.5317(14)	7.6825(15)	2.8845(6)	166.91(4)
20	15.5	7.5165(8)	7.6827(13)	2.8842(5)	166.55(3)
3.5	6.5	7.5422(27)	7.6843(28)	2.8830(11)	167.09(8)
5	6.5	7.5400(16)	7.6863(17)	2.8837(6)	167.12(5)
7.5	6.5	7.5429(14)	7.6823(15)	2.8827(6)	167.04(4)
10	6.5	7.5402(12)	7.6806(12)	2.8816(5)	166.88(4)
15	7	7.5383(6)	7.6802(6)	2.8842(2)	166.98(2)
20	6.5	7.5297(32)	7.6783(3)	2.8846(12)	166.77(10)

synthesized phases. For comparison we have also plotted in Figure 4 the measurements from a number of natural sillimanites. It is seen from Figure 4 that a nearly continuous variation in cell volume and cell edge a exists between sillimanite and mullite prepared under these conditions. A number of these results have been replotted in Figure 11 and the variation in cell volume and cell edge a is shown to be linear with the pressure of the run. Only samples subjected to pressures of 15–20 kbar showed cell measurements in the range of those shown by natural sillimanite. It may be noted that the Tem-Pres mullite has a slightly larger cell edge a than the mullite we formed by firing clay. This difference remains regardless of the pressure to which the samples have been taken.

A number of runs were made at 1300°C. These are shown in Table 4.

TABLE 5. RUNS AT 800°C AND 1000°C

Press. (Kbar)	Temp. (°C)	Time (hr)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Remarks
Starting material: fired kaolin							
0.5	800	168	7.5351(13)	7.6858(12)	2.8840(5)	167.02(3)	Hydrothermal run
3.5	800	60	7.5374(25)	7.6933(26)	2.8831(9)	167.18(7)	
5	800	60	7.5405(22)	7.6924(24)	2.8810(10)	167.11(7)	
5	800	42	7.5493(36)	7.6768(41)	2.8812(11)	166.98(10)	Starting material: Gel mixture Al ₂ O ₃ :SiO ₂ =1:1 mol %
5	1000	169	7.5272(18)	7.6869(19)	2.8839(7)	166.86(6)	
7.5	1000	120	7.5281(23)	7.6922(26)	2.8861(7)	167.12(6)	
Starting material: fired kaolin + 1 mol, excess quartz							
1	800	48	7.5399(29)	7.6893(31)	2.8831(12)	167.15(9)	Hydrothermal run
Starting material: Tem-Pres mullite							
1	800	336	7.5493(38)	7.6893(40)	2.8831(15)	167.36(12)	Hydrothermal run
10	1000	48	7.54448(23)	7.6859(24)	2.8844(9)	167.25(7)	
15	1000	47	7.5417(21)	7.6844(22)	2.8850(9)	107.19(6)	
Starting material: Tem-Pres mullite + 1 mol excess quartz							
3.5	1000	21.5	7.5456(35)	7.6883(37)	2.8834(14)	167.27(11)	
5	1000	31.5	7.5505(31)	7.6909(32)	2.8848(12)	167.52(9)	
75	1000	20.5	7.5450(29)	7.6875(30)	2.8832(11)	167.23(9)	
10	1000	17	7.5428(19)	7.6852(21)	2.8835(7)	167.15(6)	
15	1000	21.5	7.5439(17)	7.6822(17)	2.8837(6)	167.12(5)	
20	1000	21.5	7.5361(38)	7.6846(65)	2.8836(15)	166.99(14)	
Starting material: Tem-Pres mullite + 2 mol excess quartz							
3.5	1000	16.5	7.5458(17)	7.6852(18)	2.8837(7)	167.23(5)	
5	1000	15	7.5465(37)	7.6823(38)	2.8835(14)	167.17(11)	
7.5	1000	15.5	7.5445(12)	7.6816(12)	2.8823(5)	167.04(4)	
10	1000	16.5	7.5452(21)	7.6860(22)	2.8830(8)	167.19(6)	
15	1000	15	7.5459(8)	7.6819(9)	2.8836(3)	167.16(3)	
20	1000	16	7.5399(20)	7.6822(35)	2.8843(8)	167.07(7)	

Results are plotted in Figure 5 where we show again the variation of cell volume with cell edge *a*. Reactions were substantially more sluggish than at 1500°C. Even runs at 20 kbar, near the boundary between kyanite and sillimanite, yielded phases with cell constants intermediate between the end members mullite and sillimanite. Here again, the fired kaolin showed cell edge *a* slightly less than that of the Tem-Pres mullite, however the cell constants of mullite mixed with quartz appear somewhat smaller than those of mullites free from excess quartz.

A number of runs were also made at 800° and 1000°. These are itemized in Table 5 and the results plotted in Figure 6. At these lower temperatures there was only a slight tendency for cell constants to change towards those of natural sillimanite even at the highest pressures.

We have plotted in Figure 7 the variation of cell edge *c* with the cell

TABLE 6. CELL DIMENSIONS OF TREATED NATURAL SILLIMANITES AND SOME LOW TEMPERATURE SYNTHESIZED PHASES

Starting material	Pres (kbar)	Temp (°C)	Time (hr)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Kaolin ^a	20	650 ± 15	50	7.493(3)	7.679(3)	2.8946(8)	166.55
Gel mix ^a 60Al ₂ O ₃ mol % 40SiO ₂	4.8	623 ± 10	30	7.546(4)	7.686(4)	2.8850(20)	167.33
Gel mix ^a	2.9	727 ± 10	142	7.540(4)	7.688(4)	2.8861(20)	167.30
Natural sillimanite (Norwich, Conn.)	7.5	1500	20	7.5164(18)	7.6876(10)	2.884(8)	166.65(7)
Natural sillimanite (Norwich, Conn.)	11	1500	20	7.4958(12)	7.6828(15)	2.8836(7)	166.06(6)
Natural sillimanite	6.8	900	100	7.4942(15)	7.6796(12)	2.8848(7)	166.03(6)
Natural sillimanite	13.6	900	100	7.4902(13)	7.0702(12)	2.8840(6)	165.69(5)

^a data from Aramaki and Roy (1962)

volume. We show in this plot the measurements of synthetic sillimanite-mullite phases made during the course of this study as well as measurements from a number of natural sillimanites, and measurements on both phases published by other workers as reported in Table 2. This plot shows that the *c* translation, although with substantial scatter, is essentially independent of phase composition, whereas there is a continuous variation in the cell volume from mullites with the chemistry 2Al₂O₃·SiO₂, through mullites with the chemistry 3Al₂O₃·2SiO₂, on to sillimanites with the chemistry Al₂O₃·SiO₂. There is, however, some suggestion of a trend with larger values of cell edge *c* with cell volume as one proceeds from the 3:2 mullites to 2:1 mullites.

Cell dimensions of natural and treated sillimanites. The previous experimental data have shown that mullite taken to high pressures and high temperatures changed regularly in lattice dimensions toward those of sillimanite. A number of experiments were made to determine whether the reaction was reversible and whether sillimanite can be changed in lattice dimensions toward mullite. The results of these experiments are presented in Table 6 and shown in Figure 8. Natural sillimanite from

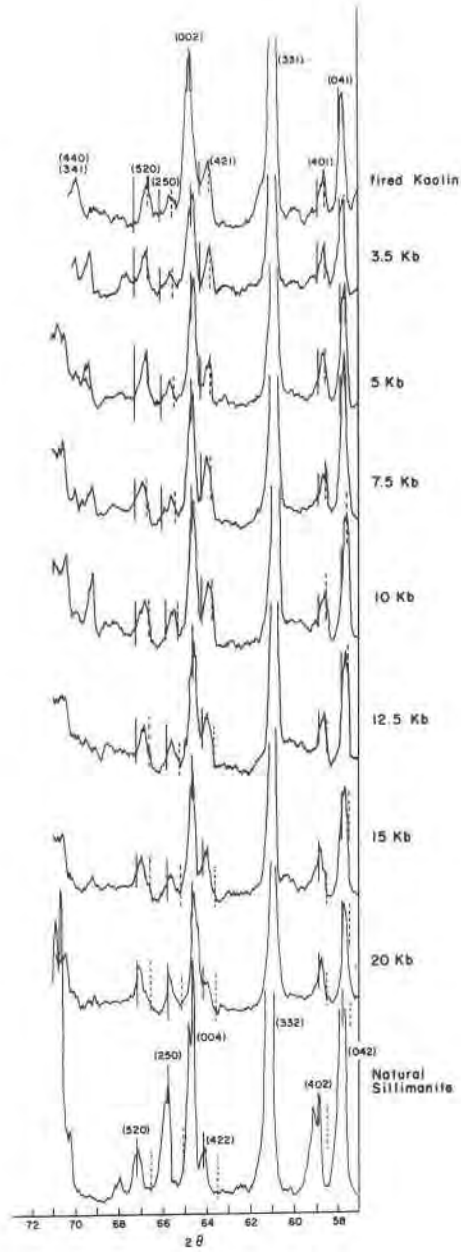


FIG. 3. Typical x-ray powder patterns of mullite-sillimanite solid solution.

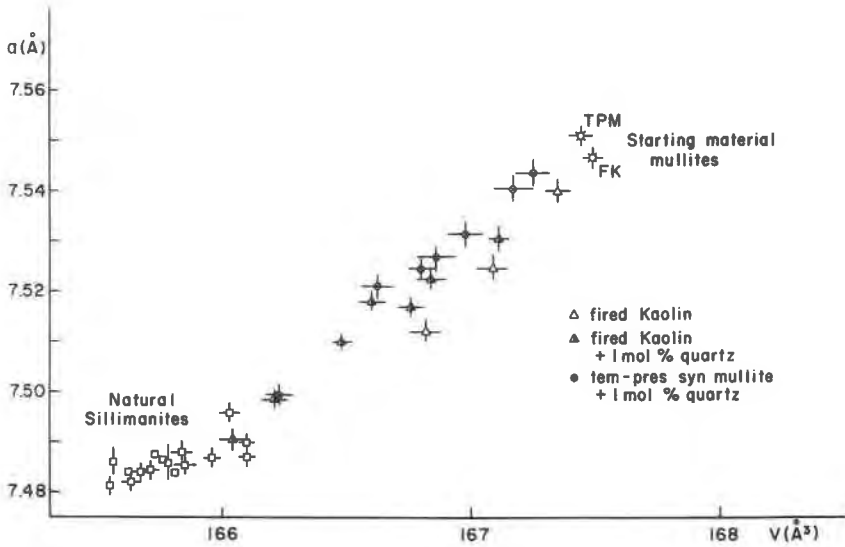


FIG. 4. Variation of cell volume with the cell edge a at 1500°C.

Norwich, Conn. held at 1500°C and 7 1/2 kbar for 20 hours changed to a phase with cell constants almost intermediate between those of natural sillimanite and a 3:2 mullite (see Fig. 11), whereas the same starting ma-

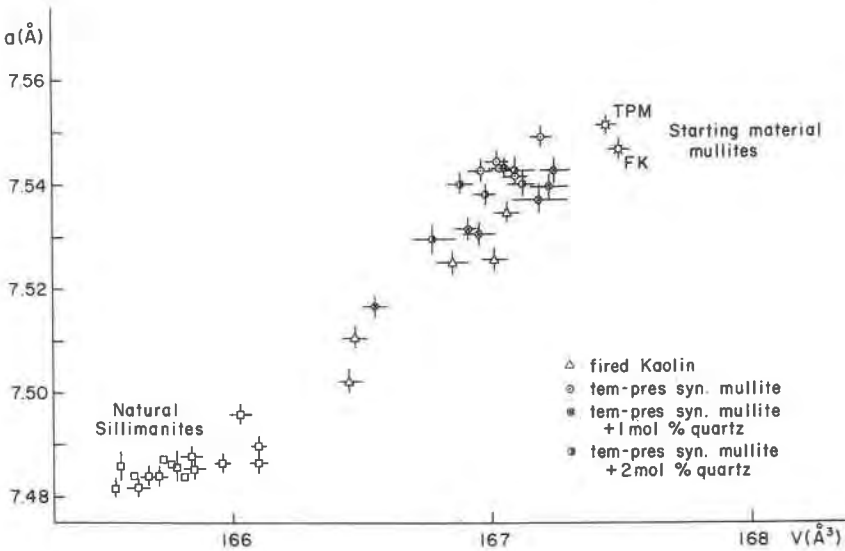


FIG. 5. Variation of cell volume with the cell edge a at 1300°C.

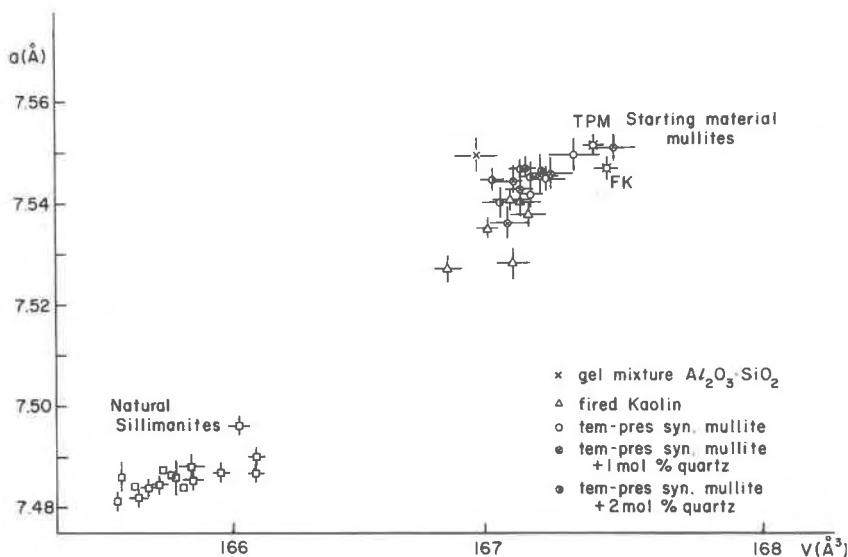


FIG. 6. Variation of cell volume with the cell edge a at 800° & 1000°C .

terial held at the higher pressure, 11 kbar for 20 hours and 1500°C , showed essentially no shift in cell volume and only a slight change in cell edge a . Another natural sillimanite held at a somewhat lower temperature and a pressure of 13.6 kbar changed in the opposite direction, i.e., its volume decreased.

Unfortunately, our starting sillimanites had quartz as an impurity. Thus it was impossible to tell if quartz was liberated during the reaction.

Infra-red spectra of the mullite-sillimanite solid solution series. Infra-red spectra of sillimanite and mullite have been published by Keller *et al.* (1952), Roy and Francis (1953) and Muller-Hesse (1960). Roy and Francis note that "mullite has a pronounced absorption spectra at 9.1 microns" and "it is evident therefore that sillimanite may be distinguished from mullite by very simple experimental techniques". We therefore investigated this technique further as a possible rapid qualitative method of distinguishing sillimanite from mullite and of perhaps locating compositions in the sillimanite-mullite series. A Perkin Elmer dual grating spectrometer with a NaCl prism was used in this investigation. The samples were milled in Nujol and applied to the NaCl plates. The spectra of a number of samples are shown in Fig. 9. The $9.1\ \mu\text{m}$ absorption band, relied upon by Roy and Francis for identification, does appear in one of our mullites made by firing kaolin but unfortunately it does not

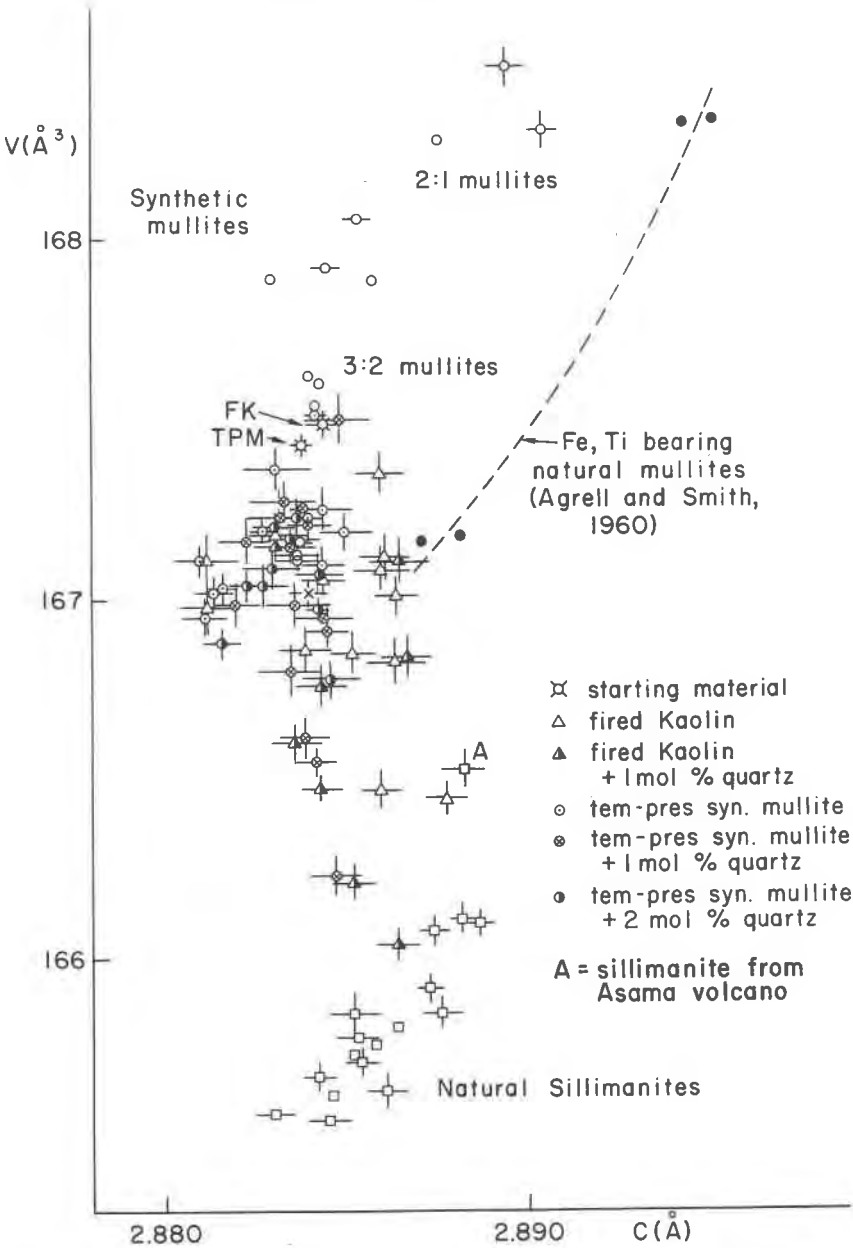


FIG. 7. Variation of cell volume with the cell edge c of synthetic and natural mullites and natural sillimanites.

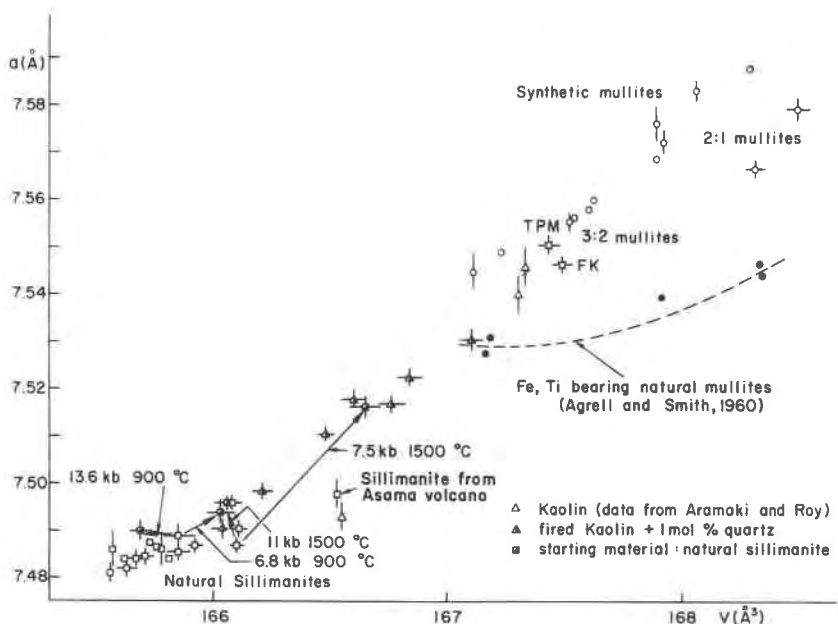


FIG. 8. Variation of cell volume with the cell edge a of synthetic and natural mullites and natural sillimanites.

appear in the mullite obtained from the Tem-Pre's Company and equally unfortunately the same absorption minima does appear in one of our natural sillimanites and in our natural sillimanite heated at 1500°C and 11 kbar for 20 hours. In the region between 12 and 15 μm sillimanite does show a number of rather narrow and apparently characteristic absorption maximum. These appear at 12.25, 13.4 and 14.4 μm whereas mullite has a much more diffuse absorption band. General progression in sharpness of fine structure in this absorption region can be noted as one progresses from mullite to sillimanite. This is consistent with mullite being a phase of high structural disorder whereas sillimanite is an ordered phase.

Lattice constants versus chemical composition. Tromel *et al.* (1957) and Gelsdorf *et al.* (1958) showed that the lattice constant a depended roughly linearly on the percentage of Al_2O_3 in various mullites, and that extrapolation to 62.9% Al_2O_3 , the composition of sillimanite, nearly gives the lattice constant a for sillimanite. Table 7 and Figure 10, which contains available published data, in general confirms this conclusion. The cell edge a of various natural mullites lie close to this extrapolated line. Agrell and Smith (1960) studied the cell dimensions of natural mullites and

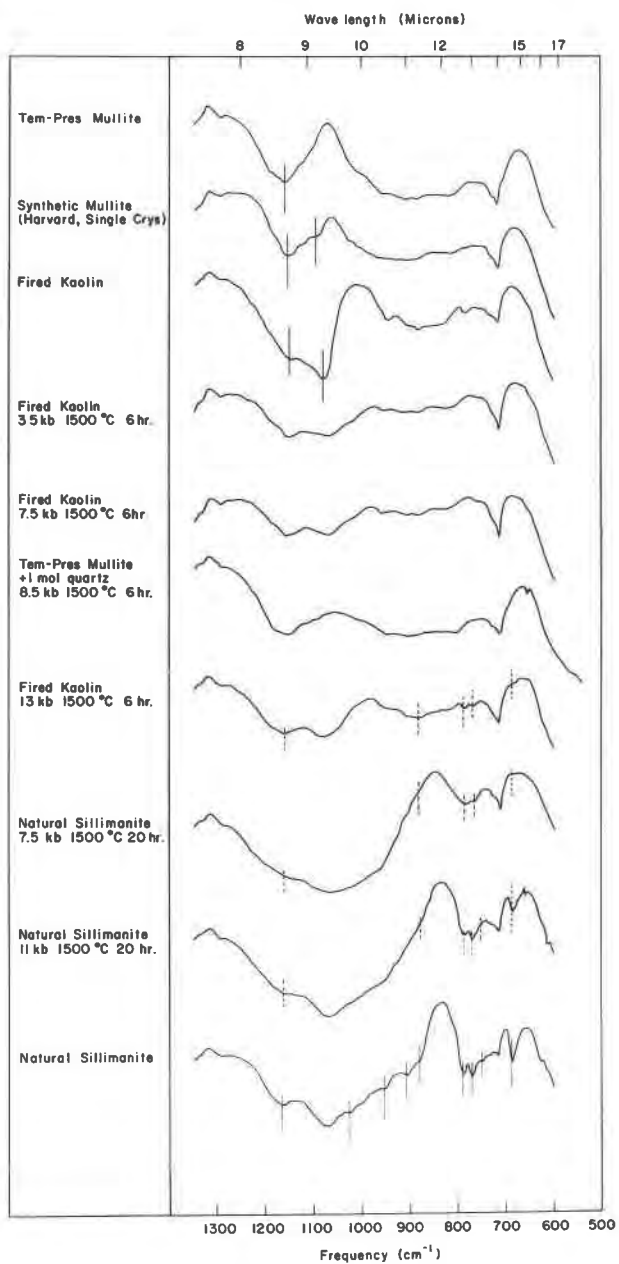


FIG. 9. Infra-red spectra of the mullite-sillimanite solid solution series.

TABLE 7. VARIATION OF UNIT CELL DIMENSIONS OF MULLITE AND SILLIMANITE WITH VARIOUS PERCENTAGE OF Al_2O_3

$\text{Al}_2\text{O}_3(\%)$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	
72	7.537				Mullite ^a
75	7.551				Mullite ^a
78	7.562				Mullite ^a
71.80	7.545(4)	7.688(4)	2.881(2)	167.11	3:2 mullite ^b
77.24	7.576(4)	7.687(4)	2.883(2)	167.89	2:1 mullite ^b
71.8	7.560	7.688	2.884	167.62	3:2 mullite ^c
73.67	7.549	7.681	2.884	167.23	1.71:1 mullite ^d
78.66 ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$)	7.583(2)	7.681(2)	2.8854(5)	168.06	Arc-fusion mullite ^e
70.07 ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2$)	7.5277	7.6913	2.8871	167.16	Natural mullite ^f
69.07 ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2$)	7.5309	7.6877	2.8882	167.18	Natural mullite ^f
70.83 ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2$)	7.5442	7.7053	2.8952	168.34	Natural mullite ^f
71.6	7.5563	7.6874	2.8842	167.54	synthetic mullite ^f
77.6	7.5686	7.6865	2.8858	167.89	synthetic mullite ^f
71.79	7.5582	7.6878	2.8843	167.60	synthetic mullite ^f

^a From data of Tromel et al. (1957)

^b From data of Gelsdorf et al. (1958)

^c From data of Murthy and Hummel (1960)

^d From data of Durovic (1962)

^e From data of Aramaki & Roy (1962)

^f From data of Agrell & Smith (1960)

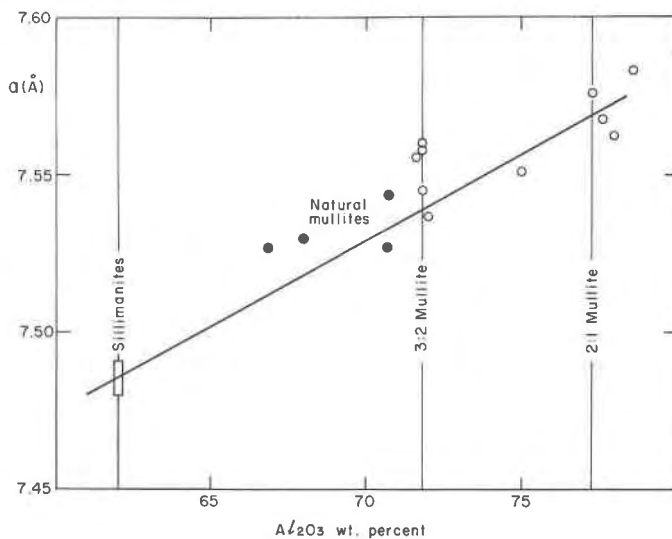


FIG. 10. Variation of cell edge a with various percentages of Al_2O_3 .

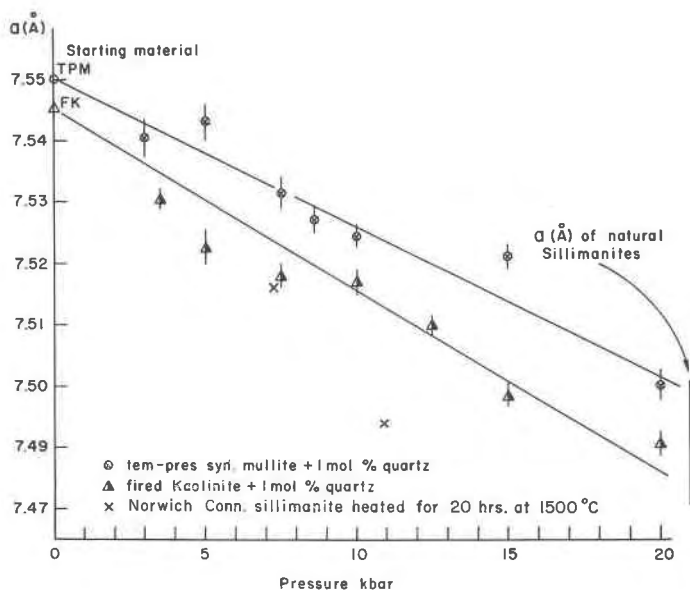


FIG. 11. Variation of cell edge a at various pressures at 1500°C.

noted two different trends: one is for iron-free synthetic mullites and the other for the iron and titanium bearing natural mullites. The c parameter and unit cell volume increase with increasing amounts of substituted iron and titanium. The variation in the cell dimensions of both sillimanites and mullites clearly depends not only on the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio but on the extent of solid substitution of Fe and Ti.

DISCUSSION

Due to the extreme fine grain size of the run products it is not feasible to determine their compositions by direct chemical analyses or on our electron probe. Lacking these data the cell parameter changes documented above are consistent with at least two different interpretations. The first would attribute the cell changes to a variable degree of Si-Al tetrahedral ordering between sillimanite (ordered) and 3:2 mullite (disordered). The second interpretation, which is thought at present to better fit the observations, attributes the cell dimension changes to a continuous, isomorphous, solid-solution between sillimanite and mullite.

If sillimanite can be disordered, it would be expected that its cell dimensions would increase slightly. Similarly 3:2 mullite, which is presumably disordered, would be expected to decrease in cell dimensions if ordering occurs. Several arguments can be raised, however, in applying

this interpretation to the observations. It has not, to the present, been demonstrated that sillimanite can in fact be disordered and mullite may be at least partially ordered as is suggested by the appearance of weak superstructure reflections in its single crystal X-ray patterns (Agrell and Smith, 1960). Under this interpretation "ordering" is produced at 1500°C with greater "disorder" produced at 1300°C, contrary to what would be expected, unless it is claimed that the rate of ordering at 1300°C prevents attainment of equilibrium. Finally, complete ordering of a 3:2 mullite should lead to a cell significantly larger than that of (ordered) sillimanite since the mullite contains more of the larger tetrahedral cation, Al.

A range of opinions on the possibility of a continuous solid solution series between sillimanite and mullite has been expressed. Konopicky (1956) noted the difficulty of determining the limit of solid solution in progressing from mullite to sillimanite. Neuhaus and Richartz (1959) suggested the impossibility of synthesizing a 5:4 mullite by the Verneuil method, i.e. at 1 atm: a conclusion in agreement with the results of this work. Tromel *et al.* (1957) and Gelsdorf *et al.*, (1958) suggested that intermediate members between 3:2 mullite and sillimanite cannot be formed at one atmosphere pressure but admit that they may form at high pressures. This was also suggested by Coes (1955) and Winkler (1957). Barta and Barta (1956) suggested that intermediate members might arise at "appropriate concentration, pressure, and temperature". Aramaki and Roy (1962) apparently excluded the possibility of intermediate members between sillimanite and 3:2 mullite; however, they do report an anomalous specimen of natural sillimanite from Asama volcano in Japan. Their data show it to have cell dimensions intermediate between mullite and sillimanite. (See Figs. 7 and 8). In addition they report the cell dimensions of a run product held for 50 hr. at 650°C and 20 kbar. The cell volume of the "anomalous sillimanite" is 166.5 Å³ which by reference to Fig. 7 can be seen to lie between those of sillimanite and mullite.

Similarly Agrell and Smith (1960) report natural mullites with composition and cell dimensions which as shown in Table 7 and Fig. 10, plot roughly half-way between sillimanite and 3:2 mullite.

In our opinion the continuous change in cell parameters observed in this study, together with observations reported in previous studies, support the contention that sillimanite and mullite are part of a continuous, isomorphous solid-solution series. In Figure 12 we have plotted some of the more recently suggested phase boundaries in the system and in addition we show hypothetical equilibrium lines in the proposed sillimanite-mullite solution series where quartz is an excess phase. Lines shown on this diagram are consistent with our experimental data and with the di-

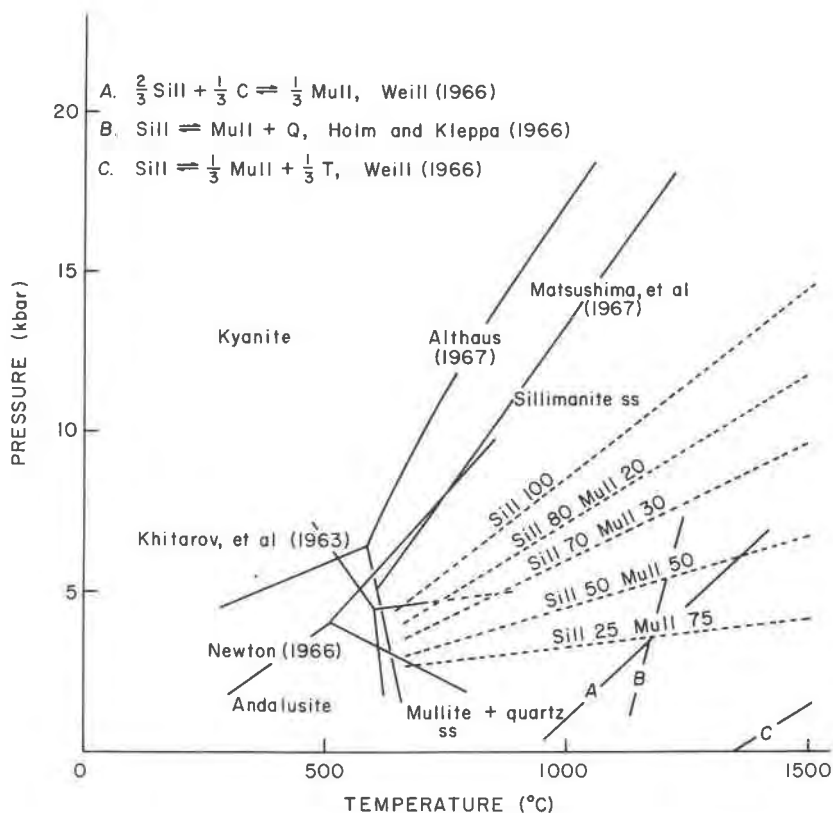


FIG. 12. Those boundaries in the system $\text{Al}_2\text{O}_3\text{-SiO}_2$ as given by various authors, with suggested equilibrium sillimanite-mullite compositions.

rection of trend of equilibrium but it should be emphasized that it is certain that we did not achieve equilibrium in any of our experiments.

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