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THERMODYNAMIC PROPERTIES OF MULLITE, ANDALUSITE, KYANITE AND SILLIMANITE[1]

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ABSTRACT

Recent experimental investigations in the system Al_2O_3-SiO_2 provide sufficient data to re-evaluate the heats and free energies of formation of the Al_2SiO_5 polymorphs (andalusite, kyanite and sillimanite) and $Al_6Si_2O_{13}$ (mullite). The calculated free energy of formation from the elements at 298.15° K, $\Delta G^\circ_{f\,298.15}$, is −583,897 cal/gfw for andalusite; −582,737 cal/gfw for kyanite; −583,351 cal/gfw for sillimanite; and −1,545,093 cal/gfw for 3:2 mullite. These results clearly indicate that previously accepted free energy values of the Al_2SiO_5 polymorphs are approximately 40 kcal/gfw too negative with respect to quartz and corundum.

The available experimental data almost certainly preclude the compatibility of quartz and corundum in igneous and metamorphic rocks or in the synthetic system. However, the assemblages *mullite-corundum*, *mullite-andalusite*, and *mullite-sillimanite* may be more common in highly aluminous metamorphic rocks than previously supposed.

INTRODUCTION

Several compilations (Richardson *et al.*, 1950; Rossini *et al.*, 1952) of thermodynamic data for inorganic compounds, contain free energies of formation for andalusite, kyanite and sillimanite calculated from the calorimetric data of Neumann (1925), indicating that the Al_2SiO_5 polymorphs are stable by 40–45 kcal/gfw with respect to the oxides. However, Neumann's results are considered unreliable in light of early experimental work on the *kyanite-sillimanite* equilibrium (Clark *et al.*, 1957; Clark, 1961), and the pressure-temperature stability relations of the Al_2SiO_5 polymorphs inferred from their third-law entropies, crystal structures, and mineral associations in metamorphic rocks. Furthermore, studies in the system Na_3AlF_6-Al_2O_3-SiO_2 (Weill, 1962) indicate that the Gibbs free energies of formation of andalusite, kyanite and sillimanite from the oxides are more nearly ±3 kcal/gfw.

Recently Khitarov *et al.* (1963), using a simple squeezer, and Bell (1963), using a shear squeezer, determined the *andalusite-kyanite-sillimanite* triple point. Both sets of results are in good agreement and consistent with the earlier work of Clark *et al.* (1957) and Clark (1961) on the stability of the Al_2SiO_5 polymorphs. In addition, the *sillimanite-mullite-quartz* equilibrium curve of Khitarov *et al.* (1963) agrees well with earlier predictions. These phase equilibria results, combined with heat capacity

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and molar volume data, are sufficient to evaluate the heats and free energies of formation of the Al_2SiO_5 polymorphs.

TREATMENT OF EXPERIMENTAL DATA

Invariant points in the Al_2SiO_5 composition plane are taken as 8600 bars, 350° C. for *andalusite-kyanite-sillimanite;* and 4090 bars, 624° C. for *quartz-mullite-andalusite-sillimanite* using a composite plot of Khitarov *et al.* (1963) and Bell's (1963) tabulated results. The *andalusite-sillimanite* and *kyanite-sillimanite* curves used in these calculations are plotted in Fig. 1. Disposition of the equilibrium curves around the invariant points is also taken from the experimental pressure-temperature data. Because of uncertainties in the entropy $S^\circ_{298.15}$ of the phases, the observed univariant slopes do not necessarily agree with the slopes calculated from entropy and volume data.

Not much latitude exists in evaluating the pressure of metastable transition of sillimanite to kyanite at 25° C. considering the excellent agreement among the data of Clark (1961), Khitarov *et al.* (1963) and Bell (1963). Using 4430 bars and the data in Table 1, the standard free energy for the reaction sillimanite = kyanite[1] at 25° C. is:

$$\Delta G^\circ_{298.15} = -\Delta V^\circ_{298.15}\int_1^{4430} dP = +614 \pm 70 \text{ cal/gfw}$$

where $V^\circ_{298.15}$ is the molar volume at 298.15°K and P is the pressure. Using the point 14.0 kb, 25° C. as being on the metastable extension of the *andalusite-sillimanite* equilibrium, the free energy of formation of sillimanite from andalusite is:

$$\Delta G^\circ_{298.15} = +546 \pm 80 \text{ cal/gfw}$$

which gives the free energy of formation of kyanite from andalusite:

$$\Delta G^\circ_{298.15} = +1160 \pm 150 \text{ cal/gfw}$$

and a calculated equilibrium pressure of 6530 bars for andalusite = kyanite at 25° C. Using these data, the calculated entropy of kyanite, $S^\circ_{298.15}$, is 21.17 ± 0.20 cal/deg-gfw. Therefore, a change in $S^\circ_{298.15(\text{kyanite})}$ of 1.15 cal/deg-gfw would be necessary to bring the low-temperature calorimetric data (Kelly and King, 1961) into agreement with the phase-synthesis and volume data. However, additional calorimetric studies are needed to resolve this discrepancy.

An equilibrium point, 4750 ± 250 bars and 700° C., given by Khitarov *et al.* (1963), combined with the entropies and volumes of the phases,

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[1] Differences in the isothermal compressibilities of the phases are small and may be neglected in these calculations. The uncertainties given here are based on the uncertainty in extrapolating the P,T data to 25°C.

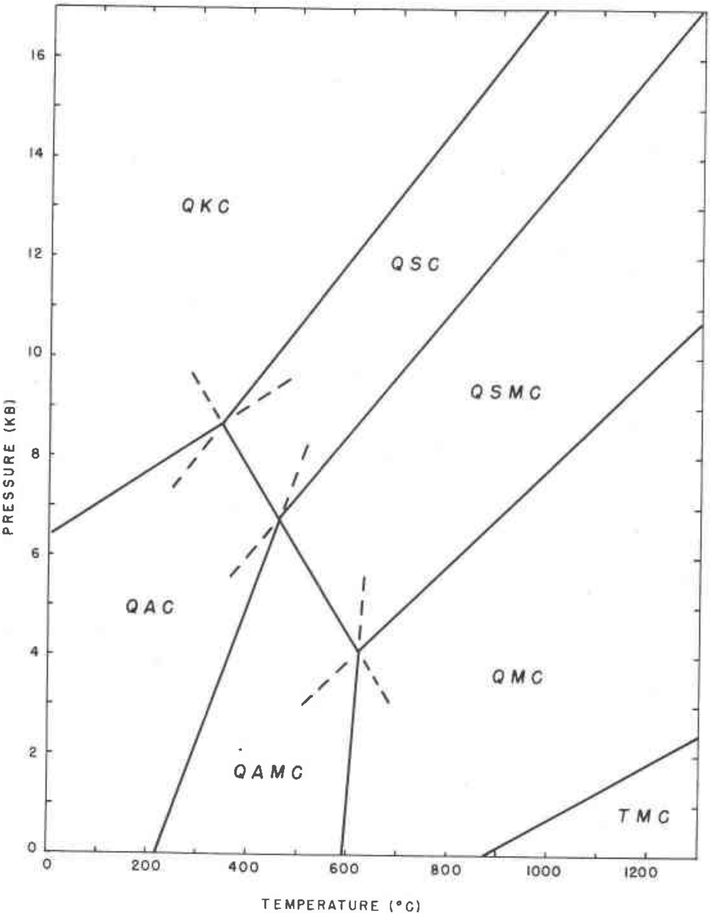

FIG. 1. Stability relations of crystalline phases in the system SiO_2-Al_2O_3 below 17 kb and 1300° C. Data for *quartz-tridymite* equilibrium from Tuttle and Bowen (1958). Equilibria involving mullite and Al_2SiO_5 are shown here as first-order phase changes, assuming that a compositional discontinuity exists between Al_2SiO_5 and mullite in the entire P,T range. Phases stable (at the appropriate composition) within the indicated P,T fields are given in order of increasing Al_2O_3: Q, quartz; T, tridymite; A, andalusite; K, kyanite; S, sillimanite; M, mullite; C, corundum.

locates the *quartz-sillimanite-mullite* curve as shown in Fig. 1. At 25° C. the metastable extension of this equilibrium beyond the invariant point *quartz-andalusite-sillimanite-mullite* is -1760 bars, giving $\Delta G°_{298.15}$ of sillimanite relative to mullite and quartz. Using the data obtained earlier, the free energy of formation of mullite and quartz from andalusite is:

$$\Delta G°_{298.15} = +1954 \pm 350 \text{ cal/gfw.}$$

TABLE 1. FREE ENERGY FUNCTION, MOLAR VOLUME, AND HEAT OF FORMATION AT 298.15° K FOR PHASES IN THE SYSTEM Al_2O_3-SiO_2

cal, calories; gfw, gram formula weight. Values in italics reported in this paper; numbers in parentheses refer to references at the end of this table

MINERAL	$-(G_T^\circ - H_{298.15}^\circ/T)$ cal/deg-gfw	$V_{298.15}^\circ$ cal/bar-gfw	$\Delta H_{f,298.15}^\circ$ cal/gfw
Corundum	12.17(1,2)	0.61114(1)	−400,400(1)
Quartz	9.88(1,2)	0.54230(1)	−217,650(1,8)
Cristobalite	10.38(1,2)	—	−216,930(1,8)
Andalusite	22.28(3,4)	1.23207(6)	*−619,158*
Kyanite	20.02(3,4)	1.05440(6)	*−618,672*
Sillimanite	22.97(3,4)	1.19307(6)	*−618,406*
3:2 Mullite	60.80(5)	3.21630(7)	*−1,636,725*

[1] Robie (1962)
[2] Kelley (1960)
[3] Kelley and King (1961)
[4] Pankratz and Kelley (1964)
[5] Pankratz *et al.* (1963)
[6] Skinner *et al.* (1961)
[7] Robie and Bethke (1962)
[8] Wise *et al.* (1963)

These results clearly demonstrate the small differences in the free energies of mullite, kyanite and sillimanite relative to andalusite. In this respect, Neumann's (1925) solution calorimetric data are in error by an order of magnitude.

To obtain standard free energies of formation from the elements, Kay and Taylor's (1960) measurements of the silica activity of liquids in the system CaO-Al_2O_3-SiO_2 are used. Kay and Taylor give the value of $a_{SiO_2}=0.44$ for the activity of silica (referred to *crystalline* SiO_2) in the liquid in equilibrium with mullite and corundum at 1550° C. Hence, the reaction to be written is:

$$3 \text{ corundum} + 2 \text{ cristobalite} = \text{mullite}$$

and at 1823° K the free energy of the reaction is:

$$\Delta G^\circ_{1823} = -RT \ln a_{SiO_2}^{-2} = -5950 \pm 400 \text{ cal/gfw.}$$

From the data in Table 1 and thermodynamic functions for Al, Si and O_2 reference states (Joint Army-Navy-Air Force Thermochemical Tables, 1960–1964), the calculated standard free energy of formation of 3:2 mullite from the elements is:

$$\Delta G^\circ_{f,298.15} = -1{,}545{,}093 \pm 1500 \text{ cal/gfw.}$$

Stoichiometric $Al_6Si_2O_{13}$ is probably not the mullite phase in equilibrium with corundum on the $CaO\text{-}Al_2O_3\text{-}SiO_2$ liquidus. However, correction of $\Delta G^\circ_{f,298.15(\text{mullite})}$ involves only the free energies of mixing of mullite solid solutions, which are probably small, and will not significantly affect these calculations.

Standard heats and free energies of formation from the elements for andalusite, kyanite, and sillimanite are calculated through the *quartz-sillimanite-mullite* equilibrium (Tables 1 and 2). Combining these results with data for quartz and corundum gives the standard free energies of formation from the oxides at 298.15° K as: −1572, −1175, −15, and −629 cal/gfw for mullite, andalusite, kyanite, and sillimanite respectively. The high-temperature thermodynamic functions in Table 2 are calculated from heat-content data obtained in recent studies of the thermodynamic properties of the aluminum silicates by Pankratz *et al.* (1963) and Pankratz and Kelley (1964). These calculations confirm the suggestions of Flood and Knapp (1957), Miyashiro (1960), Weill (1962), and Haskell and DeVries (1964) that the aluminum silicates are stable by less than 5 kcal with respect to corundum and silica, which again indicates that Neumann's (1925) heat of solution measurements are in error.

SUMMARY AND CONCLUSIONS

Numerous attempts to repeat the solution calorimetric results of Neumann (1925) have failed. The unpublished negative results obtained by F. C. Kracek of the Geophysical Laboratory, K. K. Kelley of the U. S. Bureau of Mines, D. R. Waldbaum, and other investigators indicate that no appreciable amount of Al_2SiO_5 can be dissolved in hydrofluoric acid under the normal experimental conditions of solution calorimetry. Thus Neumann's (1925) reported direct measurement of the heats of solution of Al_2SiO_5 and mullite should be regarded as discredited. The heats and free energies of formation presented in this paper are obtained indirectly and depend mainly on the data of Kay and Taylor (1960). R. A. Robie (pers. comm.) of the U. S. Geological Survey has suggested the possible use of fluorine combustion calorimetry for directly determining these heats of formation.

The uncertainty given for the free energy of formation of mullite does not include an additional uncertainty in the third-law entropy of mullite. Considering the disordered arrangement of aluminum atoms, silicon atoms, and holes in the crystal structure of mullite (Sadanaga *et al.*, 1962; Burnham, 1963) and the sluggishness of Al-Si ordering in silicates, it is very likely that the calorimetric measurements of Pankratz *et al.* (1963) have not accounted for configurational entropy at 0° K. However, two important constraints set an upper limit on $S^\circ_{298.15(\text{mullite})}$: the incompatibility of quartz and corundum in igneous and metamorphic rocks and the

TABLE 2. FREE ENERGY FUNCTION, HEAT OF FORMATION, AND GIBBS FREE ENERGY OF FORMATION OF MULLITE, ANDALUSITE, KYANITE, AND SILLIMANITE AT HIGH-TEMPERATURES AND ONE ATMOSPHERE (APPROXIMATELY 1 BAR) PRESSURE

Temperature (° K)	$-\frac{(G^\circ_T - H^\circ_{298.15})}{T}$ (cal/deg-gfw)	$\Delta H^\circ_{f,T}$ (cal/gfw)	$\Delta G^\circ_{f,T}$ (cal/gfw)	$-\frac{(G^\circ_T - H^\circ_{298.15})}{T}$ (cal/deg-gfw)	$\Delta H^\circ_{f,T}$ (cal/gfw)	$\Delta G^\circ_{f,T}$ (cal/gfw)
	MULLITE—$Al_6Si_2O_{13}$			ANDALUSITE—Al_2SiO_5		
298.15	60.80 ±0.80	−1,636,725 ±1,800	−1,545,093 ±1,500	22.28 ±0.10	−619,158 ±1,100	−583,897 ±900
400	64.11	−1,637,185	−1,513,684	23.52	−619,362	−571,808
500	70.83	−1,636,917	−1,482,828	26.05	−619,213	−559,931
600	78.75	−1,636,296	−1,452,067	29.05	−618,935	−548,101
700	87.01	−1,635,495	−1,421,429	32.19	−618,594	−536,323
800	95.24	−1,634,592	−1,390,913	35.32	−618,233	−524,597
900	103.27	−1,633,673	−1,360,496	38.37	−617,866	−512,911
1000	111.04	−1,647,761	−1,329,079	41.31	−622,503	−500,892
1100	118.52	−1,646,308	−1,297,287	44.14	−621,952	−488,759
1200	125.69	−1,644,756	−1,265,625	46.86	−621,360	−476,673
1300	132.57	−1,643,131	−1,234,699	49.47	−620,725	−464,645
1400	139.17	−1,641,449	−1,202,700	51.98	−620,041	−452,673
1500	145.51	−1,639,728	−1,171,428	54.38	−619,307	−440,741
1600	151.58	−1,637,991	−1,140,258	56.69	−618,531	−428,860
1700	157.42	−1,660,456	−1,108,988	58.92	−629,812	−416,923
1800	163.03	−1,658,650	−1,076,594	60.97	−628,907	−404,252
1900	168.43	−1,656,864	−1,044,291			
2000	173.64	−1,655,100	−1,012,106			
	KYANITE—Al_2SiO_5			SILLIMANITE—Al_2SiO_5		
298.15	20.02 ±0.08	−618,672 ±1,100	−582,737 ±900	22.97 ±0.10	−618,406 ±1,100	−583,351 ±900
400	21.25	−618,896	−570,414	24.21	−618,600	−571,334
500	23.77	−618,767	−558,305	26.74	−618,491	−559,524
600	26.76	−618,449	−546,241	29.73	−618,253	−547,755
700	29.90	−618,068	−534,236	32.84	−617,962	−536,027
800	33.03	−617,657	−522,285	35.94	−617,661	−524,345
900	36.10	−617,250	−510,387	38.96	−617,354	−512,696
1000	39.07	−621,847	−498,166	41.88	−622,031	−500,710
1100	41.92	−621,256	−485,830	44.69	−621,490	−488,605
1200	44.66	−620,604	−473,541	47.39	−620,878	−476,551
1300	47.29	−619,899	−461,323	49.98	−620,193	−464,555
1400	49.81	−619,135	−449,149	52.48	−619,439	−452,617
1500	52.23	−618,311	−437,030	54.87	−618,615	−440,724
1600	54.57	−617,425	−424,970	57.18	−617,729	−428,890
1700	56.82	−628,576	−412,865	59.41	−628,880	−417,011
1800	58.99	−627,521	−400.202	61.56	−627.825	−404,574

same incompatibility in the synthetic system. The latter of these constraints depends on the fact that $\Delta G^\circ_{f,298.15(kyanite)}$ is calculated from the mullite thermodynamic data as outlined above. The entropy of mullite, therefore, enters directly into the stability of kyanite with respect to the elements and oxides. As the entropy of mullite is increased the calculated value of the free energy of formation of kyanite is increased to the extent that kyanite is no longer stable with respect to quartz and corundum. At that point, the equilibrium *quartz-kyanite-corundum* intersects the *sillimanite-kyanite* equilibrium so that kyanite is not a stable phase for a range of temperatures and pressures above the invariant point *quartz-sillimanite-kyanite-corundum.* Further increase in the entropy of mullite increases the calculated *quartz-corundum* field at the expense of the kyanite field.

With $S^\circ_{298.15(\mathrm{mullite})} = 60.80$ cal/deg-gfw, the assemblage *quartz-corundum* is metastable, hence the equilibria *quartz-*Al_2SiO_5*-corundum* are not shown in Fig. 1. From the data in Table 1, it can be shown that the first appearance of *quartz-corundum* at the expense of Al_2SiO_5 will be in the kyanite field. However, the possibility of the metastable equilibrium *quartz-kyanite-corundum* intersecting the stable *sillimanite-kyanite* equilibrium is precluded by the recent work of Haskell and DeVries (1964) in which kyanite is shown to be stable up to its (incongruent) melting point. Clark (1961) observed the assemblage *kyanite-corundum-glass* in the same P,T region along the *kyanite-sillimanite* equilibrium curve. These data imply the appearance of the invariant point:

liquid-sillimanite-kyanite-corundum

which requires the invariant point *quartz-sillimanite-kyanite-corundum* (and the assemblage *quartz-corundum*) to be completely metastable. Moreover, from the thermodynamic data it follows that quartz and corundum are incompatible in the andalusite and sillimanite fields. This is in good agreement with the absence of the assemblage *quartz-corundum* in igneous and metamorphic rocks. The incompatibility of quartz and corundum therefore, sets an upper limit for the entropy of mullite *and* the slope of the *quartz-sillimanite-mullite* curve.

These constraints on $S^\circ_{298.15(\mathrm{mullite})}$, taken in connection with entropy and volume data for the other phases, permit a maximum value of 62.80 cal/deg-gfw which results in a change in $\Delta G^\circ_{f,298.15(\mathrm{mullite})}$ of +3100 cal/gfw and +450 cal/gfw in the free energy of the Al_2SiO_5 polymorphs. Since the free energies of andalusite, kyanite, and sillimanite relative to the elements and oxides presently depend on the thermodynamic properties of mullite, it would be desirable to have additional equilibrium data for univariant reactions in which mullite participates.

Equilibria involving mullite and Al_2SiO_5 are regarded as first-order phase changes in this paper. However, comparison of the crystal structures of mullite and sillimanite (Sadanaga *et al.*, 1962; Burnham, 1963) suggests that a continuous transition is possible in the composition range Al_2SiO_5-Al_4SiO_8. Since experimental verification of this has not been reported, it is assumed that a compositional discontinuity exists between mullite and Al_2SiO_5 as in Fig. 1.

Equilibrium thermodynamic relations of the crystalline phases in the system SiO_2-Al_2O_3 are summarized in Fig. 1. The univariant equilibria *quartz-andalusite-mullite*, *andalusite-mullite-corundum*, and *sillimanite-mullite-corundum* have been calculated from the entropy, volume and heat of formation data given in Table 1. The two latter equilibria intersect as a degenerate quadruple point with the *andalusite-sillimanite*

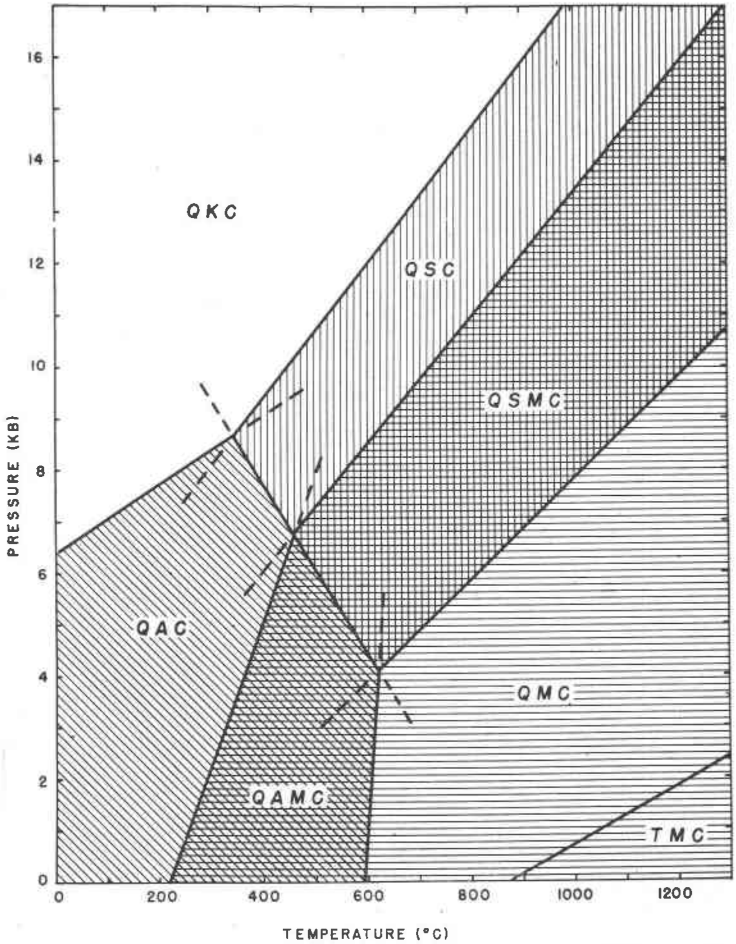

FIG. 2. Stability relations of crystalline phases in the system SiO_2-Al_2O_3 below 17 kb and 1300° C as shown in Fig. 1. The blank area outlines the kyanite stability field; horizontal ruling—the mullite field; vertical ruling—the sillimanite field; diagonal ruling—the andalusite field. Quartz and corundum are incompatible over the entire P,T range.

equilibrium at approximately 6800 bars and 460° C. With the exception of the entropy of kyanite, as discussed above, all equilibrium relations in Fig. 1 are consistent with the data in Table 1. The stability fields of the aluminum silicates are outlined in Fig. 2. Mullite is stable well into the andalusite and sillimanite fields which suggests that the assemblages *mullite-andalusite*, *mullite-sillimanite*, and *mullite-corundum* may be more common in highly aluminous metamorphic rocks than previously supposed.

The phase diagram for this system as given by Clark (1961) must be modified beyond 17 kb and 1300° C. in light of the recent work of Haskell and DeVries (1964). They reported that the equilibrium *liquid-kyanite-corundum* passes through the point 25.2 kb and 1527° C. with a positive slope of 33.8 bars/deg. The appearance of liquids under these pressures and temperatures is not surprising since the formation of "metastable" glass, quartz, and corundum from crystalline Al_2SiO_5 was observed by Clark *et al.* (1957) and Clark (1961) in the same P,T region. The resulting invariant point *liquid-sillimanite-kyanite-corundum* at 23 kb and 1450° C. is at a considerably lower temperature than the observed one-atmosphere equilibria *quartz-liquid-mullite* and *mullite-liquid-corundum* at 1595° C. and 1840° C. respectively (Aramaki and Roy, 1962). These observations, therefore, require *negative* slopes for at least some of the equilibria involving a liquid phase. The probable disposition of other possible invariant points:

quartz-liquid-sillimanite-kyanite
quartz-liquid-sillimanite-mullite
liquid-sillimanite-mullite-corundum

suggests the appearance of liquids in the anhydrous system SiO_2-Al_2O_3 at temperatures as low as 1300° C. at pressures less than 20 kb.

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