

The High Temperature Stability of Muscovite Plus Quartz

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Abstract

Standard hydrothermal experiments using synthetic crystalline starting materials were conducted in order to locate the reaction: muscovite + quartz \rightleftharpoons sanidine + sillimanite + water. The indicated equilibrium temperatures at water pressures equal to total pressure are: $595 \pm 15^\circ\text{C}$ at 1 kbar, $640 \pm 10^\circ\text{C}$ at 2 kbar, and $662 \pm 6^\circ\text{C}$ at 3 kbar. One self-consistent curve passing through 662°C , 637°C , and 603°C at 3, 2, and 1 kbar respectively is also consistent with the observed calorimetric entropy of formation of muscovite at 298.15 K. These temperatures agree with those reported by Althaus *et al.* (1970) but are systematically higher than those reported by Evans (1965). The lack of reaction reversals and kinetic arguments suggest that Evans' data may reasonably be interpreted as minimum temperatures for the reaction. The textures of the reaction products suggest that the reaction may proceed through nucleation of sanidine and aluminum silicate in the muscovite grains. If true, this mechanism might explain the lack of reaction reversals in Evans' experiments.

Introduction

The assemblage of muscovite + quartz is so common in igneous and metamorphic rocks that its stability is an important consideration in the construction of any petrogenetic grid. Several recent workers have reported experimental data for the reaction:



$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + \text{SiO}_2 = \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{SiO}_5 + \text{H}_2\text{O}$
Evans (1965) used a reaction-rate method and natural starting materials to determine the locations of the reactions involving andalusite and sillimanite. Althaus *et al.* (1970) reported data on the reaction involving andalusite which were gathered using natural starting materials in standard hydrothermal experiments. Storre and Karotke (1971) investigated the melting relations of natural muscovite + quartz in the pressure region 7-20 kbar.

For purposes of a larger study of equilibria among synthetic phases in the system K-Fe-Al-Si-O-H (Day, 1971), it seemed desirable to verify the stability of muscovite + quartz using synthetic materials wherever possible. The data presented here have been discussed in brief form previously (Day, 1970).

Experimental

A synthetic sanidine, muscovite and quartz, and a natural sillimanite were used as starting materials in this study. Silica

gels of muscovite, sanidine, and quartz compositions were prepared from nitrate solutions and tetraethylorthosilicate (TEOS) by a method similar to that described by Luth and Ingamells (1965). Muscovite was hydrothermally crystallized from dried gel at 2 kbar, 600°C for two weeks. This muscovite had moderately broad X-ray diffraction peaks characteristic of an 1M polymorph (Yoder and Eugster, 1955) which partially inverted to the 2M form during the experiment. The muscovite starting material did not produce an X-ray diffraction pattern which would permit a meaningful measurement of the unit cell parameters. Sanidine was hydrothermally crystallized from gels at 2 kbar, 700°C for two weeks. Unit cell parameters were refined according to the method of Wright and Stewart (1968) using the computer program written by Appleman, Handwerker, and Evans (unpublished). A preliminary version of this program was described by Evans, Handwerker, and Appleman (1963). Ten X-ray diffraction lines were assigned fixed indices on the basis of a preliminary refinement in which automatic indexing led to differences of less than 0.010 \AA between $d(\text{calc})$ and $d(\text{obs})$. The final refinement included only these ten lines and the results were: $a = 8.5921(20) \text{ \AA}$, $b = 13.0158(30) \text{ \AA}$, $c = 7.1789(19) \text{ \AA}$, $\beta = 116.037(19)^\circ$ and $V = 721.35(20) \text{ \AA}^3$. It is notable that the 204 and 060 lines were not included in this refinement. This sanidine lies very close to the high sanidine apex on the b - c plot of Wright and Stewart (1968).

A mixture of SiO_2 polymorphs was prepared by hydrothermally crystallizing either TEOS or floated silica powder at approximately 650°C and 2 kbar. These polymorphs rapidly inverted to quartz during the experiment. Natural sillimanite from Custer, South Dakota (Brown University Baker Collection No. 399.7) was crushed and purified by heavy liquid and magnetic techniques. X-ray diffraction scans revealed traces of possible alteration products (kaolinite?). After washing this material, these peaks were barely perceptible and did not appear in the starting mixes discussed below. As discussed at a later point, the possible

presence of these trace impurities does not affect the interpretation of these experiments.

Muscovite + quartz and sanidine + sillimanite mixtures were prepared in the weight ratios necessary for complete reaction. An aliquot of each mixture was "seeded" with 10 percent or 15 percent by weight of the other mixture. A hydrothermal experiment consisted of two sealed platinum tubes in the same reaction vessel, each of which contained pure water and a mixture of four solid phases, one mixture with 90 percent muscovite + quartz (Mix 1), the other with 90 percent sanidine + sillimanite (Mix 2).

All experiments were conducted according to standard hydrothermal procedures (Day, 1971). Chromel-alumel thermocouples were calibrated against the melting point of NaCl (800.5°C). Temperatures inside the reaction vessel at atmospheric pressure were within 2°C of the temperature measured in the external well in the bomb, and thermal gradients were less than 4°C over the length of the charge. No attempt was made to apply corrections for these sources of error. Fluctuations during the experiment were never more than $\pm 5^\circ\text{C}$. Accuracy of the temperatures reported is estimated to be no worse than $\pm 10^\circ\text{C}$. Pressures were measured with a Heise five-kilobar bourdon tube gauge. The manufacturer reports no deviations greater than five bars from dead weight piston gauges certified by the U.S. National Bureau of Standards. Pressure fluctuations during an experiment were never more than 20 bars, and during most experiments they were less than 10 bars. The accuracy of the pressures reported is estimated to be no worse than 20 bars.

Starting materials and run products were always compared both optically and by X-ray diffraction. In almost all experiments, X-ray diffraction criteria were not definitive in determining the direction of reaction, and optical criteria were most important. Small differences in refractive index were enhanced using phase-contrast microscopy, and the phases were easily identified when present as single grains.

The grain sizes of the starting materials and run products were approximately the same. Synthetic muscovite, sanidine and quartz ranged in size from 1–30 μm with an average size in the range 5–10 μm in length.

Interpretation of Run Products

Two criteria were used to identify the breakdown of muscovite + quartz to sanidine + sillimanite. First, in those experiments containing Mix 1, there was a marked decrease in the number of identifiable muscovite grains. The intensity of the (001) muscovite peak sometimes, but not always, showed a concomitant decrease. This can be explained because the crystallinity of the muscovite increases greatly in these long experiments, thus offsetting any small decreases in the intensity of the (001) due to a decrease in the amount of muscovite.

The second criterion for the dehydration of muscovite + quartz was the observation of small white inclusions in muscovite grains, interpreted as sanidine, and of needle-like inclusions, interpreted as sillima-

nite. Since the vapor phase in these experiments must have been saturated with respect to silica (Weill and Fyfe, 1964), these inclusions were interpreted as having nucleated and grown in the sanidine + sillimanite stability field. These features were identified in the muscovite grains from run products of both types of starting materials. These textures clearly indicate only that muscovite + quartz is unstable, but they do not provide information concerning the more stable assemblage.

The reaction reversal, the growth of muscovite + quartz, was much more difficult to identify conclusively. In the runs which started with 10 percent by weight of the sanidine + sillimanite mixture, it was possible to identify "rims" and intergrowths of material which appeared to be muscovite on the feldspar grains. The material, like muscovite, was gray under phase contrast conditions in $n = 1.560$ oil and sometimes had reddish tinges. It was possible that these features were merely muscovite grains which had adhered to the surface of a feldspar grain. Every attempt was made to separate the muscovite and feldspar while observing the grain continuously. In no case did vigorous movement of the grain, by moving the coverslip with a spatula, succeed in producing any relative movement of the muscovite and sanidine. Attempts to identify these textures using scanning electron microscopy were unsuccessful.

Rims and intergrowths were never observed in the companion runs which started with only 10 percent by weight of the muscovite + quartz mixture (Mix 2). It is possible that, in the runs starting with 90 percent muscovite + quartz (Mix 1), muscovite has dissolved and reprecipitated on feldspar surfaces. However, since the sharpness of muscovite X-ray diffraction lines increases rapidly in the early stages of an experiment, and since no muscovite growth features (or decomposition features) were found in runs of short duration, it is very unlikely that metastable recrystallization of muscovite in the stability field of sanidine + sillimanite can account for these textures. In addition, it is extremely unlikely that reaction of feldspar with possible traces of sillimanite alteration products could have produced these muscovite growth textures since the textures were only observed in runs starting with small amounts of sillimanite. Therefore, the observed textures are tentatively interpreted as evidence for the reaction reversal.

One experiment at 650°C, 2 kbar, produced sanidine + corundum + quartz from an unseeded

starting material of muscovite + quartz. This was interpreted as the metastable nucleation and growth of corundum + quartz instead of the stable aluminum silicate. There was no indication that the capsule had leaked. In runs which leaked and produced corundum, the corundum always had an euhedral habit whereas the corundum in this experiment occurred as rounded equant grains ranging from 1-6 μm in size.

Another experiment (C73) performed at 650°C and 3 kbar, was designed to detect the reaction:

Fe-biotite + sillimanite + quartz

= Fe-cordierite + sanidine.

The starting materials for this experiment included sanidine + sillimanite, and the reaction products contained muscovite + quartz, indicating that the experiment was performed in the muscovite + quartz stability field (Day, 1971).

The experimental data are listed in Table 1 and illustrated in Figure 1. The inferred equilibrium pressures and temperatures are compared with those obtained by Althaus *et al.* (1970) and Evans (1965) in Table 2.

Discussion

It is important to realize the difficulty of making unbiased interpretations of textural features in a multiphase mixture of grains ranging in size from 1-30 μm . If the muscovite rims on the feldspars have been incorrectly interpreted as the reaction reversal, then the data presented here represent maximum temperatures for the stability of muscovite + quartz. The following discussion accepts the premise that the textures have in fact been correctly interpreted.

With these uncertainties in mind, the data suggest that the muscovite + quartz breakdown lies at temperatures systematically higher than those reported by Evans (1965) and at substantially the same temperatures reported by Althaus *et al.* (1970). It is argued that the new data better describe the position of the univariant equilibrium because: (1) the new data are thermodynamically consistent while Evans' probably are not, and (2) Evans' experiments can be interpreted as minimum estimates of the reaction temperature. These points will be considered in turn.

Thermodynamic Considerations

Anderson (1970) has described a method of testing the thermodynamic consistency of a set of experi-

TABLE 1. Experimental Data for the Reaction*

Run	T °C	P (kbar)	Hours	Starting Mix (See Text)	Observed Changes	Direction
44	565	1	1509	2	Ms (004) appears	← ?
45	565	1	1509	1	Ms rims Sa, Sill (110) disappears	←
50	580	1	1917	2	Sa+Sill+Ms+Q(?)	n.r.**
51	580	1	1917	1	Ms rims Sa	←
48	610	1	3118	1	Ms (001) decreased inclusions in Ms	→
49	610	1	3118	2	Ms (001) decreases inclusions in Ms	→
52	625	1	1008	2	inclusions in Ms	→ ?
53	625	1	1008	1	Ms + Sa + Sill	n.r.
57	630	2	668	1	Sa-Ms intergrown	←
58	630	2	668	2	Sa+Sill+Ms+Q	n.r.
12	650	2	1351	Sa+Sill	Sa + Sill	n.r.
13	650	2	1351	Ms+Q	Ms+Sa+Cor+Q	→
C73	650	3	1004	Cd+Sa+Sill	Bi+Ms+Q+Sill(?)	←
25	656	3	1680	2	Sa+Sill+Ms	n.r.
26	656	3	1680	1	Ms rims Sa	←
22	668	3	914	2	Grain size and amount of Ms decrease	→
23	668	3	914	1	Sa increases (optically)	→
46	675	3	1887	1	Ms has inclusions	→
47	675	3	1887	2	Ms has inclusions	→

*The arrows in the right hand column indicate the direction of the inferred reaction:
Muscovite + Quartz = Sanidine + Sillimanite + Water
Ms Q Sa Sill

**n.r. = no reaction

mental data gathered at several temperatures and pressures. The method is based on the assumption that the standard heat of reaction is a constant over small intervals of temperature so that the logarithm of the equilibrium constant ($\log K$) is a linear function of the inverse temperature in that temperature interval. For a dehydration reaction among solid phases in their standard state, the equilibrium constant is equal to the activity of water. The equilibrium activity of water at the standard pressure, and therefore the equilibrium constant, may be calculated from the experimental data by applying an isothermal pressure correction on the activity of water at the experimental pressure. If the standard enthalpy of reaction is a constant, and if the data are thermodynamically consistent, a plot of ($\log K$) vs ($1/T$) should yield a straight line.

Figure 2 illustrates such plots for the data contained in Table 2. The standard state for all phases was taken as the pure phase at 3 kbar and the temperature under consideration (Standard state set B,

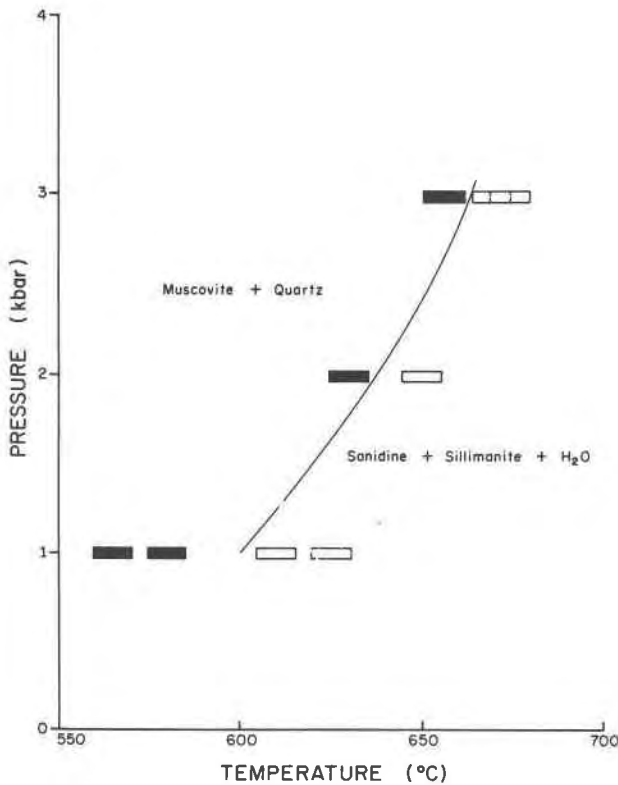


FIG. 1. Pressure and temperature coordinates of the reaction: Muscovite + Quartz = Sanidine + Sillimanite + H₂O. $P_{H_2O} = P_{Total}$. The illustrated equilibrium curve is thermodynamically self-consistent (see Fig. 2).

Anderson, 1970). Molar volumes of the pure solid phases were taken from Robie and Waldbaum (1968), and the activity of water was calculated from the fugacities reported by Burnham, Holloway and Davis (1968). Note that these are the only thermodynamic data required in order to test for self-consistency using this method. These calculations show that the data obtained at one kilobar in

TABLE 2. Temperature (°C) Coordinates of the Reaction: Muscovite + Quartz = K-feldspar + Aluminum silicate + water

Pressure (kbar)	Althaus (1970) Andalusite	Day Sillimanite	Evans (1965) Sillimanite	Andalusite
1	585 ± 15	595 ± 15	530 ^{+20^b} -10	+525 ^{+20^b} -10
2	635 ± 25	640 ± 10	605 ± 10 ^c	600 ± 10 ^c
3	651 ± 10 ^a	640 ± 6	635 ± 10 ^c	640 ± 15
4	672 ± 12		665 ± 10 ^c	675 ± 15

a. Data in Table 3 (Althaus, *et al.*, 1970) assumed in error
 b. Pressure = 1050 bars
 c. Errors assigned by this writer

this study and in the Althaus study are thermodynamically consistent with those obtained at the higher pressures. On the other hand, the data obtained by Evans (1965) at one kilobar may be judged thermodynamically consistent with the higher pressure data only if the most extreme possible temperature values of the data are considered. In fact, Evans (1965, caption to Figure 10) prefers a calculated temperature at one kilobar to the experimental points.

Thermodynamic parameters estimated from the present data are also consistent with published values.

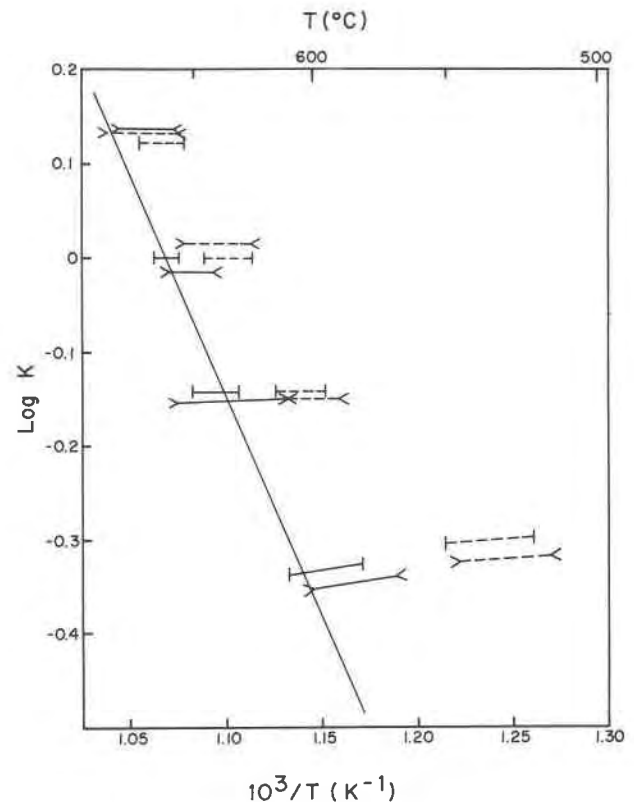


FIG. 2. Logarithm of the equilibrium constant versus reciprocal temperature for the reaction: Muscovite + Quartz = K-feldspar + Aluminum Silicate + H₂O. Dashed lines illustrate Evans' data, solid lines, those of Althaus *et al.*, and this work. Lines terminated using vertical bars represent data gathered using sillimanite, those terminated with the symbols (> <) represent data gathered using andalusite. At the standard pressure, 3 kbar, log K = 0 for all experiments. However, the andalusite data have been offset from this value for clarity in presentation. One self-consistent reaction curve has been constructed through the sillimanite data presented in this paper (3 kbar, 662°C; 2 kbar, 637°C; 1 kbar, 603°C). The slope of this curve is consistent with the entropy of formation of muscovite (298 K, 1 atm) which is calculated from the data tabulated by Robie and Waldbaum (1968).

Table 3 summarizes the estimated Gibbs energy, entropy and enthalpy of formation from the elements at 298.15 K for muscovite (O:H = 12:2 per mole). The quoted errors are the maximum variations permitted by the experimental data. The Gibbs energy of formation was estimated according to the method outlined by Fisher and Zen (1971) using the thermodynamic parameters listed in Table 4. The entropy of formation was estimated by combining the entropies of formation listed in Table 4 with the entropy of reaction calculated according to the method described by Chatterjee (1970).

The parameter G'' (Chatterjee, 1970) needed in the entropy calculation was obtained from the tabulated values of G^* (Fisher and Zen, 1971) using the relation:

$$G'' = G^* + \Delta V_s(P - 1)$$

where ΔV_s is the volume change of solids in the reaction and P is the equilibrium pressure. The entropy of formation of muscovite calculated in this way agrees within the limits of error with the value listed in Table 4. The enthalpy of formation was calculated by difference using the relation:

$$\Delta G + T\Delta S = \Delta H$$

Evans' (1965) data were analyzed by the same methods. The estimated Gibbs energy of formation agrees with that reported in Table 3. However, only one solution for the entropy of formation of muscovite is consistent with all of Evans data (as reported in Table 2). This value ($-295 \text{ cal K}^{-1} \text{ mol}^{-1}$) is somewhat lower than expected and is consistent with the lower observed slope of his reaction curve. If the one-kbar data are eliminated, however, no disagreement is necessary.

If the slope of the andalusite-producing reaction is taken as 36 bar K^{-1} (Althaus *et al.*, 1970) and the

TABLE 3. Estimated and Published Thermodynamic Parameters (298 K, 1 bar) for Muscovite^a

	This Work	Previous Estimates
G_f° kcal mol ⁻¹	-1339.9 ± 2.4	-1340 ^b
S_f° cal K ⁻¹ mol ⁻¹	-303.7 ± 7.2	-305.5 ^c
H_f° kcal mol ⁻¹	-1430.4 ± 4.5	-1431 ^b

a. See text for details.

b. Estimated by Zen (1970) using procedures similar to that employed here.

c. Robie and Waldbaum (1968) 1 atm data.

TABLE 4. Thermodynamic Parameters Used in the Derivation of Data in Table 3^a

	G_f° (kcal mol ⁻¹)	S_f° (cal K ⁻¹ mol ⁻¹)	V (cal bar ⁻¹ mol ⁻¹)
Muscovite		-305.47	3.3630
Quartz	-204.646	-43.62	0.5423
Sanidine	-892.263	-174.79	2.6063
Sillimanite	-583.599	-117.56	1.1926

^aAll parameters were taken from Robie and Waldbaum (1968).

intersection of this reaction with the andalusite-sillimanite equilibrium is taken as approximately 4 kbar and 680°C (Richardson *et al.*, 1969), then a slope of 40 bar K^{-1} for the sillimanite-producing reaction may be calculated from the thermodynamic data of Robie and Waldbaum (1968). This is equivalent to a temperature divergence of only about 3°C/kbar between these two reactions. Since the data of Althaus *et al.* (1970) for the andalusite-producing reaction and these data for the sillimanite-producing reaction were obtained using different methods for the detection of reaction, their close agreement is further evidence for the self-consistency of the data. Their close agreement is also evidence that the possible presence of fibrolite in the starting material has not significantly changed the inferred temperatures of the sillimanite-producing reaction (*cf.* Holdaway, 1971).

A corollary of this close expected and observed agreement is that little useful information concerning the andalusite-sillimanite equilibrium can be derived from data on the stability of muscovite and quartz (*cf.* Holdaway, 1971; Newton, 1966). The only restrictions on the data must be the relative slopes of the andalusite-producing and sillimanite-producing reactions. If this is taken into account, then manipulation of straight curves in Figure 2 shows that the Day-Althaus data permit intersections at least as low as one kilobar and place no upper pressure limit. Likewise, the Evans (1965) data permit intersections over the entire pressure range of the data.

The discussion above indicates that the present data are thermodynamically self-consistent, are consistent with the available thermodynamic data, and are in agreement with the data reported by Althaus *et al.* (1970). Evans' reaction curve is probably not thermodynamically self-consistent and, on the basis of the calculated entropy of formation for muscovite, probably has a pressure-temperature slope which is too small.

Comparison of Experiments

Evans' experiments were based on the weight change displayed by a single crystal of aluminum silicate which has been reacted with a powder of muscovite + quartz + aluminum silicate + K-feldspar in the presence of water. All experiments were conducted for a fixed time so that a weight change is proportional to a reaction rate. The temperature at which the observed weight changes or the inferred reaction rate becomes zero must be the equilibrium temperature. A typical set of data (Evans, 1965, Figure 8) is reproduced as Figure 3. Notice that the reproducibility of the experiments is at best 0.05 mg and that an increase in temperature does not necessarily lead to a smaller weight loss. The percent reproducibility of points might be improved with increased duration of the experiments.

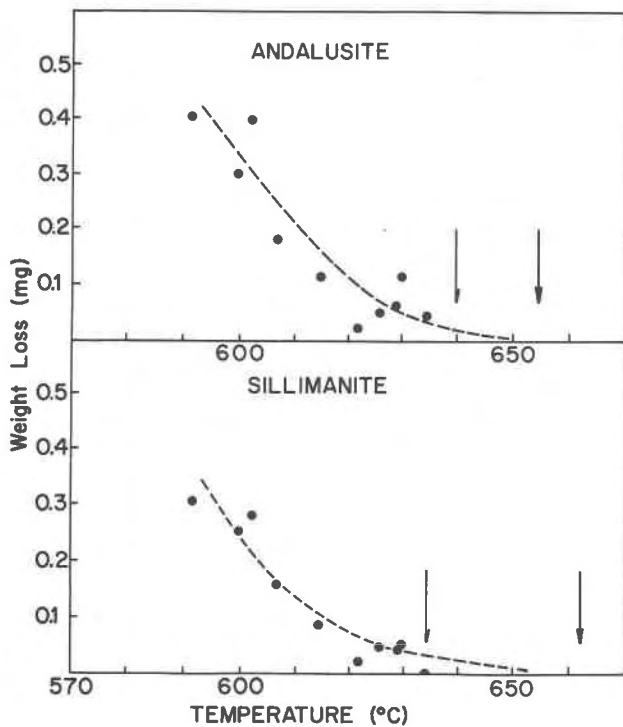


FIG. 3. Weight changes undergone by andalusite and sillimanite crystals in the presence of powder of muscovite (<200 mesh), quartz (<325 mesh), and adularia (<325 mesh). Water pressure 3 kbar, time 70 hours. After Evans (1965). The single-headed arrows point to Evans' reported temperature based on a linear extrapolation of the data. The double-headed arrows indicate equilibrium temperatures reported in this paper and by Althaus *et al.* (1970). The dashed lines indicate possible curvilinear extrapolations and have been added by this writer. The curvilinear extrapolations are near the maximum limit of error reported by Evans.

The most important observation with regard to Evans' experiments is that they are unreversed. That is, significant growth of the aluminum silicate crystal at the expense of muscovite + quartz was never observed. By this criterion alone, Evans' data may be interpreted as minimum estimates of the reaction temperatures. Evans has also assumed a linear extrapolation of his data to zero weight loss. It is argued below that this procedure can also lead to a minimum estimate of the temperature because, in fact, there are good reasons to believe that the reaction rate should approach the equilibrium temperature in an asymptotic manner.

Experimental petrologists have long noticed that reaction rates decrease significantly near the equilibrium temperature. This has usually been expressed by a zone surrounding the reaction trace in which experiments of long duration lead to no reaction. The casual suspicion that decreases in the rate are exponential in this region is substantiated by classical rate theory and by limited amount of experimental data.

Classical rate theory (see, for example, Fyfe *et al.*, 1958, or various physical chemistry texts) suggests that reaction rates for most processes are exponential functions of temperature. For small extents of reaction, exponential decreases of reaction rate towards the equilibrium temperature have been demonstrated for the hydration of periclase (temperature increases as equilibrium is approached) and the dehydration of brucite (temperature decreases towards equilibrium) (Fyfe *et al.*, 1958), and for the aragonite to calcite transition (temperature decreases towards equilibrium) under dry conditions (Davis and Adams, 1965) and hydrothermal conditions (Metzger and Barnard, 1968). It is likely that the rates for other reactions and reaction mechanisms also decrease exponentially as the equilibrium temperature is approached.

In Figure 3, curves have been drawn which approach the equilibrium temperature asymptotically and which are consistent with the reproducibility of Evans' data. These curvilinear extrapolations lead to substantially higher estimates of the equilibrium temperatures which are near the upper limits of error assigned by Evans on the basis of linear extrapolations of the data.

The reproducibility of Evans' (1965) data and of data for other reactions gathered by similar methods (Fyfe and Hollander, 1964; Holdaway, 1966; Kerrick, 1968; Thompson, 1970) often does not permit

differentiation between a linear or a higher order curve. However, in view of the rate data discussed above, the absence of reaction reversals in the muscovite data, and the absence of any direct knowledge of the mechanism for this dehydration reaction, a curvilinear extrapolation of Evans' data must remain a likely possibility.

Textural features of run products from this work suggest a possible explanation for the fact that Evans observed no significant weight gains of aluminum silicate crystals. Muscovite grains in the presence of quartz were observed to contain abundant inclusions of what was interpreted as sanidine and aluminum silicate when held at temperatures in the sanidine + sillimanite field. The presence of quartz in the charge assures the rapid saturation of the fluid with silica in some form (Weill and Fyfe, 1964). With silica readily available, it appears that sanidine and aluminum silicate may develop, not by precipitation from solution onto pre-existing nuclei, but by a process akin to homogeneous nucleation and growth in the original muscovite grain. If this is in fact true, it is clear that no significant growth of a pre-existing aluminum silicate crystal will be observed.

The presence of rims of muscovite on sanidine grains suggest that muscovite + quartz grow by precipitation of the constituents from solution. Even if the Al-Si framework of the feldspar serves as a nucleation site for the muscovite, some transport of alumina from grain to grain is necessary. It is most likely that this occurs via the vapor phase through dissolution of the aluminum silicate crystals. Thus, weight losses of a single aluminum silicate crystal would be expected.

Evans (1965) and Althaus *et al.* (1970) both used natural sodium-bearing muscovites as starting materials. Both of these materials were presumably the 2M form of muscovite. The presence of small amounts of sodium would decrease the thermal stability of muscovite + quartz with respect to the sodium-free assemblage used in the present experiments. The extent of this decrease is not precisely known, but it is likely to be only a very few degrees. The close agreement of the present data with those of Althaus *et al.* tends to substantiate this view. The run products of the present experiments include both the 1M and 2M forms of muscovite. If the 1M form is metastable with respect to the 2M form under the conditions of these experiments (Velde, 1965), then the 1M-bearing assemblage should have a lower thermal stability than the equivalent 2M-bearing

assemblage. Such an effect would not explain the differences between Evans' data and that presented here.

In view of the lack of reaction reversals and the uncertainty in the linear extrapolation of the data to zero reaction rate, the results obtained by Evans (1965) may be reasonably interpreted as minimum temperatures for the reaction. Because of the difficulty in making unambiguous interpretations, the data presented in this work could represent maximum temperatures for the reaction. However, if the textural interpretations are correct, it is argued that the present data are preferred because they are thermodynamically consistent while Evans' are not.

Note Added in Proof. Kerrick (1972, *Amer. J. Sci.* **272**, 946-958) has recently reported another determination of the upper thermal stability of muscovite plus quartz using natural starting materials and methods similar to those employed by Evans (1965). His results ($605 \pm 10^\circ\text{C}$, 2 kbar) confirm those of Evans and are substantially lower than those reported here and by Althaus *et al.* (1970). The range of temperatures reported for this equilibrium at low pressures suggests that the problem is not yet resolved and that there may be systematic differences among the results obtained by the different methods.

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References

- ALTHAUS, E., E. KAROTKE, K. H. NITSCH AND H. G. F. WINKLER (1970) An experimental re-examination of the upper stability limit of muscovite plus quartz. *N. Jahrb. Mineral. Monat. Jahrg.* **1970**, 325-336.
- ANDERSON, G. M. (1970) Some thermodynamics of dehydration equilibria. *Amer. J. Sci.* **269**, 392-401.
- BURNHAM, C. W., J. R. HOLLOWAY, AND N. F. DAVIS (1969) Thermodynamic properties of water to 1,000°C and 10,000 bars. *Geol. Soc. Amer. Spec. Pap.* **132**, 96 pp.
- CHATTERJEE, N. D. (1970) Synthesis and upper stability of paragonite. *Contrib. Mineral. Petrology*, **27**, 244-257.
- DAVIS, B. L., AND L. H. ADAMS (1965) Kinetics of the calcite-aragonite transformation. *J. Geophys. Res.* **70**, 433-441.
- DAY, HOWARD (1970) Redetermination of the stability of

- muscovite + quartz. *Geol. Soc. Amer. Abstr. Programs*, **2**, 535.
- (1971) *A theoretical and experimental study of some equilibria in the system K-Fe-Al-Si-O-H*. Ph.D. Dissertation, Brown University, Providence, Rhode Island.
- EVANS, B. W. (1965) Application of a reaction rate method to the breakdown equilibria of muscovite and muscovite + quartz. *Amer. J. Sci.* **263**, 647–667.
- EVANS, H. T., D. E. APPLEMAN, AND D. S. HANDWERKER (1963) The least squares refinement of crystal unit cell with powder diffraction data by an automatic computer indexing method. (abstr.) *Program Annu. Meet. Amer. Crystallogr. Ass.* March 28, 1963, Cambridge, Mass., pp. 42–43.
- FISHER, J. R., AND E-AN ZEN (1971) Thermochemical calculation from hydrothermal phase equilibrium data and the free energy of H₂O. *Amer. J. Sci.* **270**, 297–314.
- FYFE, W. S., AND M. A. HOLLANDER (1964) Equilibrium dehydration of diasporite at low temperatures. *Amer. J. Sci.* **262**, 709–712.
- , F. J. TURNER, AND J. VERHOOGEN (1958) Metamorphic reactions and metamorphic facies. *Geol. Soc. Amer. Mem.* **73**.
- HOLDAWAY, M. J. (1966) Hydrothermal stability of clinozoisite plus quartz. *Amer. J. Sci.* **264**, 643–667.
- HOLDAWAY, M. J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *Amer. J. Sci.* **271**, 97–131.
- KERRICK, D. M. (1968) Experiments on the upper stability limit of pyrophyllite at 1.8 kilobars and 3.9 kilobars water pressure. *Amer. J. Sci.* **266**, 204–214.
- LUTH, W. C., AND C. O. INGAMILLS (1965) Gel preparation of starting materials for hydrothermal experimentation. *Amer. Mineral.* **50**, 255–258.
- METZGER, W. J., AND W. M. BARNARD (1968) Transformation of aragonite to calcite under hydrothermal conditions. *Amer. Mineral.* **53**, 295–300.
- NEWTON, R. C. (1966) Kyanite-andalusite equilibrium from 700° to 800°C. *Science*, **153**, 170–172.
- RICHARDSON, S. W., M. C. GILBERT, AND P. M. BELL (1969) Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria; the aluminum silicate triple point. *Amer. J. Sci.* **267**, 259–272.
- ROBIE, R. A., AND D. R. WALDAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 Bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* **1259**.
- STORRE, B., AND E. KAROTKE (1971) An experimental determination of the upper stability limit of muscovite + quartz in the range 7–20 kbar water pressure. *N. Jahrb. Mineral, Monat. Jahrg.* **1971**, 237–240.
- THOMPSON, A. B. (1970) A note on the kaolinite-pyrophyllite equilibrium. *Amer. J. Sci.* **268**, 454–458.
- VELDE, B. (1965) Experimental determination of muscovite polymorph stabilities. *Amer. Mineral.* **50**, 436–449.
- WEILL, D. F., AND W. S. FYFE (1964) The solubility of quartz in H₂O in the range 1000–4000 bars and 400°C–500°C. *Geochim. Cosmochim. Acta*, **28**, 1243–1255.
- WRIGHT, T. L., AND D. B. STEWART (1968) X-ray and optical study of alkali feldspar. I. Determination of composition and structural state from refined unit cell parameters and 2V. *Amer. Mineral.* **53**, 38–87.
- YODER, H. S., AND H. P. EUGSTER (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta*, **8**, 225–280.
- ZEN, E-AN (1971) Standard (298K, 1 bar) enthalpy and Gibbs free energy of formation for 8 minerals, and 298 K, 1 bar third law entropy for 6 minerals. *Trans. Amer. Geophys. Union*, **54**, 381.

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