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APPLICATION OF A REACTION-RATE METHOD TO THE BREAKDOWN EQUILIBRIA OF MUSCOVITE AND MUSCOVITE PLUS QUARTZ

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ABSTRACT. Data on the breakdown equilibria of muscovite, particularly in the presence of quartz, have been obtained by an experimental method based on reaction rates. Pure muscovite decomposes to K-feldspar, corundum, and water at about 680°C and 2 kilobars water pressure, and natural muscovites begin to decompose in the region 630°C to 650°C. The addition of quartz reduces the stability field of muscovite by approximately 80°C at 2 kilobars. The positions of the three univariant curves, in which the products of reaction are respectively andalusite, sillimanite, and kyanite, together with K-feldspar and water, have been determined between 1 and 4 kilobars water pressure. An invariant point, where muscovite, quartz, K-feldspar, sillimanite, andalusite, and water coexist, occurs between 2 kilobars and 600°C and 3 kilobars and 640°C. Kyanite and mullite + quartz are considerably less stable than andalusite or sillimanite in the 2 kilobar–650°C region. The pair corundum + quartz is always less stable than at least one of the three Al_2SiO_5 polymorphs. The coexistence of muscovite and high-quartz is only possible under metamorphic conditions of water pressure equal to total pressure.

INTRODUCTION

A state of equilibrium is defined as a state of rest (for example, Lewis and Randall, 1961, p. 16). To determine the equilibrium conditions for a system in which a reaction is possible, it is therefore only necessary to find under what conditions the net reaction velocity is zero. Experimental equilibrium studies continually make use of this definition, although the rate-measuring device is commonly quite crude and rarely capable of indicating anything but direction. This proves adequate when reactions proceed in reasonable time. For sluggish reactions, the rate measurements have to be refined (for example, Greenwood, 1963). An improvement in sensitivity of up to three orders of magnitude is possible with the rate method proposed by Fyfe (1960), which utilizes the change in weight of a reaction participant in the form of a single crystal. This method has been successfully applied to the equilibrium: diaspore ⇄ corundum + water (Fyfe and Hollander, 1964).

This paper presents the results of a rate study to determine the equilibrium conditions for the reactions:

$$\begin{array}{lllllll}
KAl_3Si_3O_{10}(OH)_2 & & \rightleftarrows & KAlSi_3O_8 & + \; Al_2O_3 & + \; H_2O & \\
\quad\text{muscovite} & & \rightleftarrows & \text{potassium feldspar} & + \;\text{corundum} & + \;\text{water} & (1) \\
KAl_3Si_3O_{10}(OH)_2 & + \; SiO_2 & \rightleftarrows & KAlSi_3O_8 & + \; Al_2SiO_5 & + \; H_2O & \\
\quad\text{muscovite} & + \;\text{quartz} & \rightleftarrows & \text{potassium feldspar} & + \;\text{andalusite} & + \;\text{water} & (2) \\
\quad\text{muscovite} & + \;\text{quartz} & \rightleftarrows & \text{potassium feldspar} & + \;\text{sillimanite} & + \;\text{water} & (3) \\
\quad\text{muscovite} & + \;\text{quartz} & \rightleftarrows & \text{potassium feldspar} & + \;\text{kyanite} & + \;\text{water} & (4)
\end{array}$$

Although Yoder and Eugster (1955) and Crowley and Roy (1964) have demonstrated the reversibility of reaction (1), their proposed univariant curves were based not on reaction reversals but on the interpretation of runs made on starting mixtures of relatively high free energy. A critical evaluation of their results shows that there is still a gross uncertainty in the stability field of muscovite. Hitherto, reactions (2) to (4) have not received a successful experimental treatment, although experiments on the reaction leading to mullite

+ potassium feldspar + water have been conducted by Yoder and Eugster (1955) and Segnit and Kennedy (1961). These workers indicated that the influence of quartz on the field of stability of muscovite is to reduce it by about 15°C. On the other hand, Miyashiro (1960) has argued that this figure should be in excess of 100°C, and Weill (in press) suggests a reduction of about 75°C at 2 kilobars on the basis of work in the system Al_2O_3–SiO_2–Na_3AlF_6. The reaction of muscovite with quartz is used to define metamorphic facies and to draw isograds. This work is an attempt to fill in some much needed lines on our petrogenetic grid.

THE RATE METHOD, ADVANTAGES AND LIMITATIONS

The rate method used herein determines the rate of a reaction as a function of temperature at fixed pressure. Equilibrium exists at that temperature where the rate extrapolates to zero. The change in weight of a participant in the reaction in the form of a single crystal is used as the measure of rate. Since significant weight changes can be detected down to 0.02 of a milligram, the rate method has a sensitivity of the order 10^{-3} of complete reaction or even greater if powdered charges of more than 20 or 30 milligrams are employed. The superiority of the method over the conventional optical and X-ray examination of charges is obvious.

The rate method is equally suited to stable and metastable equilibria, since both are states of rest. Many equilibria in the subsolidus region are not readily amenable to study because they include phases which are exceedingly difficult to grow (for example, sillimanite, andalusite, et cetera). The rate method is able to circumvent this difficulty by deriving equilibrium information from the solution of such phases rather than their growth.

A requirement of the method is that the solution of the single crystal in the fluid of the charge makes a negligibly small contribution to its total change in weight. This is certainly true in the cases of corundum (Morey, 1957) and the aluminosilicates but is not necessarily so for quartz or feldspar. However, the charge includes finely powdered material containing the same ionic species as the crystal, and this can be expected to reduce the solubility of the crystal to effectively zero (Fyfe and McKay, 1962). Furthermore, there is no known substance whose solubility in water, above the critical region, decreases with increasing temperature; this is the pattern typical of the present series of experiments. The incongruent solution of Al_2SiO_5 to corundum and SiO_2 in water will certainly not *decrease* with increasing temperature.

A further requirement is that the recorded weight changes be a consequence only of the reaction under consideration. Direct proof is usually not possible; so little reaction takes place that detectable changes in the powder arising therefrom cannot be expected. The phase growing on the single crystal can sometimes be identified: for example, a coating of blue corundum on a colorless corundum crystal occurs above the equilibrium temperature of reaction (1). An alternative proof is to substitute one of the other reactants as the single crystal phase and arrive at the same equilibrium temperature. This was successfully done for adularia and corundum in equilibrium (1). The possibility of growth of phases outside those in the reaction can be eliminated in the majority of cases. In the first place, the seeding serves to bias against any such eventuality. Consider reaction (1), where a single crystal of corundum was used. There is no known phase of Al_2O_3 composition more stable than corundum under the PT conditions of the experiments. No aluminum hydrate is stable. nor is pyrophyllite. The only possibility that accounts for the loss of corundum is that it reacts with the feldspar and water. If in fact the product is any phase or assemblage of phases other than 2M muscovite (for example, 1M muscovite), then the equilibrium temperature for this reaction will be lower at any given pressure than the equilibrium temperature for reaction (1) (where the muscovite is 2M), and the zero extrapolations of the prograde and retrograde rate plots will be separated in temperature. This was found to be the case only when the feldspar and muscovite compositions differed appreciably.

Single crystals of Al_2SiO_5 were used to examine reactions (2), (3), and (4). The loss in weight of one of the Al_2SiO_5 crystals (for example, sillimanite) could conceivably be explained as due to conversion to a more stable Al_2SiO_5 (for example, andalusite). However, the more stable Al_2SiO_5 (andalusite) itself behaves in much the same way as the other polymorphs, and so, short of assuming the existence of some unknown Al_2SiO_5 polymorph more stable than the well-known three, this explanation can be rejected. The PT conditions are high enough to exclude the growth of pyrophyllite. The only reasonable explanation for the loss of Al_2SiO_5 is that it is due to reaction with the feldspar and water. With no nucleation barriers. and indeed an immense surface area of 2M muscovite and quartz available, it is inconceivable that any less stable equivalents of this assemblage could form under the PT conditions of the experiments. Provided that gels and other highly reactive starting mixtures are avoided, there is generally no difficulty in producing 2M muscovite and quartz hydrothermally.

Of the three rate controlling steps, solution, nucleation, and growth, the barrier of nucleation is eliminated. It may be asked why, when one of the reactants is a single crystal, any reaction at all takes place when the rates for that system are known to be very slow, even with powders of less than 10 microns (for example, reaction (1), compare Yoder and Eugster, 1955, p. 241). The sensitivity of the method is part of the explanation. However, in general the real reason would seem to be that neither the solution nor the growth of the phase for which the single crystal has been substituted is the rate controlling factor. In the case of reaction (1), it will be seen that the substitution of the single crystal of corundum instead of its powder has not served to reduce the reaction rate below the limit of detectability even in a 3-day run within 20°C of the equilibrium temperature. The solution of feldspar is unlikely to be the rate controlling step (in view of the solution rates found by Morey and Hesselgesser, 1951), which leaves the growth of muscovite as the only possible control. The slow growth rates of andalusite and sillimanite are evident in runs above the equilibrium temperatures of reactions (2) and (3). The control below the equilibrium temperature is presumably, again, the rate of growth of muscovite. Thus, the success of the rate method is best assured if the single crystal phase is not the reactant that is rate-controlling. For practical reasons, this recommendation was not entirely followed in the present work.

As with all experimental studies, certain final tests of reliability are possible: (1) boundary slopes check satisfactorily with available thermodynamic data, (2) the results are not inconsistent with reliable experimental results on overlapping systems, and (3) the results are not at variance with what can reasonably be deduced geologically. The success of the present work is measured in these terms throughout the later discussion.

EXPERIMENTAL DETAILS

The single crystals used for weighing were pure synthetic corundum in rod form, pale blue kyanite and gem quality andalusite from Minas Gerais, Brazil, sillimanite from Oconee, South Carolina, and synthetic mullite of composition $2Al_2O_3 \cdot SiO_2$ made by the A. C. Sparkplug Company. Powders were made from a $2M_1$ muscovite, monoclinic adularia, microcline (analyses in table 1), and colorless vein quartz. Natural materials have been preferred in this study, to facilitate control of grain size, degree of crystallinity, and freedom from contaminants.

Table 1

Chemical composition of muscovite, microcline, and adularia

	1	2	3
SiO_2	44.69		
TiO_2	0.87		
Al_2O_3	31.50		
Fe_2O_3	4.50		
FeO	1.08		
MgO	0.99		
CaO	0.02		
BaO	0.32		
MnO	0.03		
Na_2O	0.71	2.38	0.3
K_2O	10.45	13.9	15.8
P_2O_5	0.04		
H_2O+	4.40		
H_2O-	0.47		
F	0.10		
Sum	100.17		
O=F	0.04		
Total	100.13		

1. $2M_1$ muscovite, pegmatite, New York. Univ. Calif. Berkeley colln. #15463 (Ms_{91} Pa_9).
2. Pink microcline perthite, pegmatite, Ontario, Univ. Calif. Berkeley colln. #16846 ($Or_{80}Ab_{20}$).
3. Colorless adularia, Switzerland ($Or_{97}Ab_3$).

Fixed weights (commonly 30 mg) of a homogenized powdered mixture of muscovite, feldspar, and, when appropriate, quartz were sealed with the accurately weighed single crystal and 0.05 of a milliliter of distilled water in one-eighth inch diameter silver tubes for fixed run-times (70, 71, or 168 hours)

TABLE 2

Summary of experimental runs

Reaction	Crystal	Pressure	Powdered materials all plus 0.05 ml water	Average weight of crystal	Total weight of powder	Time	Text-fig.	Number of runs
1	corundum	2 kb	microcline, muscovite	125 mg	20 mg	70 hours	1	14
	corundum	2 kb	adularia, muscovite	”	”	”	2	8
								5
	corundum	3 kb	adularia, muscovite	”	”	”	3	5
	adularia	2 kb	muscovite, corundum	45 mg	30 mg	”	4	5
2	andalusite	1050 bars	muscovite, adularia, quartz	39 mg	30 mg	168 hours	6	7
3	sillimanite			54 mg	”	”	”	”
2	andalusite	2 kb	” ” ”	50 mg	”	70 hours	7	19
3	sillimanite		” ” ”	55 mg	”	”	”	10
4	kyanite		” ” ”	150 mg	”	”	”	13
	mullite		” ” ”	5 mg	”	”	”	6
2	andalusite	3 kb	” ” ”	35 mg	”	”	8	10
3	sillimanite		” ” ”	19 mg	”	”	”	”
2	andalusite	4 kb	” ” ”	30 mg	”	71 hours	9	4(+4)
3	sillimanite		” ” ”	17 mg	”	”	”	4(+5)

in cold-seal hydrothermal pressure vessels. For the muscovite system (1), the desired run conditions were approached by following the estimated equilibrium curve as closely as possible. For the muscovite-quartz systems, it was soon established that the rates of growth of the Al_2SiO_5 polymorph and K-feldspar were very much slower than the rates for the reverse direction. Accordingly, run temperatures and pressures were approached from the high temperature side of the estimated reaction curve. With stainless-steel bombs a water quench terminated the run; with inconel alloy bombs a compressed air quench was used while pressure was controlled as at the start of the run.

Fresh mineral powders were used for every run, but the same Al_2SiO_5 crystal was used for the entire series of runs at any given pressure. Blue corundum deposited on the synthetic colorless corundum, as a result of "impurities" in the natural muscovite, was removed with molten potassium pyrosulphate before proceeding with subsequent runs. Temperatures, measured with chromel-alumel thermocouples, possibly err 5°C on the high side due to thermal gradients. Pressures were indicated with a Bourdon gauge and are believed to be accurate to within 50 bars of the stated value. At the end of every run the silver capsule was checked for possible leakage by ballooning under gentle heat. Crystals were cleaned of adhering particles by boiling in water or, better, immersing in water in an ultrasonic cleaning bath. Weighing was carried out on a Mettler M5 microbalance in a temperature and humidity controlled room with an estimated day-to-day reproducibility of ± 0.01 of a milligram. Experience showed that the error caused by an insufficiently cleaned crystal might amount to no more than about 0.02 of a milligram; in most cases it was probably much less than this. Breakage of the aluminosilicate crystals along cleavages proved to be surprisingly rare.

REACTION (1): MUSCOVITE ⇄ K-FELDSPAR + CORUNDUM + WATER

Table 2 summarizes the series of experimental runs made for the entire study. Run temperatures and weight changes may be read off the appropriate diagram. All other variables were held constant for each series of runs. Reaction (1) was examined at water pressures of two (figs. 1, 2, and 4) and three kilobars (fig. 3). The first test of the suitability of the rate method to this equilibrium was made using a microcline with a bulk composition of $Or_{80}Ab_{20}$ (table 1). The same adularia ($Or_{97}Ab_3$) was used throughout all subsequent work.

K-feldspar in the form of microcline.—In view of the presence of albite as a phase in the perthitic microcline, no attempt will be made to interpret the results (fig. 1) too closely, save to note that the corundum weight changes indicate a muscovite-forming reaction below 625°C and the reverse above 645°C. The newly formed corundum is impure and forms a blue coating on the initially colorless corundum rod.

K-feldspar in the form of adularia.—The substitution of adularia ($Or_{97}Ab_3$) for microcline results in a higher equilibrium temperature at 2 kilobars water pressure (fig. 2). This temperature is interpreted as that at which the forward and reverse reaction rates are equal, or, alternatively, as the decomposition temperature for a muscovite intermediate in composition be-

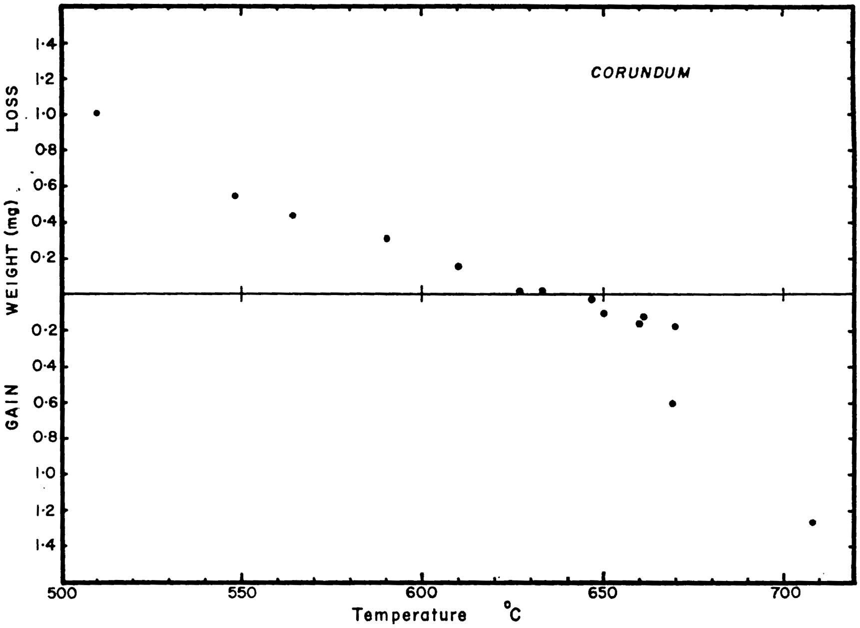

Fig. 1. Weight changes undergone by a corundum crystal in the presence of powder of microcline (200-325 mesh) and muscovite (<200 mesh), and water. Water pressure 2 kilobars, time 70 hours. These runs are those described by Evans and Fyfe (1962).

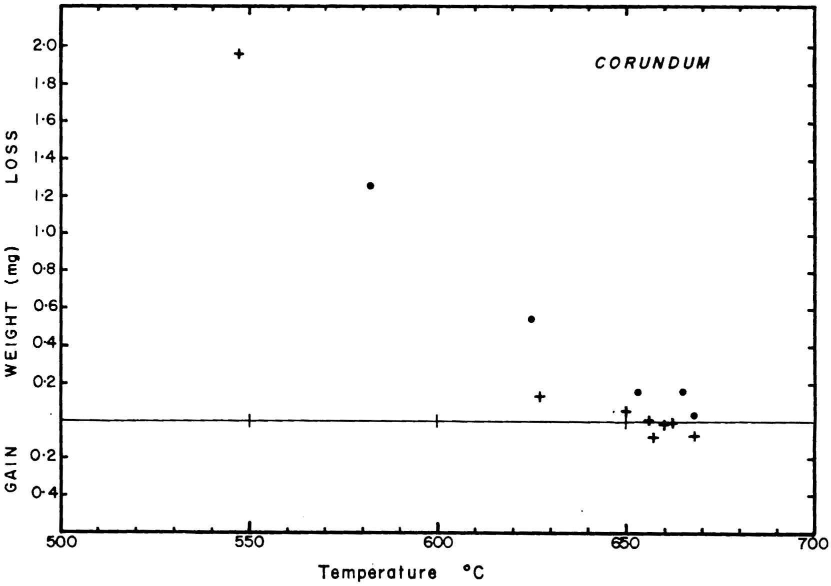

Fig. 2. Weight changes undergone by a corundum crystal in the presence of powder of adularia (crosses 200-300 mesh, dots <325 mesh) and muscovite (<200 mesh), and water. Water pressure 2 kilobars, time 70 hours.

tween natural muscovite ($Ms_{91}Pa_9$) and nearly pure muscovite(the composition in equilibrium with $Or_{97}Ab_3$, corundum, and water). The two series of runs plotted in figure 2 used the same materials except for adularia sized 200-325 mesh in one case and less than 325 mesh in the other. The increased surface energy of the feldspar due to the inclusion of ultra-fine grains would appear to enhance muscovite's stability by roughly 10°C (MacDonald, 1955, p. 248-250; Fyfe, Turner, and Verhoogen, 1958, p. 69-72). While the lower equilibrium temperature of 660°C was obtained with grain sizes similar to those used in the microcline runs, the higher intersection temperature of 670°C resulted from the use of ultra-fine material on both sides of the reaction and is thought to give a better estimate of the true equilibrium relations. It seems safe to extrapolate the small distance to pure muscovite and suggest a temperature of 680°C for its upper limit of stability at 2 kilobars water pressure.

At 3 kilobars, muscovite of composition between Ms_{91} and $Ms_{>97}$ decomposes at about 700°C (fig. 3), and accordingly a figure of 710°C may be regarded as appropriate for pure muscovite at this pressure. An increase in equilibrium temperature of 30°C therefore takes place between two and three kilobars.

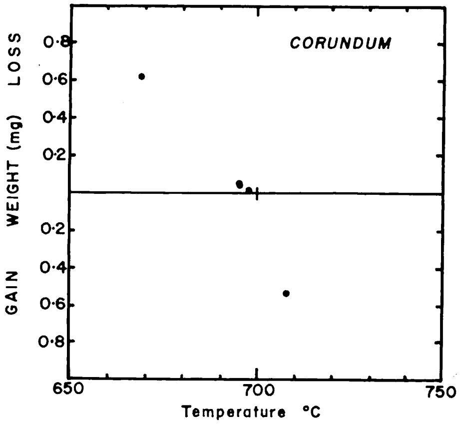

Fig. 3. Weight changes undergone by a corundum crystal in the presence of powder of adularia (<325 mesh) and muscovite (<200 mesh), and water. Water pressure 3 kilobars, time 70 hours, 5 runs. There are two points at 695°C practically superimposed.

Adularia single crystal, muscovite + corundum powder.—A short series of 5 runs (fig. 4) was made as a qualitative check on those reported above. Figure 4 should be compared with figure 2. The actual values of the weight changes cannot be meaningfully compared, except on a gross basis. A possible 0.15 of a milligram of adularia (Morey and Hesselgesser, 1951) could have dissolved in the 0.05 of a milliliter of water, but anything approaching this amount is unlikely, for reasons already stated (p. 648). The agreement in equilibrium temperature (bearing in mind grain-size influences), while not perfect, is sufficiently close to indicate that the interpretation given of the earlier runs in this system was sound.

Other natural muscovites.—Four other analyzed natural muscovites, from high-grade pelitic schists, were found to break down to corundum and feldspar between 630°C and 650°C at 2 kilobars, although the precision necessary to show how this varied with composition was lost owing to the use of powders carefully sieved to avoid any grain-size bias. Anorthoclase (K_2O = 2.61 percent) served as a feldspar nucleus.

Equilibrium curve for Reaction (1).—The gradient of the proposed equilibrium curve (fig. 5) between two and three kilobars (2½ kb and 695°C)

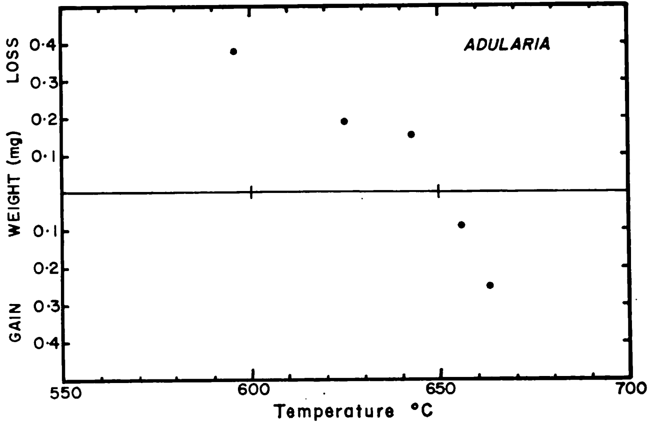

Fig. 4. Weight changes undergone by an adularia crystal in the presence of powder of corundum (200-325 mesh) and muscovite (100-325 mesh), and water. Water pressure 2 kilobars, time 70 hours.

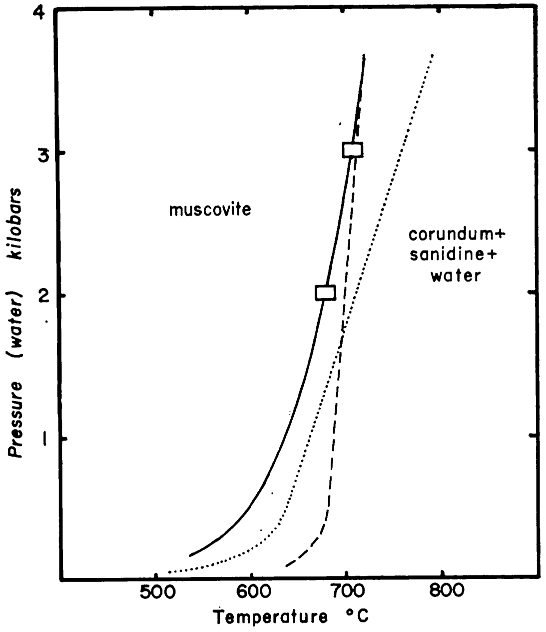

Fig. 5. Equilibrium phase diagram for the decomposition reaction of K-muscovite. Solid curve from this study, the extrapolation to 1000 bars (636°C) and 500 bars (598°C) having been made by graphical integration of entropy and volume terms. Dashed curve from Crowley and Roy (1964); dotted curve from Yoder and Eugster (1955).

suggests a reaction entropy of 19 (± about 5) cal/mole deg. using PVT data from Kennedy (1950). The entropy data, which is now available for all phases in this reaction (Weller and King, 1963; Pankratz, 1964; Kelley, 1960; Kelley and King, 1961; Pistorius and Sharp, 1960), gives ΔS_r under the same conditions equal to 18 cal/mole deg. It is inconceivable that such agreement could be obtained fortuitously from some process in the charge other than that under study.

There are no very large disagreements between the curve proposed here and those previously published (fig. 5). Nevertheless, the new curve is recommended since both earlier curves (Yoder and Eugster, 1955; Crowley and Roy, 1964) represent what are basically synthesis fields for muscovite (Fyfe, 1960, p. 553-556), and neither exhibits the sort of curvature in the range 1/3 to 2 kilobars that is demanded by the changes in volume and entropy of the mole of water in the reaction (see, for example, typical hydration equilibrium curves in Fyfe, Turner, and Verhoogen, 1958, fig. 34; or MacDonald, 1955, fig. 1). The gradient of Crowley and Roy's curve (15°C from 1 to 2 kb) cannot be correct because either the computed ΔV_r or ΔS_r would have to be wrong by a factor of three. Crowley and Roy's curve approaches the present one at 3 kilobars and above simply because reaction rates, and hence the accuracy of synthesis methods of equilibrium determination, are enhanced by higher water pressures.

REACTIONS (2), (3), AND (4): MUSCOVITE + QUARTZ ⇄ K-FELDSPAR + ALUMINUM SILICATE + WATER

Reactions (2) and (3), with andalusite and sillimanite respectively, were studied at 1050, 2000, 3000, and 4000 bars water pressure (figs. 6, 7, 8, and 9). Reaction (4), leading to kyanite formation, was examined at 2 kilobars, together with some runs on a similar reaction forming mullite of composition $2Al_2O_3 \cdot SiO_2$ (fig. 7).

The pattern of weight changes shown by the aluminosilicate crystals, enclosed with muscovite, adularia, quartz, and water, consists of a nearly linear

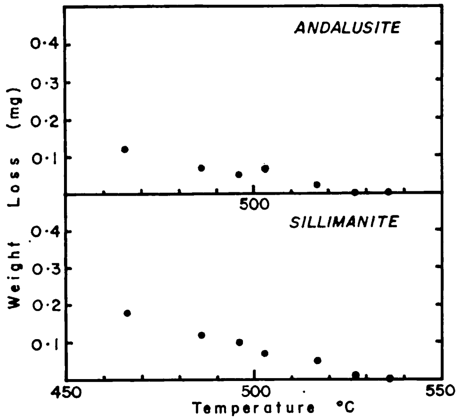

Fig. 6. Weight changes undergone by andalusite and sillimanite crystals in the presence of powder of muscovite (<200 mesh), quartz (<325 mesh), and adularia (<325 mesh), and water. Water pressure 1050 bars, time 1 week.

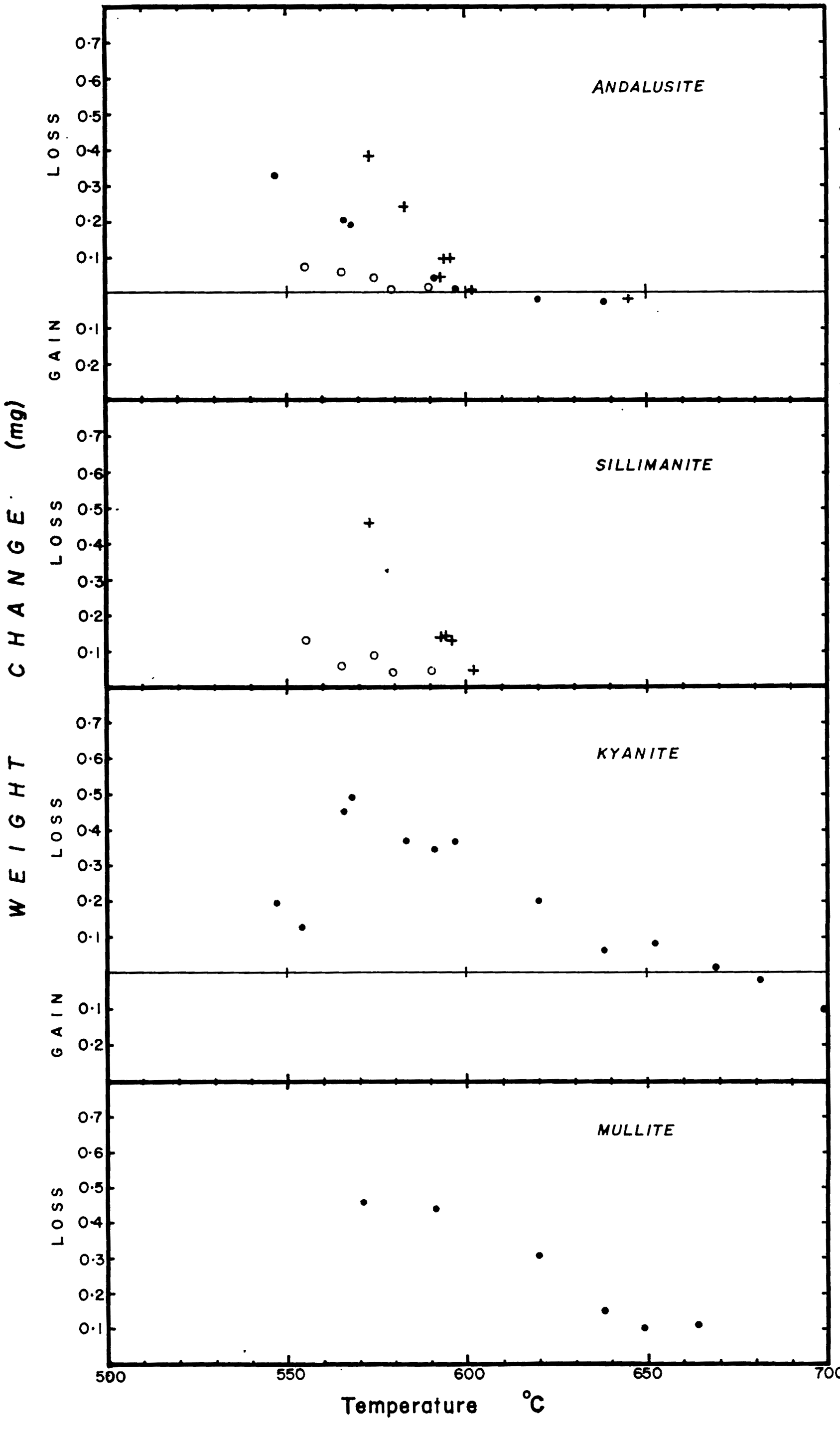

Fig. 7. Weight changes undergone by andalusite, sillimanite, kyanite, and mullite crystals in the presence of powder of muscovite (dots and crosses <140 mesh, circles 100-325 mesh), quartz (dots and circles 200-325 mesh, crosses <325 mesh), and adularia (dots and circles 200-325 mesh, crosses <325 mesh). Water pressure 2 kilobars, time 70 hours.

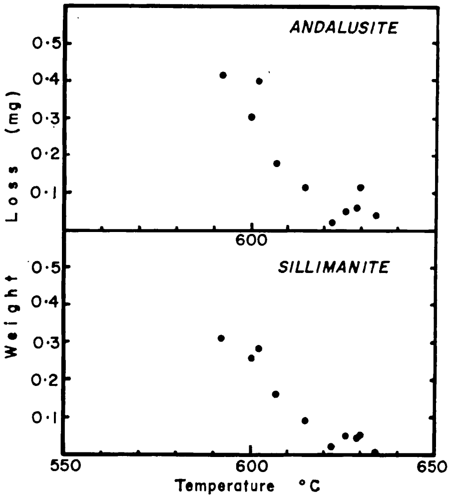

Fig. 8. Weight changes undergone by andalusite and sillimanite crystals in the presence of powder of muscovite (<200 mesh), quartz (<325 mesh), and adularia (<325 mesh). Water pressure 3 kilobars, time 70 hours.

decrease in weight loss with increasing temperature until the zero weight-loss axis is reached, followed by negligible or significant weight grains depending upon the polymorph in question. The intersection of the weight-loss curve with the temperature axis is regarded as giving the equilibrium temperature for the reaction. It is clearly not an asymptotic relationship. Above the equilibrium temperature the andalusite- and sillimanite-forming reactions either do not proceed at all or are so slow that the weight grains lie within the limits of experimental error. There is no nucleation and growth of sillimanite or andalusite within the powder of the charge. The weight gain exhibited by the kyanite crystal above 675°C at 2 kilobars (fig. 7) was not confirmed as due necessarily to the growth of kyanite, although it is very likely that it was.

The equilibrium points shown by figures 6 to 9 have been assembled in table 3, and the same data have been used in the construction of the phase diagram (fig. 10). Aside from errors in temperature and pressure measurement and control, the uncertainty attending these equilibrium points may be judged from figures 6 to 9 as lying between ±5°C and ±10°C except where stated otherwise in table 3. The determined equilibria are those below which muscovite and quartz will form from adularia, aluminum silicate, and water. The possibility of Na-K exchange between the muscovite and the feldspar during the experiments is clearly a factor having a possible influence over the solid solution compositions to which the equilibrium points refer. Generally, the $20\bar{1}$ reflection of the feldspar increased up to 0.02° 2θ (quartz internal standard), indicating gains of up to 2 percent albite in solid solution, while the 0 0 10 reflection of the muscovite decreased up to 0.04° 2θ (fluorite internal standard), indicating losses of up to 2 percent paragonite. These changes are small

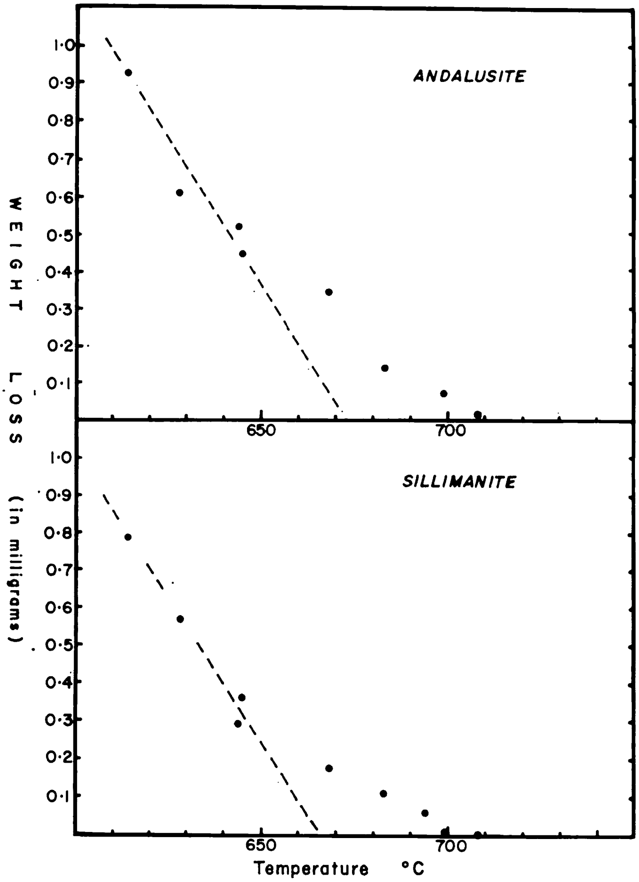

Fig. 9. Weight changes undergone by andalusite and sillimanite crystals in the presence of powder of muscovite (<200 mesh), quartz (<325 mesh), and adularia (<325 mesh). Water pressure 4 kilobars, time 71 hours.

fractions of the total ion exchange necessary for complete equilibration of the mica and feldspar. During a run at a temperature where, for example, $Or_{96}Ab_4$ should be in equilibrium with sillimanite, quartz, muscovite, and water, K-Na ion exchange would stop the reaction when the original Ab_3 alkali feldspar had been converted to Ab_4. Nevertheless, in the present experiments, a mica-forming reaction will take place, as evidenced by the loss in weight of the Al_2SiO_5 single crystal, up to that temperature at which $Or_{97}Ab_3$ is in equilibrium with the other phases in the reaction. Since the rate for the prograde reaction is effectively zero, the Al_2SiO_5 weight loss can be interpreted unambiguously. The equilibrium points obtained refer then to the reaction of quartz with practically pure muscovite (Ms 97 percent). X-ray diffractograms of the product powders also confirm the absence of such phases as corundum, mullite, et cetera.

TABLE 3

Equilibrium temperatures and pressures for the breakdown reactions of muscovite obtained from the rate plots, figures 2-3 and 6-9

Water pressure	Temperature °C			
	System: muscovite + quartz			System: muscovite
	(2)	(3)	(4)	
1050	525 + 20 - 10	530 + 20 - 10		
2000	600	605	675	680
3000	640 ± 15	635		710
4000	675 ± 15	665		
	Reaction leading to mullite formation at 2000bars: 680 ± 20			

Reactions (2), (3), and (4) leading to andalusite, sillimanite, and kyanite, respectively.

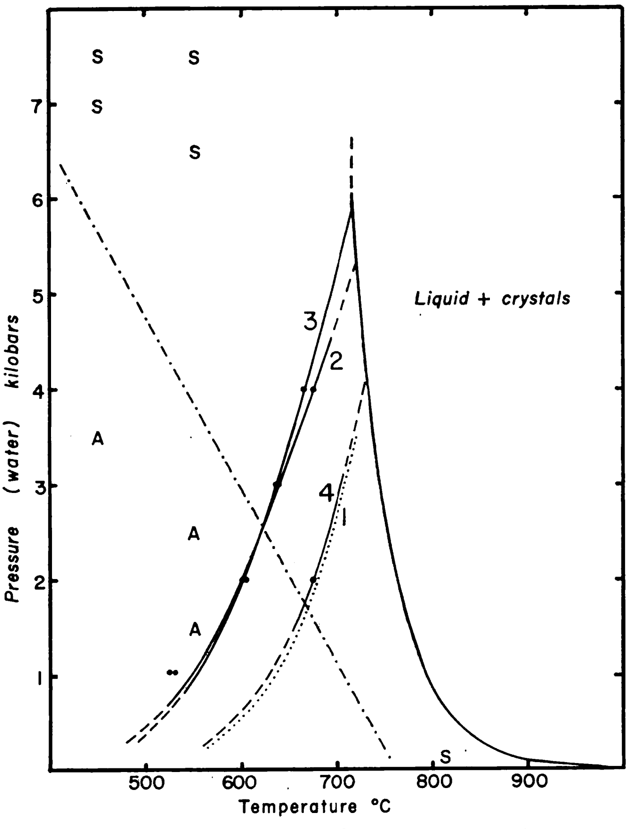

Fig. 10. Equilibrium phase diagram for the system: muscovite + quartz. Numbers correspond to the reactions as listed on page 647. Reaction (4) is entirely metastable; reaction (2) is stable below 2½ kilobars, while reaction (3) is stable above 2½ kilobars. The field of liquid is from Shaw (1963). A and S indicate the field of stability of andalusite and sillimanite in the system Al_2SiO_5, after Bell (1963) and Weill (ms), and the dot-dash line represents an estimate of the boundary conditions for these minerals. The calculated curves for reactions (2) and (3) are preferred in the low pressure region.

In order to induce the highest possible rates, all runs carried out at 1050, 3000, and 4000 bars utilized fine-grained powders less than 200 mesh and in some cases 325 mesh (table 2). At 2 kilobars some additional runs were made with fully sieved powders (muscovite 100-325, quartz and adularia 200-325 mesh) in order to check the equilibrium temperatures uninfluenced by grain-size effects. A comparison of the results (fig. 7, andalusite and sillimanite plots) shows that any grain-size bias of the equilibrium conditions in the experiments at other pressures is likely to have been very small (under 10°C say). It is also seen that the rates were enhanced an order of magnitude by this procedure.

The interpretation of the 4 kilobar experiments (fig. 9) is based only on those runs below 660°C, since the charge contains an assemblage of minerals that can be expected to begin melting at this temperature (Luth, Jahns, and Tuttle, 1964). The pattern of weight changes above this temperature is not understood. Certainly the measurements cannot offer any information on the hydration reaction that is of interest here. Above 710°C considerable melt forms, and this adheres in large quantities to the aluminosilicate crystals.

Excellent self-consistency is immediately apparent from the equilibrium points plotted in figure 10. The results are further tested by some simple thermodynamic considerations and by comparing the implications of the results with independent data on the system Al_2SiO_5 in the following paragraphs.

The gradients of the univariants for reactions (2) and (3) are slightly gentler than for the quartz-free system: from figure 10, roughly 40°C and 35°C respectively for the pressure change 2 to 3 kilobars, compared to approximately 30°C for the breakdown of muscovite alone. Differences of almost exactly these amounts (actually 80 percent and 90 percent of the slope [dP/dT] of equilibrium [1]) are to be expected on the basis of the ΔV and ΔS of the coupling reaction: quartz + corundum $\rightleftarrows$ Al_2SiO_5, calculated from data in Skinner, Clark, and Appleman (1961), Kelley (1960), Kelley and King (1961), and Pankratz and Kelley (1964). A reaction entropy of 15 ± 2 cal/mole deg is obtained when the Clausius-Clapeyron relation is applied to the gradient of the curve for the andalusite reaction at $2\frac{1}{2}$ kilobars and 625°C, whereas the entropy data (Kelley, 1960; Kelley and King, 1961; Pankratz, 1964; Pankratz and Kelley, 1964; Weller and King, 1963; Pistorius and Sharp, 1960) suggest a figure of 16.7. Similarly, ΔS for the sillimanite-forming reaction at the same pressure and temperature from the gradient in figure 10 is 18 ± 3 cal/mole deg, whereas the computed figure is 17.0. The curve for the kyanite-forming reaction has been drawn parallel to the curve for muscovite alone in figure 10 because the effects on dP/dT of the reduction in entropy and volume caused by coupling the reaction: quartz + corundum $\rightleftarrows$ kyanite almost exactly cancel.

It is possible to derive estimates of the relative free energies of the aluminosilicates from a comparison of the univariant curves for reaction (1) with reactions (2), (3), and (4). The change in free energy of reactions (2), (3), and (4) at any P and T is equal to that of (1) plus that of the coupling reaction:

$$SiO_2 + Al_2O_3 \rightleftarrows Al_2SiO_5 \qquad (5)$$

At 2 kilobars and 680°C, reaction (1) has $\Delta G = 0$ (table 3), and hence ΔG_5

may be equated in turn to ΔG_2, ΔG_3, and ΔG_4, which can be estimated for these conditions using the univariant curves and the relation $\frac{\delta(\Delta G)_P}{\delta T} = -\Delta S$. Reaction entropies of 17.0, 17.4, and 15.1 cal/mole deg can be assumed at 2 kilobars for reactions (2), (3), and (4) respectively (entropy references given on p. 661). The following estimates for ΔG_5 thus apply to 680°C and 2 kilobars: –1360 calories in the case of andalusite, –1300 calories for sillimanite, and –150 calories for kyanite (at least the last two figures in each of these computations are uncertain). The reaction: $SiO_2 + 2Al_2O_3 \rightleftarrows 2Al_2O_3 \cdot SiO_2$ (mullite) would appear to be very close to equilibrium. From these figures $\Delta G_{\text{sillimanite} \rightarrow \text{kyanite}}$ is about 1150 calories at 680°C and 2 kilobars. Using the relation $\frac{\delta(\Delta G)_T}{\delta P} = \Delta V$, substituting –5.45 cm^3 for ΔV (Skinner, Clark, and Appleman, 1961) and ignoring compressibility, the pressure increase necessary to reduce this free energy change to zero is about 9 kilobars. This indicates kyanite-sillimanite equilibrium at 11 kilobars and 680°C, which, considering the approximations and assumptions, agrees very satisfactorily with an extrapolation of Clark's (1961) curve and a fix at 11 kilobars and 550°C reported by Bell (1963).

The intersection of reaction curves (2) and (3) between 640°C and 3 kilobars[1] gives rise to an invariant point in the system muscovite + quartz, where sillimanite, andalusite, K-feldspar, quartz, muscovite, and water are stable. The sillimanite-andalusite boundary so determined agrees very satisfactorily with that of Bell (1963) but is just a little too high in temperature in comparison with the boundary proposed by Weill (in press).

The present results on the stability of mullite + quartz relative to the aluminosilicates (giving relative free energies similar to those obtained for reaction [5]) are in complete agreement with Weill (in press). Nor is any inconsistency necessarily involved in Aramaki and Roy's (1963) conversion of mullite to corundum + quartz in the 600°C–4 kilobar region. Mullite possesses greater molar volume and almost certainly greater entropy than the oxide pair and will accordingly tend to be stabilized with increase in temperature or decrease in pressure or both, so that it is quite possible for the reaction: mullite $\rightleftarrows$ corundum + quartz to be in equilibrium at 680°C and 2 kilobars.

The reliability of the rate-method results, having been tested in numerous ways, may be regarded as adequate for a number of conclusions to be advanced. The addition of quartz effects a reduction of about 80°C to the stability field of muscovite at 2 kilobars. There are metastable fields relative to kyanite or mullite, together with K-feldspar and water, that are coincident or

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[1] For reasons unknown, the scatter of points in figure 8 (3 kb runs) is worse than at other pressures, and interpretation in terms of the 3 kilobar equilibrium temperatures is difficult. It is clearly critical for the relative stability of andalusite and sillimanite. Some assistance in interpretation may, however, be had by noting that in eight of the runs at 3 kilobars the sillimanite crystal lost less weight than the anadalusite, and in only one run were the losses reversed. At 2 kilobars, on the other hand, the sillimanite crystal lost more weight than the andalusite in all eleven runs where the comparison is possible.

less than 10°C lower than that for muscovite alone. Reaction (2) provides the stable limit for muscovite + quartz at 1050 and 2000 bars, while reaction (3) assumes this role at 3 and 4 kilobars.

ΔG for reaction (5) was shown to be negative at 2 kilobars and 680°C for all three Al_2SiO_5 polymorphs. Since ΔV_5 is positive for sillimanite and andalusite and negative for kyanite (1.1, 3.4, and –4.3 cm^3 respectively), neither increase nor decrease in pressure alone will enable a true field of stability for corundum + quartz to appear on the phase diagram for the Al_2SiO_5 system. Nor will a lowering of temperature enhance the stability of the oxide pair, since all three aluminosilicates, kyanite in particular, have lower entropy at 680°C. In the other direction we find that ΔS for reaction (5) in the case of sillimanite (–0.53 cal/mole deg at 1000°K and –0.32 at 1300°K) is insufficient by a factor of 4 or 5 to change the sign of ΔG before the true field of mullite is reached. Probably, in any case, only a small rise in temperature above 680°C is needed for mullite itself to be more stable than corundum + quartz. Thus, if the muscovite results are accepted, there is no possible field of stability for corundum + quartz on the phase diagram of the Al_2SiO_5 system (compare Aramaki and Roy, 1963). Weill (ms) arrived at a similar conclusion. Although the structurally extensive variety of starting materials used by Aramaki and Roy is stressed by them, it is unfortunate that it was not sufficiently extensive to include sillimanite, andalusite, and kyanite, the only phases likely, on geological grounds, to possess lower free energy than corundum + quartz.

Segnit and Kennedy's diagram (1961, fig. 1) for the reaction: muscovite + quartz $\rightleftarrows$ sanidine + mullite + water is essentially in agreement with Yoder and Eugster's results (1955). Both studies utilized starting mixtures of kaolin, amorphous silica, and potassium silicate and indicated apparent equilibrium at about 700°C and 2 kilobars. This is only 20°C higher than the admittedly uncertain figure for this equilibrium obtained in this study (table 3). The synthesis field for muscovite + quartz is thus approximately equivalent to the metastable field for these minerals relative to mullite, sanidine, and water. This agreement, as also argued by Yoder and Eugster (p. 263), may well be a result of the ready growth of sanidine and mullite at low temperatures, which meant that some of those runs finally reported as producing muscovite and quartz actually passed through an earlier stage of sanidine ± mullite, thereby reversing the reaction. It would seem that, unless growth rates of andalusite and sillimanite are in some way considerably accelerated, any direct approach to the question of the influence of quartz on the stability field of muscovite will inevitably give a misleading answer.

Winkler (1957), Winkler and von Platen (1958), and Althaus and Winkler (1962), in conducting hydrothermal experiments on a variety of natural starting materials, give data for some reactions in which muscovite and quartz participate. Since the addition of any phase or phases, for example, biotite, chlorite, plagioclase, K-feldspar, halite, carbonate, et cetera to muscovite and quartz can, if at all, only reduce the field of stability of muscovite + quartz, the reaction temperatures obtained by these workers should represent minima for the quartz-muscovite system. At 2 kilobars water pressure they describe reactions in which muscovite, quartz, and other phases are replaced by higher temperature assemblages, ranging from below 600°C to about 670°C. There exists therefore an inconsistency of 70°C when comparison is made with the present work (compare table 3 or fig. 10). This has arisen in part at least because the aluminosilicate phase produced by the reaction in Winkler and co-workers' experiments is "sillimanite-mullite" (possibly a disordered sillimanite or mullite) and not andalusite or sillimanite which are more stable. Insufficient run-times may also be part of the explanation, because it is the author's experience with standard powder runs in the muscovite system that run-times of a month are insufficient to give a clear indication of reaction direction when the temperature is within about 30°C of the probable equilibrium temperature.

CONCLUSIONS

The univariant equilibria defining the various breakdown reactions of K-muscovite described above are shown in figure 10. Assuming that natural muscovites react fractionally over a temperature interval, the curves in figure 10 will give upper limits for natural muscovites, and decomposition of natural muscovites is likely to begin considerably below these curves. The beginning-of-melting curve for the system sanidine–quartz–water (Shaw, 1963) intersects the stable univariant muscovite + quartz $\rightleftarrows$ sillimanite + sanidine + water at about 6 kilobars and 715°C. Above these conditions, muscovite in the presence of quartz melts to liquid plus crystalline phases, such as corundum, sillimanite, or quartz, depending on the quartz content of the system (Segnit and Kennedy, 1961). Under conditions of P_{total} equal P_{H_2O}, andalusite plus K-feldspar have a limited field of stability, comprising a triangular area with a maximum pressure of 2½ kilobars. Coexisting sillimanite and K-feldspar have a wide range of possible PT conditions, the field being limited primarily by the onset of melting. In a system lacking quartz, muscovite is stable to some 80°C higher than in the presence of quartz. A stability field for corundum + quartz in the system Al_2SiO_5 is ruled out.

The alternative assemblages, muscovite + quartz and orthoclase + Al_2SiO_5, have a significance in metamorphic facies. The stable univariant for the decomposition of muscovite in the presence of quartz obtained in this work may be taken as defining the upper limits of physical conditions for the hornblende–hornfels facies (Fyfe, Turner, and Verhoogen, 1958, p. 206) and the sillimanite–almandine–muscovite subfacies of the amphibolite facies (Turner and Verhoogen, 1960, p. 548). It remains to be seen exactly what effect other phases (for example, biotite, plagioclase) have on this reaction which is one now widely recognized in high-grade regional metamorphism, particularly in the eastern United States (Heald, 1950; Chapman, 1952; Barker, 1961, 1962; Lundgren, 1962; Guidotti, 1963).

Under conditions of P_{H_2O} less than P_{total}, the field of stability of muscovite + quartz is reduced. This possibility has to be entertained seriously in cases of polymetamorphism (including retrograde metamorphism), but it is not necessarily true during the initial metamorphism of a pile of sediments when a sequence of dehydration reactions continuously supplies water to the pore spaces, which at the higher grades of metamorphism become vanishingly small. A field of stable coexistence of muscovite and high-quartz is precluded when Yoder's (1950) high-low quartz inversion curve is compared with figure 10, except possibly when P_{H_2O} is equal to P_{total} (the field boundaries converge to within the limits of experimental error, in the region 5 kilobars-700°C). It is interesting to note that Guidotti (1963, p. 782) records quartz with the prism-free dipyramidal habit occurring in small migmatitic lenses in the vicinity of the sillimanite + potash-feldspar isograd in the Bryant Pond quadrangle, Maine. Unfortunately, this morphology does not provide conclusive proof of former high-quartz, since it is not rare in low-quartz (Frondel, 1962, p. 119-120), but it is suggestive of high-quartz, and there is a temptation to make use of the implications.

Since it is in equilibrium with quartz, the occurrence of predominantly hydroxyl-containing muscovite as a primary phase in magmatic granites would appear to require a water pressure of at least 3½ to 4 kilobars (compare, Yoder and Eugster, 1955, p. 266).

It seems not unreasonable to conclude that the reaction rate method has been particularly successful in the case of the muscovite breakdown reactions. More information on the relative stabilities of the Al_2SiO_5 minerals in the particularly interesting low temperature region in the vicinity of the triple point could be obtained by applying similar rate techniques to the equilibria:

$$\text{paragonite} + \text{quartz} \rightleftarrows \text{albite} + Al_2SiO_5 + \text{water}$$

and

$$\text{pyrophyllite} \rightleftarrows 3\ \text{quartz} + Al_2SiO_5 + \text{water}.$$

Because of extremely small weight losses, the writer has had little success so far with the reaction:

$$\text{paragonite} \rightleftarrows \text{albite} + \text{corundum} + \text{water}.$$

It seems that reaction rates in this system may be of an order of magnitude slower than in the muscovite system. This may be why the author's figure for muscovite breakdown at 2 kilobars is only 35°C below Yoder and Eugster's (1955) figure, whereas he is able to form corundum and albite from paragonite at 590°C and 2 kilobars water pressure, a good deal lower therefore than Eugster and Yoder's (1954) 660°C, which was presumably also derived from synthesis runs.

It is not difficult to find other potential applications for the reaction rate method. With grain sizes carefully controlled, it could provide quantitative information on the surface energy of fine-grained crystalline material. The temperature of inversions apparently impossible to reverse experimentally, for example, microcline-orthoclase and orthoclase-sanidine, might be amenable to study through the use of appropriate simple reactions such as those examined here, where only the structural state of the feldspar is allowed to vary. Finally, there is scarcely a limit to the number of reactions of significance in metamorphism that could be profitably examined on these lines.

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