

Stability of the Assemblage Muscovite-Calcite-Quartz

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Abstract

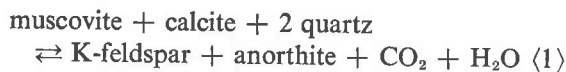
Equilibrium data have been obtained for the reaction $KAl_3Si_3O_{10}(OH)_2 + CaCO_3 + 2SiO_2 \rightleftharpoons KAlSi_3O_8 + CaAl_2Si_2O_8 + CO_2 + H_2O$. Under the conditions where fluid pressure equals total pressure and the $CO_2:H_2O$ ratio in the fluid is 1:1, the equilibrium temperatures are $606 \pm 5^\circ C$ at 7 kbar, $584 \pm 4^\circ C$ at 6 kbar, $559 \pm 9^\circ C$ at 5 kbar, $533 \pm 7^\circ C$ at 4 kbar and $475 \pm 20^\circ C$ at 2 kbar. Using 0.93 ± 0.03 cc/gm as the specific volume of CO_2 , the calculated enthalpy of reaction at $584^\circ C$ and 6 kbar is 49.6 ± 6.0 kcal/mole.

Within experimental error, the equilibrium $T-X_{CO_2}$ curve at 6 kbar fluid pressure is symmetrical about $X_{CO_2} = 0.5$ with points for $570^\circ C$ at $X_{CO_2} = 0.22 \pm 0.03$ and 0.78 ± 0.05 , and for $555^\circ C$ at $X_{CO_2} = 0.11 \pm 0.02$ and 0.88 ± 0.02 . The 6 kbar isobaric invariant point at the intersection of the muscovite-calcite-quartz reaction with the reaction $zoisite + CO_2 \rightarrow anorthite + calcite + H_2O$ is placed at $550^\circ C$ and $X_{CO_2} = 0.09 \pm 0.03$. There is no evidence for any fluid immiscibility in the CO_2-H_2O system under the conditions of this study. The symmetry of the 6 kbar $T-X_{CO_2}$ equilibrium curve suggests that the fluid mixing may be nearly ideal.

The calculated effect of the addition of an albite component to the anorthite is to move the muscovite-calcite-quartz \rightleftharpoons K-feldspar-anorthite equilibrium to lower temperatures and to move the zoisite \rightleftharpoons anorthite-calcite equilibrium to more water-rich fluid compositions. The occurrence of the stable assemblage, zoisite-plagioclase ($An < 60$)-K-feldspar, at 6 kbar fluid pressure requires that the vapor phase be more water-rich than $X_{CO_2} = 0.03$.

Introduction

Muscovite-calcite-quartz is a common metamorphic assemblage for greenschist facies rocks in alternating sequences of pelitic schists and impure calcitic or dolomitic limestones. The equivalent high temperature assemblage, K-feldspar-calcic plagioclase, can occur in calc-silicate rocks anywhere above the greenschist facies. In non-calcareous rocks and in calc-silicates the assemblage K-feldspar-sodic plagioclase can occur over an even larger range of metamorphic grade. Reaction (1), which relates the two assemblages in the sodium-free system, is:



The wide range of metamorphic grade over which this and similar reactions to zoisite-K-feldspar and grossular-K-feldspar can occur is due primarily to the broad natural variations in fluid and plagioclase compositions. At constant pressure the temperature maximum for this reaction occurs when the plagioclase is An_{100} and the fluid composition is $X_{CO_2} = X_{H_2O} = 0.5$ (Greenwood, 1967b).

Several mixed-volatile reactions involving CO_2 and H_2O have been determined previously by other workers. With the exception of some preliminary data from Bailey (1964) on the reaction, 3 dolomite + K-feldspar + $H_2O \rightleftharpoons$ phlogopite + 3 calcite + 3 CO_2 , none of the reactions determined have involved potash as a component and few have involved alumina. The applications of these data have therefore been limited, for the most part, to the metamorphism of siliceous dolomites. The determination of mixed-volatile equilibria involving K_2O and Al_2O_3 as additional components increases the variety of calcareous rocks to which experimental data can be applied. In particular, the data are useful in regions of calcareous rocks interbedded with pelites. Some of the intensive variables determined for the relatively simple calcareous rocks in these areas can then be applied to the more complex pelites.

Experimental Techniques¹

The equilibrium for reaction (1) has been reversibly determined in horizontal, 1-3/8" O.D. \times 12"

¹ See Table 1 for an explanation of symbols used in this paper.

TABLE 1. Symbols Used

T	: Temperature
P	: Pressure - fluid pressure equal to total pressure
$X_{\text{CO}_2}, X_{\text{H}_2\text{O}}$: Mole fraction CO_2 or H_2O in the vapor phase
a_i^j	: Activity of component i in phase j
f_i	: Fugacity of component i in a vapor phase at T and P
f_i^0	: Fugacity of pure component i in a vapor phase at T and P
ΔZ	: Represents the change in some function Z between two sets of P, T, X_{CO_2} conditions
H^*, S^*	: The enthalpy or entropy of reactions where all the phases are at T and P
H^*	: The enthalpy of reaction where the solid phases are at T and P and the vapor phase is the ideal gas at T and $P = 1$

long, cold-seal, hydrothermal bombs using crystalline starting materials. Sanidine, anorthite, and muscovite were synthesized from gels at 600°C and 2 kbar. Cell parameters given in Table 2 were determined using annealed CaF_2 ($a_0 = 5.4620\text{\AA}$) and NaF ($a_0 = 3.5670\text{\AA}$) as internal standards. Multiple scans were made at $1/2^\circ/\text{min.}$ and all lines were measured at peak top using $\text{CuK}\alpha_1$ radiation. Other starting materials were Brazilian optical grade quartz and Mallinckrodt reagent grade CaCO_3 (Lot KRJ).

Pressures were measured with Heise bourdon tube gauges and are presumed accurate to ± 50 bars. Water was used as the pressure medium for all experiments. Temperatures were measured with external chromel-alumel thermocouples calibrated against a standard thermocouple inside the bomb at one atmosphere. All experiments and calibrations of the external thermocouples were performed using a filler rod. The standard thermocouple was calibrated by D.T.A. methods against the melting points of dry NaCl , KCl , and CsCl . The temperature values reported are accurate to $\pm 3^\circ\text{C}$.

Fluid compositions were controlled in the capsule by including weighed amounts of $\text{Ag}_2\text{C}_2\text{O}_4$ and H_2O

TABLE 2. Unit Cell Dimensions for Synthetically Prepared Minerals

Mineral	a_0 (Å)	b_0 (Å)	c_0 (Å)
Muscovite (1M)	5.211(.006)	8.989(.004)	10.278(.006)
Sanidine	8.606(.003)	13.016(.003)	7.168(.002)
Anorthite	8.171(.003)	12.871(.003)	14.158(.005)

Mineral	α	β	γ	$V(\text{\AA})^3$
Muscovite (1M)	$101^\circ 41.2'(5.7')$			471.5(.6)
Sanidine	$116^\circ 1.1'(1.9')$			721.6(.3)
Anorthite	$93^\circ 9.1'(2.1')$	$116^\circ 52.8'(2.4')$	$91^\circ 11.5'(2.0')$	1336.0(.6)

initially separated from the sample in the opposite end of the capsule. Reaction to $\text{Ag}^\circ + \text{CO}_2 + \text{H}_2\text{O}$ was complete before the bomb reached the run temperature, and the amount of fluid generated was approximately 30 wt percent of the charge. At the completion of each run, the fluid composition was determined by puncturing the capsule and measuring the weight loss due to the escape of CO_2 , and then drying the capsule and determining the weight loss of H_2O (Johannes, 1967). Tests of the method using a reaction that consumed H_2O and produced CO_2

TABLE 3. Results of Experiments

Run No.	Duration	$T^\circ\text{C}$	X_{CO_2}	Reactants	Products
1000 Bar Experiments					
167-69	14 d	458	.43	Mu Cc Q	Mu Cc Q (An) (Ksp)
2000 Bar Experiments					
6-69	9 d	506	.46	Mu Cc Q	Mu Cc Q An Ksp
111-69	23 d	499	.49	Mu Cc Q	Mu Cc Q (An) (Ksp)
25-72	55 d	448±5	.48	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
4000 Bar Experiments					
146-69	11 d	546	.44	Mu Cc Q	Mu Cc Q An Ksp
151-69	15 d	541	.44	Mu Cc Q	Mu Cc Q An Ksp
30-72*	20 d	519	.46	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
66-72	24 d	528	.50	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
6000 Bar Experiments					
42-72	21 d	547	.47	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
67-72	23 d	537	.49	An Ksp (Mu)	An Ksp Mu Cc Q
95-72	20 d	569	.51	Mu Cc Q	Mu Cc Q (An) (Ksp)
8000 Bar Experiments					
26-72	10 d	552	.48	An Ksp (Mu)	Mu Cc Q An Ksp
31-72	10 d	576	.48	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
36-72	30 d	602	.50	Mu Cc Q	An Ksp (Mu) (Cc) (Q)
47-72	21 d	550	.92	Mu Cc Q	Mu Cc Q (An) (Ksp)
48-72	21 d	550	.72	An Ksp (Mu)	An Ksp Mu Cc Q
51-72	27 d	561	.24	An Ksp (Mu)	An Ksp Mu Cc Q
52-72	27 d	561	.72	An Ksp (Mu)	An Ksp Mu Cc Q
55-72	27 d	580	.49	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
57-72	13 d	566	.12	Mu Cc Q	Mu Cc Q An Ksp
61-72	22 d	573	.42	An Ksp (Mu)	An Ksp Mu Cc Q
62-72	22 d	571	.58	An Ksp (Mu)	An Ksp Mu Cc Q
64-72	22 d	549	.82	An Ksp (Mu)	An Ksp Mu Cc Q
71-72	20 d	550	.13	An Ksp (Mu)	Mu Cc Q An Ksp
74-72	19 d	540	.09	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
79-72	15 d	587	.49	Mu Cc Q	Mu Cc Q (An) (Ksp)
87-72	21 d	560	.07	Mu Cc Q	Zo Ksp Mu Q
91-72	19 d	575	.22	Mu Cc Q	Mu Cc Q (An) (Ksp)
92-72	19 d	575	.79	Mu Cc Q	Mu Cc Q (An) (Ksp)
93-72	19 d	588	.35	Mu Cc Q	Mu Cc Q (An) (Ksp)
96-72	17 d	593	.52	Mu Cc Q	Mu Cc Q (An) (Ksp)
103-72	11 d	539	.065	Mu Cc Q	Mu Cc Q Zo Ksp
105-72	72 d	572	.32	An Ksp (Mu)	An Ksp (Mu) (Cc)
106-72	72 d	574	.72	An Ksp (Mu)	An Ksp (Mu) (Cc)
109-72	75 d	561	.16	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
111-72	75 d	561	.80	An Ksp (Mu)	An Ksp (Mu) (Cc)
112-72	66 d	581	.35	Mu Cc Q	Mu Cc Q An Ksp
113-72	66 d	581	.72	Mu Cc Q	Mu Cc Q (An) (Ksp)
7000 Bar Experiments					
33-72	17 d	628	.51	Mu Cc Q	An Ksp Mu Cc Q
38-72	17 d	604	.49	An Ksp (Mu)	An Ksp (Mu) (Cc) (Q)
39-72	17 d	616	.51	Mu Cc Q	Mu Cc Q An Ksp
49-72	26 d	610	.52	Mu Cc Q	Mu Cc Q An Ksp

Mu = muscovite; Cc = calcite; Q = quartz; An = anorthite; Ksp = K-feldspar; Zo = zoisite; parentheses indicate less than 10% of a phase; X_{CO_2} = mole fraction CO_2 in a CO_2 - H_2O vapor phase.

*Pressure was 4100 ± 100 bars.

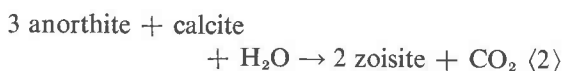
indicate reliability to better than 0.02 mole fraction over the range of fluid compositions and amounts of fluid used in this study (Hewitt, 1970).

Mixtures of starting materials were prepared with stoichiometric amounts of reactants. Anorthite-sanidine mixtures were also seeded with 5 percent synthetic muscovite in order to promote reaction. Phases were identified primarily by X-ray diffraction methods. Optical methods were also used successfully in the determination of low levels of reaction to muscovite-calcite-quartz.

Discussion

Reaction (1) has been reversed at $X_{\text{CO}_2} = 0.50 \pm 0.06$ over the pressure range 2–7 kbar (Figure 1). At 6 kbar fluid pressure, the equilibrium bracket is $584 \pm 4^\circ\text{C}$. From the Clausius-Clapeyron relation, the $H \rightarrow$ and $S \rightarrow$ at this temperature and pressure are $49,600 \pm 6000$ cal/mole and 57.9 ± 7.0 cal/mole-deg respectively. The specific volume of CO_2 used in the calculations is $0.93 \pm .03$ cc/gm (V. Wall and C. Wayne Burnham, The Pennsylvania State University, personal communication, 1973). These reported errors in $H \rightarrow$ and $S \rightarrow$ represent an estimated 5 percent possible error in the volume of the fluid due to mixing and a 7 percent possible error in the determination of the slope of the equilibrium boundary.

Figure 2 shows an equilibrium curve consistent with the reversal brackets for reaction (1) at 6 kbar fluid pressure for varying fluid composition in the system $\text{CO}_2\text{-H}_2\text{O}$. Within the errors of the determinations, the curve is symmetrical about $X_{\text{CO}_2} = 0.5$. Anorthite-K-feldspar is the stable high-temperature assemblage over most of the range of X_{CO_2} values. Zoisite-K-feldspar is the stable high-temperature assemblage in two runs at low X_{CO_2} . On the basis of these two runs, a curve for reaction (2),



has been placed on Figure 2. The location of this reaction represents only a minimum value for X_{CO_2} , because reversibility has not been demonstrated. It is in good agreement with the unreversed data of Storre and Nitsch (1972). However, some reversed experimental data determined by Johannes and Orville (personal communication) indicate that the true equilibrium may lie at values of X_{CO_2} that are 0.02–0.04 higher.

The effects of pressure on the $T\text{-}X_{\text{CO}_2}$ positions

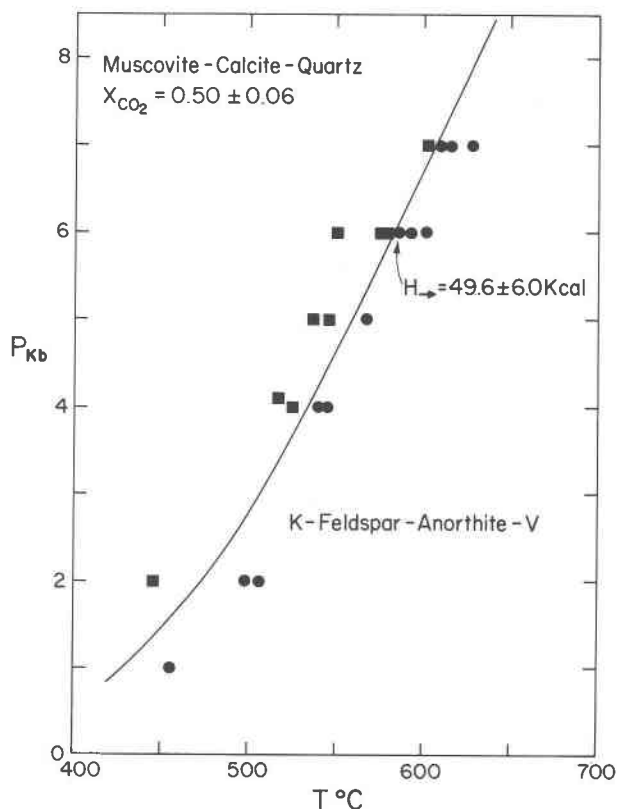


FIG. 1. Data for reaction (1) under the conditions $P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = P_T$, and X_{CO_2} equal to the stoichiometric fluid composition. Circles represent conditions where K-feldspar-anorthite-vapor form from muscovite-calcite-quartz; squares represent conditions where muscovite-calcite-quartz form from K-feldspar-anorthite-vapor.

of the above equilibria are shown in Figure 3. The shape of the curve for reaction (1) has been held constant and the temperatures changed as a function of pressure according to the equilibrium in Figure 1. Data for reaction (2) have been reversibly determined at 7 kbar by Johannes and Orville (1972). The 5 kbar curve for reaction (2) represents unreversed data from Storre and Nitsch (1972). Even though the invariant point appears to be moving rapidly towards more CO_2 -rich fluids with increasing pressure, the occurrence of zoisite-K-feldspar indicates the presence of very CO_2 -poor metamorphic fluids. Johannes and Orville (1972) place the invariant point at 7 kbar at 570°C and $X_{\text{CO}_2} = 0.17$. Using their data on reaction (2) and the data presented here on reaction (1), the invariant point is placed at 585°C and $X_{\text{CO}_2} = 0.17$ at 7 kbar. The 15°C difference between the two points is probably within the combined experimental errors.

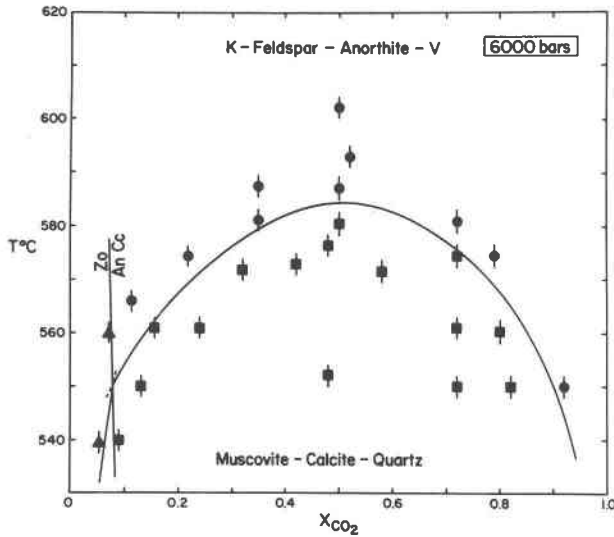


FIG. 2. Data for reaction (1) under the condition $P_{\text{fluid}} = P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = P_{\text{solid}} = 6$ kbar. Circles represent conditions where K-feldspar-anorthite-vapor form from muscovite-calcite-quartz; squares represent conditions where muscovite-calcite-quartz form from K-feldspar-anorthite-vapor; triangles represent conditions where zoisite-K-feldspar-vapor form from muscovite-calcite-quartz. Approximate reaction curves for reaction (2) and the reaction $3 \text{ muscovite} + 4 \text{ calcite} + 6 \text{ quartz} \rightleftharpoons 2 \text{ zoisite} + 3 \text{ K-feldspar} + 4 \text{ CO}_2 + 2 \text{ H}_2\text{O}$ are drawn in on the basis of the two runs producing zoisite.

Low-pressure P - V - T data on the CO_2 - H_2O system (Greenwood and Barnes, 1966; Greenwood, 1967a) indicate that ideal mixing is approximated at temperatures above 500°C and pressures below 2 kbar. Although the actual mixing behavior cannot be determined from the symmetrical shape of the T - X curve for reaction (1) at 6 kbar, the data are consistent with nearly ideal mixing of the fluid and certainly rule out the possibility of fluid immiscibility under these conditions. If the mixing behavior in the CO_2 - H_2O system is nearly ideal at pressures up to 6 or 7 kbar for temperatures in excess of 550°C , then the feasibility of calculations of equilibrium curves and the extrapolation of the experimentally determined curves are greatly enhanced.

Ryzhenko and Volkov (1971) have extrapolated fugacity coefficients for CO_2 and a number of other gases up to 10 kbar and 1000°C on the basis of reduced-variable equations. Figure 4 has been constructed using their values for f_{CO_2} and the data from Burnham, Holloway, and Davis (1969) for the fugacity of water. Ideal mixing behavior has been assumed for the fluid and all the equilibrium data have been corrected to a constant solid pressure equal to 6 kbar.

Using only the data collected for 6 kbar $P_{\text{fluid}} = P_{\text{solid}}$, a good fit is obtained for the equilibrium line. The calculated $H^* \rightarrow$ from this line at 584°C is 49.4 ± 3 kcal/mole. This corresponds to an $H \rightarrow \approx 48$ kcal/mole and is in good agreement with the $H \rightarrow$ derived previously from the slope of the P - T curve. When the data at 4, 5, and 7 kbar are included with the 6 kbar data, the curve fit is much poorer. It is possible to construct a line through the reversal brackets, but some of the data points are so close to this line that it seems very unlikely that they should have reacted at all. Furthermore, the slope of the line yields an $H \rightarrow$ that is not consistent with the P - T data. There are three obvious possible explanations for the inconsistency of the data determined at different pressures: (1) the experimental data do not represent equilibrium; (2) the assumption of ideal mixing is invalid; (3) the fugacity data used for CO_2 are in error.

The first reason is rejected on the basis of the good reversibility of the reaction. Even if the reaction is metastable the relationship between $\ln f$ and $1/T$ should still be linear over the temperature interval involved and consistent with the P - T curve. The assumption of ideal mixing is definitely subject to some uncertainty. However, because the 6 kbar data with varying $\text{CO}_2/\text{H}_2\text{O}$ ratios plot in a consistent manner, it is unlikely that non-ideality is the whole

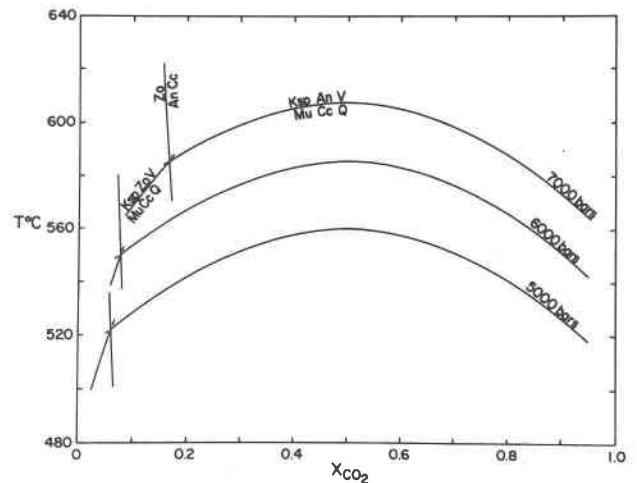


FIG. 3. Variation with pressure of reactions (1) and (2) and the isobaric invariant point formed at their intersection. The shape of reaction (1) has been held constant with the 6 kbar curve shown in Figure 2 and the variation with temperature has been taken from Figure 1. The positions of reaction (2) have been taken from the data of this paper, Johannes and Orville (1972), and Storre and Nitsch (1972).

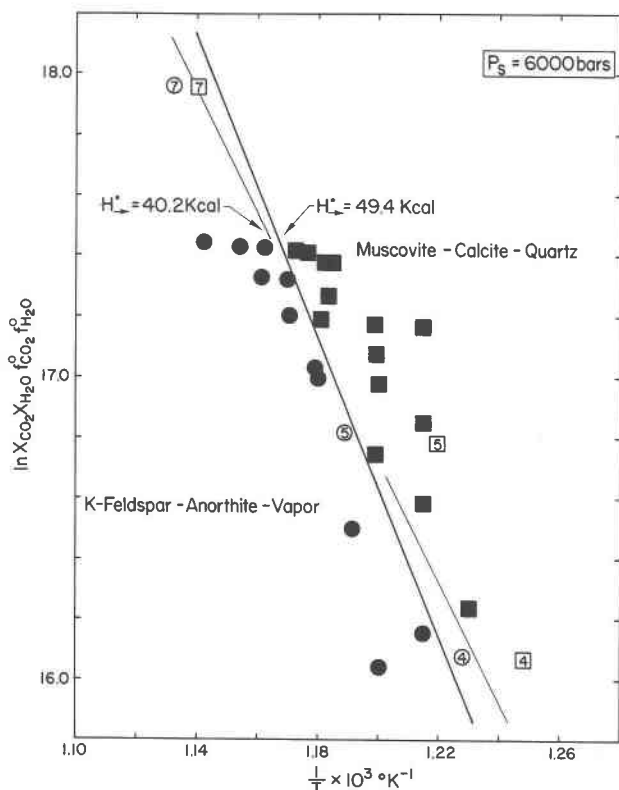


FIG. 4. Data for reaction (1) plotted on a $\ln f_{\text{CO}_2} f_{\text{H}_2\text{O}} - 1/T$ diagram corrected to a solid pressure equal to 6 kbar. Ideal mixing has been assumed in calculating values for f_{CO_2} and $f_{\text{H}_2\text{O}}$. Circles represent conditions where K-feldspar-anorthite-vapor form from muscovite-calcite-quartz; squares represent conditions where muscovite-calcite-quartz form from K-feldspar-anorthite-vapor; solid symbols represent data determined at 6 kbar fluid pressure; open symbols represent data determined at 4, 5, and 7 kbar fluid pressure. The dark equilibrium line is drawn to fit only the 6 kbar data and the light line is drawn to fit all the data.

cause of the discrepancy. The most likely error lies in the values for f_{CO_2} . Extrapolated reduced variable equations often do not give accurate predictions of fugacities at high pressures. Apparently the fugacity data at 6 kbar are good enough over a small temperature range to yield a consistent plot for the experimental data at that pressure, but the slope of fugacity *vs* pressure is incorrect so that there is poor agreement among the data at different pressures.

The effect of changing the activity of anorthite by introducing an albite component must normally be taken into consideration whenever the reaction data are applied to the interpretation of natural systems. When soda is added to the system, the equilibrium constant for reaction (1) becomes

$$K = \frac{f_{\text{CO}_2} f_{\text{H}_2\text{O}} \cdot a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} \cdot a_{\text{KAlSi}_3\text{O}_8}^{\text{K-feldspar}}}{a_{\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2}^{\text{muscovite}} \cdot a_{\text{CaCO}_3}^{\text{calcite}} \cdot (a_{\text{SiO}_2}^{\text{quartz}})^2}$$

In the carbonate-bearing rocks investigated by the author (Hewitt, 1973), the soda contents of the micas and alkali-feldspars were low, whereas the plagioclase composition was highly variable. If it is assumed that the activities of CaCO_3 , SiO_2 , KAlSi_3O_8 , and $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ are close to unity and/or cancel each other, then the effect of adding sodium to the plagioclase at constant P and X_{CO_2} can be calculated simply from the $\ln f$ *vs* $1/T$ plot in Figure 4. Using Orville's (1972) activity data for $\text{CaAl}_2\text{Si}_2\text{O}_8$, the change in temperature for the reaction at 6 kbar and $X_{\text{CO}_2} = 0.50$ is -15°C for An_{60} and -33°C for An_{40} . This change in the T - X curve is shown in Figure 5.

A similar analysis can be applied to reaction (2). At constant temperature and pressure equation (1) must hold for the decrease in X_{CO_2} due to the addition of Na to the plagioclase.

$$\Delta \ln \frac{f_{\text{CO}_2}}{f_{\text{H}_2\text{O}}} = \Delta \ln a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^3 \quad (1)$$

If ideal mixing of CO_2 and H_2O is assumed in the fluid, and if we make our standard state the equi-

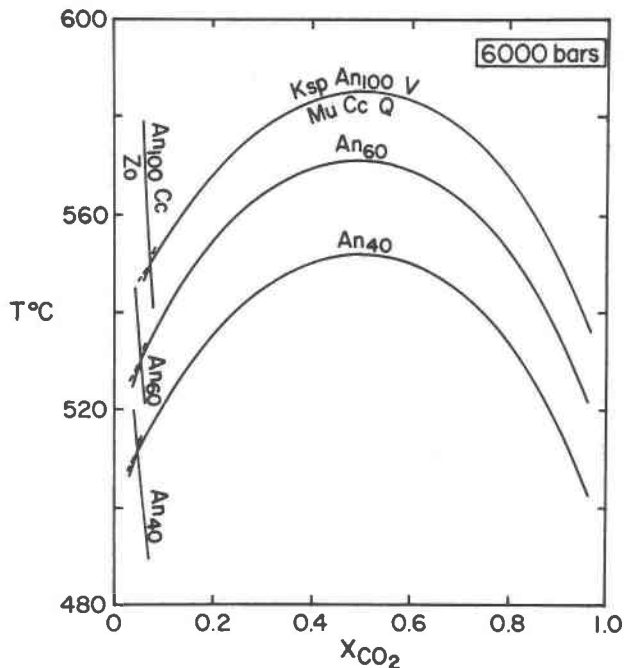


FIG. 5. Calculated equilibrium variation due to the addition of an albite component to the plagioclase phase in reactions (1) and (2) at $P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = P_T = 6$ kbar.

librium for pure anorthite (*denotes the standard state), equation (1) can be simplified to the following:

$$\Delta \ln \frac{X_{\text{CO}_2} f_{\text{CO}_2}^{\circ}}{X_{\text{H}_2\text{O}} f_{\text{H}_2\text{O}}^{\circ}} = \Delta \ln a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^3 \quad (2)$$

$$\frac{X_{\text{CO}_2}^*}{1 - X_{\text{CO}_2}^*} \frac{1 - X_{\text{CO}_2}}{X_{\text{CO}_2}} = a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{-3} \quad (3)$$

Again using Orville's (1972) activity data for $\text{CaAl}_2\text{Si}_2\text{O}_8$, the change in equilibrium at 550°C and 6 kbar is from $X_{\text{CO}_2}^* = 0.09$ for pure anorthite, to $X_{\text{CO}_2} = 0.03$ for An_{60} , to $X_{\text{CO}_2} = 0.01$ for An_{40} (Fig. 5). It is apparent that, for pressures below 7 kbar and temperatures greater than $\sim 450^\circ\text{C}$, the assemblage zoisite-K-feldspar-Na-plagioclase is stable only under conditions of low activity of CO_2 . This could occur simply by having H_2O -rich binary mixtures of CO_2 and H_2O or by having large fractions of another species such as CH_4 in the vapor.

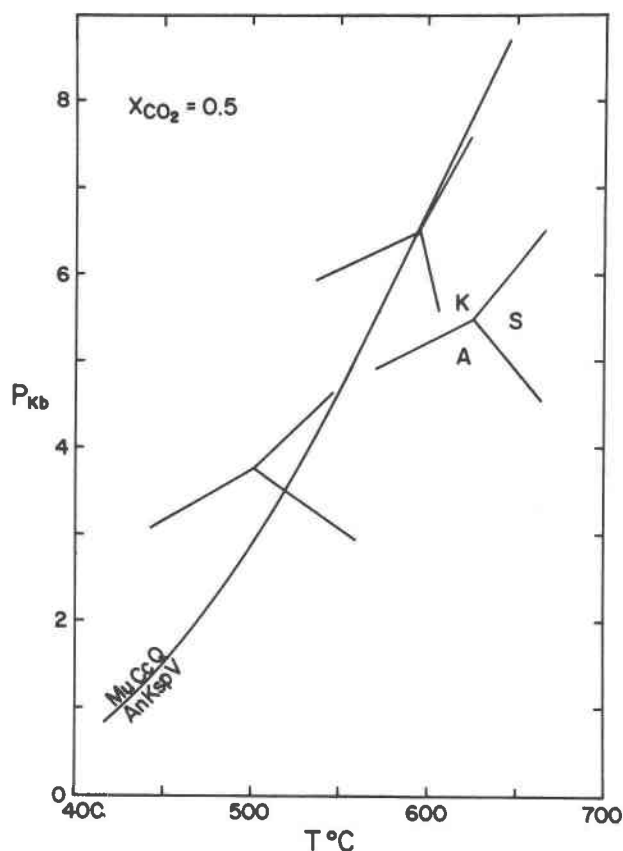


FIG. 6. Comparison of the equilibrium data for reaction (1) at $X_{\text{CO}_2} = X_{\text{H}_2\text{O}} = .5$ with the aluminum silicate triple points postulated by Althaus (1967), Richardson *et al* (1969), and Holdaway (1971) (listed in order of decreasing pressure).

Aside from the direct application of these experimental determinations to the metamorphism of calc-silicates (Hewitt, 1973), the data on the equilibrium of reaction (1) provide a possible check for consistency with the postulated positions of the aluminum silicate triple point. Based on the author's experience, it is questionable whether the assemblage muscovite-calcite-quartz is stable under metamorphic conditions where sillimanite is stable. Figure 6 shows the relation of the muscovite-calcite-quartz maximum with the recently determined triple points. The higher pressure triple points of Althaus (1967) and Richardson, Gilbert, and Bell (1969) are consistent with the assemblage not occurring at sillimanite grade. Holdaway (1971) puts the triple point at lower pressure and temperature and his data predict rare occurrences of muscovite-calcite-quartz in sillimanite-bearing terrains. The occurrence would be rare because any addition of Na to the plagioclase or change in the fluid composition would move reaction (1) to lower temperatures than Holdaway's triple point. Unfortunately, negative evidence is not conclusive in this situation. It will be necessary to observe muscovite-calcite-quartz in sillimanite grade rocks in order to give a basis for preference in the Al_2SiO_5 triple points.

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