American Mineralogist, Volume 60, pages 391–397, 1975

Stability of the Assemblage Phlogopite–Calcite–Quartz

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Abstract

Equilibrium data for the reaction $5KMg_3AlSi_3O_{10}(OH)_2 + 6CaCO_3 + 24SiO_2 \rightarrow 3Ca_2Mg_5Si_8O_{22}(OH)_2 + 5KAlSi_3O_8 + 6CO_2 + 2H_2O$ have been determined reversibly over the pressure range of 2–8 kbar. For $X_{CO_2} = 0.75$ in the fluid the equilibrium curve lies at 664 ± 18°C at 8 kbar, 600 ± 25°C at 6 kbar, 540 ± 15°C at 4 kbar, and 475 ± 15°C at 2 kbar. The enthalpy of reaction at 600°C and 6 kbar is 91 ± 12 kcal. The T–X_{CO_2} curve at 6 kbar, calculated assuming ideal fluid mixing from a log $f_{CO_2}{}^6 f_{H_2O}{}^2 - 1/T$ plot of the data, places the equilibrium at $X_{CO_2} = 0.58$ and 0.81 at 600°C, $X_{CO_2} = 0.41$ and 0.95 at 575°C, $X_{CO_2} = 0.28$ and 0.98 at 550°C, $X_{CO_2} = 0.20$ and 0.99+ at 525°C, and $X_{CO_2} = 0.13$ and 0.99+ at 500°C.

The intersection of this reaction with the reaction anorthite + calcite + $H_2O \rightleftharpoons$ zoisite + CO_2 is indifferent in the end member system at 6 kbar. The common occurrence in the natural system of the assemblage present at the intersection of these reactions indicates that additional components raise the equilibrium temperature of the ph-cc-qtz reaction relative to that of the reaction muscovite + calcite + quartz → anorthite + K-feldspar + CO_2 + H_2O. Although the assemblage ph-cc-qtz is more stable at high X_{CO_2}, and less stable at low X_{CO_2}, than the mu-cc-qtz assemblage in the pure system, the addition of other components favors the relative stability of ph-cc-qtz over the whole range of X_{CO_2}.

Introduction

Reaction ⟨1⟩ has been investigated previously by Hewitt (1970) and Hoschek (1973).

$$5 \text{ phlogopite} + 6 \text{ calcite} + 24 \text{ quartz} \rightleftharpoons$$
$$3 \text{ tremolite} + 5 \text{ K-feldspar} + 6CO_2 + 2H_2O \quad \langle 1 \rangle$$

As with other experimental investigations involving tremolite at relatively low temperatures (for example, see Skippen, 1971; Metz, 1970) the reactions are sluggish and require very long run times and/or seeding before reasonable reversed brackets can be obtained. The small, but significant, differences between the data presented here and those of Hoschek (1973) are important if we are to understand the phase relations in the synthetic system K_2O–Al_2O_3–CaO–MgO–SiO_2–CO_2–H_2O and its natural analogs.

Experimental Methods

The equilibrium for Reaction ⟨1⟩ has been determined reversibly using standard cold-seal hydrothermal techniques. Horizontally mounted 12″ long Rene 41 bombs with diameters ranging from 1″ to 1⅜″ OD were used for all experiments. Water was the pressure medium for all runs except the 8 kbar runs, which were pressurized with argon. Pressures up to 7 kbar were measured using Heise Bourdon tube gauges. The 8 kbar pressures were measured with a Harwood bulk modulus cell calibrated up to 7 kbar against a Heise Bourdon tube gauge.

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 DTA methods against the melting points of dry NaCl, KCl, and CsCl.

In all runs conducted previous to 1972, the fluid compositions were controlled in the capsule by including weighted amounts of synthetic $ZnCO_3$, SiO_2, and H_2O, initially separated from the sample in the opposite end of a 1¼″ long platinum capsule. Fluids in all later runs were generated using weighed amounts of $Ag_2C_2O_4$ and H_2O rather than the zinc mixture. Reaction to $Zn_2SiO_4 + CO_2 + H_2O$ or $Ag^\circ + CO_2 + H_2O$ was complete before the bomb reached the run temperature, and the amount of fluid generated was approximately 30 wt percent of the charge. Emission spectrographic analysis of the run products, phlogopite-calcite-quartz-tremolite-K-feldspar, that occurred in a run using the $ZnCO_3$–SiO_2 carbon dioxide generator at 2000 bars, 530°C, and $X_{CO_2} = 0.50$ showed no detectable Zn (<200 ppm). These data and the good agreement of the data using the two different CO_2 generators indicate that Zn contamination is not a source of error.

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 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).

All runs were made with crystalline starting materials. Descriptions of the different phases are given below.

Quartz: Natural Brazilian optical grade quartz

Calcite: Mallinckrodt reagent grade $CaCO_3$ (Lot KRJ)

Phlogopite: Crystallized at 800°C and 1 kbar from an oxide mix of $K_2Si_4O_9$, MgO, γ-Al_2O_3, H_2O, and SiO_2 glass

Sanidine: Crystallized from a gel at 600°C and 2 kbar

Tremolite 1 (Richville): Fluorine-rich tremolite from Richville, New York. Analysis given in Table 1.

Tremolite 2: Synthetic tremolite crystallized by successive runs at 600–700°C and 2–4 kbar in which the first run was 50 percent Richville tremolite–50 percent oxide mix. The second run was 50 percent products from the first run–50 percent oxide mix, *etc.* The OH/F ratio in the final products was always at least 7:1 and probably greater than 10:1 considering that the crystallizations were done with an excess of pure water. Optical and X-ray investigation showed no recognizable diopside in the synthetic material.

Tremolite 3 (Gouverneur): H_2O-rich tremolite from Gouverneur, New York (Engel #A-14-10). Analysis given in Table 1.

TABLE 1. Analyses of Natural Tremolites

	Richville Tremolite*	Gouverneur Tremolite**
SiO_2	56.76	57.76
Al_2O_3	1.84	.64
TiO_2	.08	.05
Fe_2O_3	.21	.00
FeO	.21	.14
MnO	.05	.06
MgO	24.15	24.73
CaO	11.59	13.27
Na_2O	1.62	.29
K_2O	.64	.09
H_2O^+	.86	2.38
F	1.51	.26
B_2O_3	.23	--
	99.70	99.67
Less O = F	.64	.11
	99.06	99.56

*Analyst E. Lillie **Analyst C. Engel

Cell parameters of the phlogopite, Richville tremolite, and sanidine given in Table 2 were determined using annealed CaF_2 (a = 5.4628(5)Å) as an internal standard. Multiple scans were made at 1/2° per min and all lines were measured at peak top using Cu$K\alpha_1$ radiation. The unit cell parameters were refined using the LSUCR program of Appleman and Evans (1973).

Mixtures of starting materials were prepared with stoichiometric amounts of reactants. Phlogopite-calcite-quartz mixtures were seeded with 5 percent Richville tremolite in order to promote reaction. Tremolite-K-feldspar mixtures used either the nearly pure natural hydroxy-tremolite from Gouverneur or the synthetic tremolite described previously. No variations in the equilibrium could be observed in reversal experiments using these two tremolites in the starting mixtures.

Identification of the occurrence of Reaction (1) is very difficult near the equilibrium curve because of the general sluggishness of the reaction. Growth of tremolite from phlogopite-calcite-quartz can be detected optically at low levels of reaction because it forms elongated crystals (maximum $Z \wedge C = 17°$, $n_\alpha = 1.605 \pm 0.004$) usually growing from the original tremolite seeds. The length-to-width ratio of the new tremolite is always 50 or greater. K-feldspar was detected by X-ray diffraction and could only be detected in runs well above the equilibrium curve.

Several reaction points are determined solely by the optical presence of newly formed tremolite. This is certainly not the optimal situation for reaction determination, but it is felt to be fairly reliable in these circumstances because of the positive identification of K-feldspar in runs slightly farther from the reaction curve where larger amounts of the same kind of tremolite can be identified with the K-feldspar.

Detection of the reversal reaction to phlogopite-calcite-quartz is even more difficult. All reversal determinations in this study are based on the production of optically identifiable calcite ($n_\omega < 1.665$). The amount of reaction is always less than 5 percent and neither quartz nor mica has been observed. The validity of these reversals rests on the assumption that no other reaction is producing the calcite.

In this system the most likely alternatives to account for calcite production would be the reactions of a diopside impurity in the starting material (Reactions ⟨2⟩ and ⟨3⟩), and by the formation of talc, calcite, and quartz according to Reaction ⟨4⟩.

⟨2⟩ diopside + V → tremolite + calcite + quartz

⟨3⟩ diopside + K-feldspar + V → phlogopite + calcite + quartz

⟨4⟩ tremolite + V → talc + calcite + quartz

As previously noted the first alternative is not possible because great care was taken to be certain that no diopside was present in the starting material. Aside from the lack of talc in any experiment in this study, Reaction ⟨4⟩ is unlikely because it would appear from Skippen's (1974) data that the experiments were conducted within the stability field of tremolite. The argument presented later in the paper that Reactions ⟨1⟩ and ⟨4⟩ cannot intersect under most metamorphic conditions further substantiates this interpretation.

Results

All the equilibrium data collected are given in Table 3. The results of the experiments carried out in a small range of fluid compositions around the thermal maximum for Reaction ⟨1⟩ are shown in Figure 1. The equilibrium *P–T* curve is linear or nearly linear over the range of conditions studied. The calculated enthalpy and entropy of reaction at 600°C and 6 kbar are 91 ± 12 kcal and 104 ± 14 cal/deg respectively. These calculations use the molar volume data of Robie *et al* (1966) for the solid phases, of Burnham, Holloway, and Davis (1969) for H_2O, and a specific volume for CO_2 of 0.93 ± .03cc/gm at 600°C and 6 kbar (V. Wall and C. Wayne Burnham, The Pennsylvania State University, personal communication, 1973). Ideal mixing has been assumed for the fluid. The reported errors in the enthalpy and entropy of reaction (H→ and S→) include only the variations due to the uncertainty of the equilibrium curve position within the brackets.

TABLE 2. Unit Cell Parameters of Starting Materials

	Phlogopite	K-feldspar	Richville Tremolite*
a(Å)	5.317(1)	8.606(3)	9.858(2)
b(Å)	9.203(2)	13.016(3)	18.026(3)
c(Å)	10.310(2)	7.168(2)	5.271(1)
β(deg)	99.92(1)	116.02(3)	104.78(2)
V(Å)^3	496.9(1)	721.6(3)	905.6(2)

*Georg Troll - personal communication

Comparison of these data with those of Hoschek

TABLE 3. Experimental Data

Run Number	T°C	Starting Material*	X_{CO_2}	Run Duration (days)	Products*
		2000 bar Experiments			
45-69	504±2	$PCQT_1$	.60±.02	49	$PCQT_1T$
90-69	460±2	T_2KP	.70±.03	47	T_2KCP
92-69	450±2	$PCQT_1$	.02±.01	47	$PCQT_1KT$
121-69	478±2	$PCQT_1$	.11±.01	40	$PCQT_1KT$
125-69	488±5	$PCQT_1$	.37±.01	52	$PCQT_1KT$
127-69	488±5	$PCQT_1$	.69±.03	52	$PCQT_1KT$
128-69	488±5	$PCQT_1$	.88±.05	52	$PCQT_1KT$
		4000 bar Experiments			
17-69	564±4	$PCQT_1$	.64±.03	7	$PCQT_1KT$
19-69	554±4	$PCQT_1$	.63±.03	7	$PCQT_1KT$
40-69	549±2	$PCQT_1$	.64±.03	45	$PCQT_1KT$
29-72**	518±2	T_2KP	.62±.02	20	T_2KCP
		6000 bar Experiments			
2-73	623±3	$PCQT_1$	.75±.03	102	$PCQT_1T$
5-73	574±4	T_2KP	.75±.03	101	T_2KCP
7-73	549±2	$PCQT_1$	.21±.02	96	$PCQT_1KT$
9-73	593±2	$PCQT_1$	.23±.02	95	$PCQT_1KT$
		7000 bar Experiments			
24-72	652±2	$PCQT_1$	.74±.03	20	$PCQT_1T$
		8000 bar Experiments			
32-69	681±5	$PCQT_1$	.65±.10	2	$PCQT_1KT$
34-69	646±5	T_3KP	.65±.10	2	T_3KCP

*Mineral abbreviations; P=synthetic phlogopite; C=calcite; Q=quartz; K=synthetic K-feldspar; T_1=Richville tremolite; T_2=synthetic tremolite; T_3=Gouverneur tremolite; T=tremolite formed by reaction

**Pressure was 4100 bars

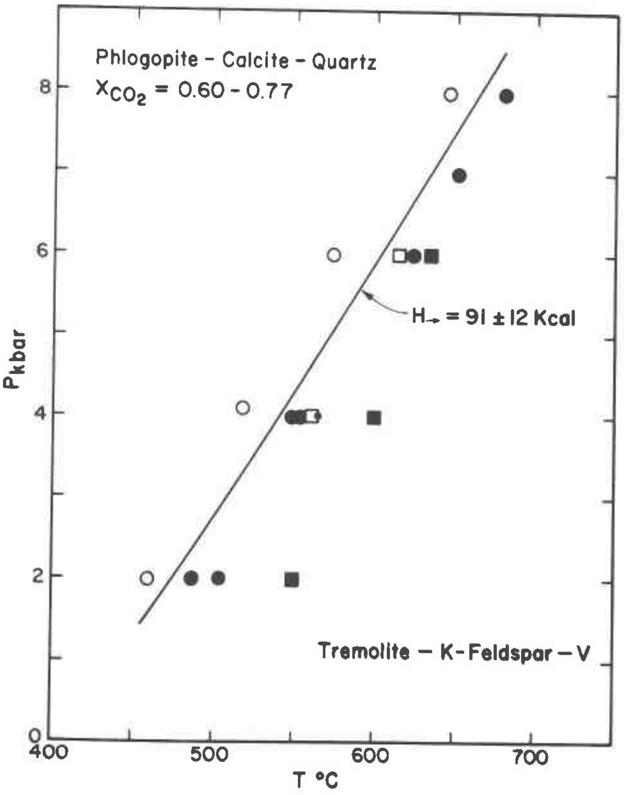

FIG. 1. *P-T* plot of the equilibrium data determined for fluid compositions near the thermal maximum at X_{CO_2} = 0.75. Open symbols indicate reaction to phlogopite-calcite-quartz; closed symbols, to tremolite-K-feldspar-vapor. Squares represent data from Hoschek (1973).

(1973) shows a disagreement of from 20 to 50°C in the position of the equilibrium curve over the pressure range 2-6 kbar. Careful consideration of the problem indicates that the probable source of the disagreement lies in the different experimental techniques. The optical method for the determination of the growth of tremolite plus K-feldspar is felt to be more reliable for small amounts of reaction than is the crystal weight-change method. The weight-change method requires a very thorough knowledge of all possible reactions in the system. Determination of reaction to phlogopite-calcite-quartz by this method is only possible if the starting material is absolutely free from diopside or other phases that would react within the stability field of tremolite-K-feldspar.

The effect of the presence of fluorine in the Richville tremolite seeds used in this study has also been considered. Munoz and Eugster (1969) and Troll and Gilbert (1972) have shown that phlogopite preferentially takes up fluorine from an aqueous phase with respect to tremolite. Because this bonded fluorine is concentrated in the phlogopite, HF will always occur on the right hand side of a balanced Reaction ⟨1⟩. The presence, therefore, of fluorine in the tremolite seeds should not lower the equilibrium but, if anything, raise it.

A log $f_{CO_2}{}^6 f_{H_2O}{}^2 - 1/T$ plot of all data given in Table 3 is shown in Figure 2. Ideal mixing of the vapor has been assumed and the fugacity data for H_2O and CO_2 have been taken from Burnham *et al* (1969) and Mel'nik (1972), respectively. All the data have been corrected to a solid pressure equal to 6000 bars. The H*→ (solid phases at temperature and pressure and vapor phase at temperature and 1 atmosphere) calculated from this plot is 92 ± 9 kcal. A comparison of this value with the enthalpy of reaction calculated from the Clausius-Clapeyron relation cannot be made because of the lack of high pressure enthalpy data for the large amount of CO_2 involved in the reaction; however, the difference between H*→ and H→ should not be very great and the two values would seem to be in good agreement.

Using the log $f_{CO_2}{}^6 f_{H_2O}{}^2 - 1/T$ curve (Fig. 2), the T-X_{CO_2} equilibrium curve for Reaction ⟨1⟩ has been calculated and plotted in Figure 3. The shape of the curve agrees nicely with the data of Hoschek (1973), but as in Figure 1 the curve presented here lies at slightly lower temperatures for all values of X_{CO_2}.

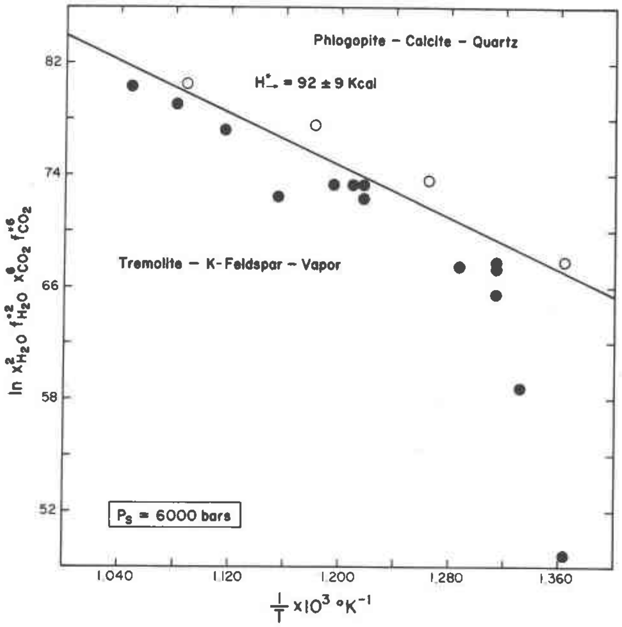

FIG. 2. A log $f_{CO_2}{}^6 f_{H_2O}{}^2 - 1/T$ plot of all equilibrium data for Reaction ⟨1⟩ assuming ideal mixing in the fluid and corrected to P_{solid} = 6 kbar. Open symbols indicate reaction to phlogopite-calcite-quartz; closed symbols, to tremolite-K-feldspar.

Discussion

Carmichael (1970) and Hewitt (1973b), among others, have described the reaction biotite + calcite + quartz $\rightleftharpoons$ amphibole + K-feldspar + vapor as a common reaction in amphibolite facies terranes containing rocks of mixed pelitic and calcareous compositions. The assemblage containing both products and reactants frequently occurs over a broad area, indicating that varying metamorphic fluid compositions and/or varying compositions of the solid phases must be taken into consideration in any interpretation of metamorphic environments.

Aside from experimental determinations the effects of varying fluid compositions can be qualitatively estimated using the approach of Greenwood (1967); more quantitative treatments can be carried out in those systems where thermochemical data are available for the volatile phases.

The effects of varying compositions of the solid phases are not so well known. Carmichael (1970) estimated, on the basis of the natural element distribution in several biotite-calcite-quartz-amphibole-K-feldspar reaction assemblages, that TiO_2 and F increase the stability of biotite-calcite-quartz whereas Al_2O_3 and Na_2O decrease that stability field. The effect of FeO was shown to be dependent on the amount of Al_2O_3. A comparison of Carmichael's original data with those of Hewitt (1973b) shows that even some of these conclusions may be oversimplifications of a more complex system behavior. It seems clear that a great deal more experimental and observational data are needed before the detailed effects of additional components on this reaction are well known.

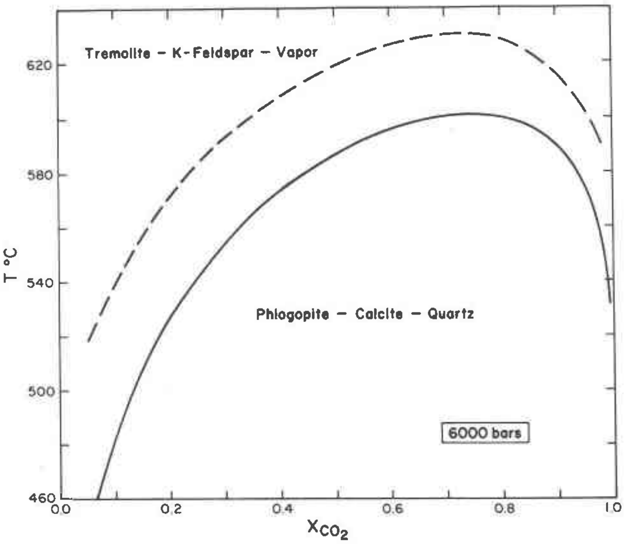

FIG. 3. *T-X* curve at 6 kbar calculated from the $\log f_{CO_2}{}^6 f_{H_2O}{}^2 - 1/T$ plot in Figure 2. Ideal mixing has been assumed for the fluid. The dashed curve represents the data of Hoschek (1973).

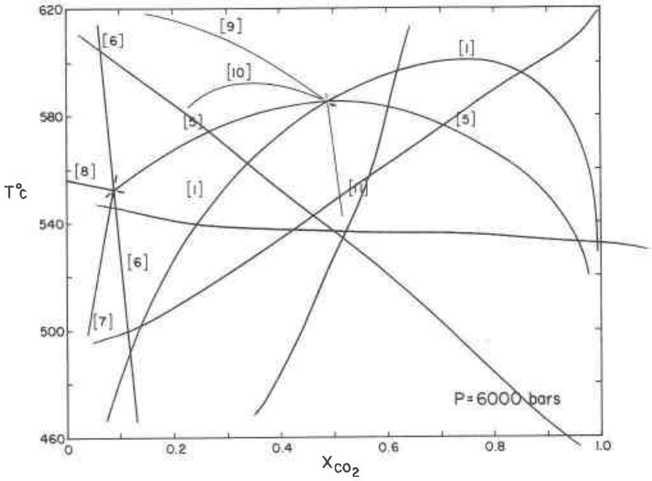

FIG. 4. Phase relations at 6 kbar involved at the intersection of the following equilibria for which some experimental data are available:

⟨1⟩ phlogopite + calcite + quartz $\rightleftharpoons$ tremolite + K-feldspar + vapor
⟨5⟩ muscovite + calcite + quartz $\rightleftharpoons$ K-feldspar + anorthite + vapor (Hewitt, 1973a)
⟨6⟩ zoisite + CO_2 $\rightleftharpoons$ anorthite + calcite + H_2O (Johannes and Orville, 1972; Storre and Nitsch, 1972; Hewitt, 1973a)
⟨7⟩ muscovite + calcite + quartz $\rightleftharpoons$ zoisite + K-feldspar + vapor (Johannes and Orville, 1972; Hewitt, 1973a)
⟨8⟩ muscovite + zoisite + quartz $\rightleftharpoons$ anorthite + K-feldspar + vapor (Johannes and Orville, 1972)

No data are available for the following reactions and their positions are only approximate.

⟨9⟩ muscovite + tremolite $\rightleftharpoons$ phlogopite + anorthite + K-feldspar + quartz + vapor
⟨10⟩ muscovite + calcite + tremolite $\rightleftharpoons$ phlogopite + anorthite + K-feldspar + vapor
⟨11⟩ muscovite + tremolite + CO_2 $\rightleftharpoons$ phlogopite + anorthite + calcite + quartz + H_2O

Figure 4 shows the experimentally determined relationships at 6 kbar for Reactions ⟨1⟩, ⟨5⟩, and ⟨6⟩.

$$\text{muscovite} + \text{calcite} + \text{quartz} \rightleftharpoons \text{anorthite} + \text{K-feldspar} + \text{V} \quad \langle 5 \rangle$$

$$\text{zoisite} + CO_2 \rightleftharpoons \text{anorthite} + \text{calcite} + H_2O \quad \langle 6 \rangle$$

There are two important points of interest in this diagram. First, the intersection between Reactions ⟨5⟩ and ⟨1⟩ substantiates the observation (Hewitt, 1973b) that at low to moderate values of X_{CO_2} muscovite is stable to higher temperatures with calcite and quartz than is phlogopite. The opposite holds at high values of X_{CO_2}. Second, the intersection between Reactions ⟨1⟩ and ⟨6⟩ must be indifferent. Because of the stability of the assemblage tremolite-muscovite there are no bulk compositions where both Reactions ⟨1⟩ and ⟨6⟩ can occur simultaneously in the pure system at this pressure. However, this assemblage, biotite-calcite-quartz–amphibole–K–feldspar–plagioclase–zoisite–vapor, commonly occurs in natural systems containing additional components such as FeO and Na_2O (Carmichael, 1970; Hewitt, 1973b). This can happen only if the intersection of Reactions ⟨1⟩ and ⟨6⟩ lies at temperatures above those for invariant point *I*. Under these conditions the intersection is no longer indifferent. There are three likely methods by which this would occur. First, the addition of sodium to the plagioclase has been shown by Hewitt (1973a) to lower the equilibrium temperature of Reaction ⟨5⟩ and to move invariant point *I* to more water-rich fluid compositions. Assuming that the sodium entering the other phases is negligible, the addition of sodium to the plagioclase would cause Reactions ⟨1⟩ and ⟨6⟩ to intersect above invariant point *I* only when the plagioclase compositions are quite sodic (An_{20} or less). Second, the equilibrium temperature of Reaction ⟨1⟩ can be raised relative to invariant point *I* by the addition of other components such as TiO_2 and perhaps FeO and F (Carmichael, 1970). Third, the addition of Fe_2O_3 to the zoisite moves invariant point *I* to more CO_2-rich fluid compositions and, therefore, closer in temperature to Reaction ⟨1⟩.

Analyses of phases from both the Whetstone Lake Area (Carmichael, 1970) and southwestern Connecticut (Hewitt, 1973b), where the biotite-calcite-quartz reaction has been described coexisting with plagioclase-epidote, indicate that all three methods are commonly in effect and that the complexity of the problem is still further increased by the addition of small amounts of sodium to the alkali feldspar and amphibole. Data are obviously too sparse at this time to assess quantitatively the effects of all of these variables. However, it is clear that the assemblage phlogopite-calcite-quartz-tremolite-K-feldspar-zoisite-anorthite-vapor is not stable under typical amphibolite facies conditions, but that the addition of other components commonly present in mixed pelite-carbonate rocks tends to stabilize the natural assemblage by differential movement of the reactions involved.

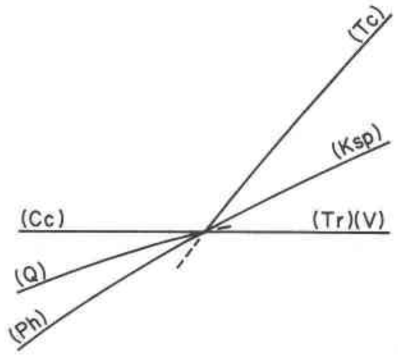

FIG. 5. The isobaric invariant point that is generated in the system $KAlO_2$–CaO–MgO–SiO_2–CO_2–H_2O if Reactions ⟨1⟩ and ⟨4⟩ intersect. Based on natural occurrences the vapor absent reaction formed at this intersection can only occur at very low temperatures.

(Tc) phlogopite + calcite + quartz $\rightleftharpoons$ tremolite + K-feldspar + vapor
(Ph) (Ksp) talc + calcite + quartz $\rightleftharpoons$ tremolite + vapor
(Tr) (Cc) (V) talc + K-feldspar $\rightleftharpoons$ phlogopite + quartz
(Q) talc + calcite + K-feldspar $\rightleftharpoons$ phlogopite + tremolite + vapor

The data presented here can also be used to place a limit on the position of Reaction ⟨4⟩. This reaction and Reaction ⟨1⟩ cannot intersect at any reasonable metamorphic pressure or temperature. If intersection were to occur, the invariant point shown in Figure 5 would be generated and the vapor-absent reaction talc + K-feldspar → phlogopite + quartz would radiate from that point. The absence of natural occurrences of the assemblage talc-K-feldspar indicates that this reaction could only occur at very low temperatures. Because of this, it appears that the data of Skippen (1971, 1974) on Reaction ⟨4⟩ are the most compatible with the data presented here.

Acknowledgments

The author would like to thank Drs. D. Burt and J. B. Thompson, Jr. for their suggestions made during the preparation of the manuscript, and Dr. P. Toulmin III for critically reviewing the manuscript. This research has been supported by the Earth Sciences Section, National Science Foundation, Grant GA-32267.

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Manuscript received, August 16, 1974; accepted for publication, January 6, 1975.