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THE REACTION: DOLOMITE + QUARTZ + WATER = TALC + CALCITE + CARBON DIOXIDE

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ABSTRACT. The formation of talc and calcite from dolomite and quartz has been studied in water-carbon dioxide mixtures at temperatures from 400° to 520°C at a total pressure of 2000 bars. If account is taken of the solid solution of $MgCO_3$ in calcite, the reaction may be written:

$$\frac{3(1-b)}{(1-a-2b)}\ \underset{\text{dolomite}}{[(1+a)CaCO_3\ (1-a)MgCO_3]} + \underset{\text{quartz}}{4SiO_2} + H_2O =$$

$$\frac{3(1+a)}{(1-a-2b)}\ \underset{\text{calcite}}{[(1-b)CaCO_3\ bMgCO_3]} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 3CO_2$$

The equilibrium curve passes approximately through the points:

$$X_{CO_2} = 0.2,\ T = 415°C;\ X_{CO_2} = 0.4,\ T = 450°C;\ X_{CO_2} = 0.6,\ T = 475°C;$$
$$\text{and } X_{CO_2} = 0.8,\ T = 500°C.$$

The reaction involves coexisting dolomite and calcite, and consequently the free energy change of the reaction is dependent on the solid solubility of $MgCO_3$ in calcite. Data of previous investigators have been used to derive the activity coefficient of $MgCO_3$ in calcite, giving:

$$\ln\gamma^{C}_{MgCO_3} = (1-X^{C}_{MgCO_3})^2\,(2.1718 - 1.8960\,X^{C}_{MgCO_3})$$
$$0 \leqslant X^{C}_{MgCO_3} \leqslant 0.18$$

This equation and data on the composition of coexisting calcite and dolomite have been used to determine the standard free energy change of the reaction. This free energy change is:

$$\Delta G_R = 64{,}700 - 119.3\,T \qquad (1\text{ bar, °K, cal})$$

Talc forms as the first step in the metamorphism of siliceous dolomites only in the absence of potassium and aluminum. Presence of aluminum alone leads to the early formation of chlorite, and presence of both leads to early formation of phlogopite.

INTRODUCTION

The reaction:

$$\underset{\text{dolomite}}{3\,CaMg(CO_3)_2} + \underset{\text{quartz}}{4SiO_2} + H_2O = \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \underset{\text{calcite}}{3\,CaCO_3} + 3\,CO_2$$

has been cited as the initial step in the metamorphism of siliceous dolomites (Tilley, 1948). This is a report of an experimental study of the reaction in supercritical H_2O–CO_2 mixtures.

The reaction has been studied previously by Metz and Winkler (1963). In their experiments, known amounts of dolomite, quartz, and water were reacted in sealed tubes, and the maximum extent of reaction determined at particular temperatures and total pressures. From the amount of dolomite consumed they calculated the composition of the H_2O–CO_2 fluid in equilibrium with dolomite, quartz, talc, and calcite. Their technique did not permit the observation of the reverse reaction. This study verifies the reversibility of the reaction and is in agreement with their results.

An excellent study by Skippen (ms) outlines equilibria in the system CaO–MgO–SiO_2–H_2O–CO_2. He discusses the relationship of this particular reaction to other equilibria in the system.

Greenwood (1961, 1962, 1967) has described experimental methods and outlined the theory of equilibria involving solids and a coexisting binary fluid. His experimental technique has been followed in this work.

EXPERIMENTAL TECHNIQUE

Starting materials for the experiments were synthetic minerals prepared from Baker and Adamson Reagent grade basic magnesium carbonate, magnesium oxide, and calcium carbonate, and natural quartz from Lisbon, Maryland.

Dolomite was prepared at 1000 bars, 600°C, and $X_{CO_2} = 0.6$ from a mixture of reagent $CaCO_3$ and magnesite. The magnesite was obtained by recrystallizing basic magnesium carbonate at 500 bars P_{CO_2} and 600°C.

Step-scanning a powder mount of the synthetic dolomite with an X-ray diffractometer showed it contained a trace of magnesium calcite. The measured spacing of the dolomite (104) peak was obtained using the diffractometer and oscillating against the (101) peak of Lisbon quartz. The quartz peak was taken to have a d-spacing of 3.343 A. The result was dolomite d(104) (measured) $= 2.885 \pm 0.002$ A, corresponding to stoichiometric dolomite (Goldsmith and Graf, 1958).

Talc was synthesized from magnesium oxide and Lisbon quartz. Reagent $CaCO_3$ was used directly as calcite. The natural quartz was crushed and washed and used with no further treatment. Distilled water and Matheson 99.99 percent CO_2 made up the fluid phase.

Two separate mixtures, one of dolomite and quartz, the other talc and calcite, were used in each experiment. Aside from the trace of calcite in the dolomite, runs were not seeded. With the exceptions of runs H22, H23, and H24, each run had a small amount of quartz placed in the bottom of the bomb to buffer the activity of SiO_2.

Temperatures were measured with chromel-alumel thermocouples in wells in the side of each bomb. The bomb thermocouples were calibrated in place against a standard previously checked against melting points of NBS standard zinc, lead, aluminum, and reagent NaCl. A Leeds and Northrup 16 point recorder monitored each bomb temperature, and periodic checks were made with a Leeds and Northrup K-3 potentiometer.

Barber-Coleman "on-off" type controllers maintained furnace temperatures to ± 3°C or better. Maximum temperature uncertainties, including calibration, thermal gradient, and one-half the control fluctuation were usually ± 5°C. These are listed in table 1.

Pressures were measured on a calibrated Ashcroft bourbon tube gauge and were constant to ± 20 bars.

The experimental technique has been described by Greenwood (1961, 1967). Starting mixtures are supported in open platinum capsules in 25 cc Morey bombs. After the bombs are placed in the furnace, sufficient CO_2 is pumped in to keep the carbonates stable until the bomb reaches the desired temperature. The CO_2 pressure is adjusted, and water pumped in to bring the fluid to the desired composition and pressure.

TABLE 1

Experimental results

Run	Duration (days)	Pressure (bars)	Temp. (°C)	X_{CO_2} (±0.003)	$\log_{10}\frac{(f_{CO_2})^3}{f_{H_2O}}$	Material		Percent Reaction
						Initial	Final	
H25	17	2000	410 ± 5	0.145	5.551	D + Q T + C	D + Q T + C	0
H32	17	2000	400 ± 5	0.164	5.736	D + Q T + C	D + Q T + C + D + Q	5
H9	20	1000	401 ± 4	0.176	5.010 (2000 b)	D + Q T + C	D + Q + T + C T + C	7
H27	19	2000	478 ± 5	0.318	6.514	D + Q T + C	D + Q + T + C T + C	68
H22*	12	2000	440 ± 5	0.360	6.790	D + Q T + C	D + Q T + C + D	16
H45	67	2000	436 ± 5	0.388	6.917	D + Q T + C	D + Q T + C + D + Q	8
H50	34	2000	453 ± 4	0.417	6.990	D + Q T + C	D + Q T + C	0
H46	67	2000	450 ± 5	0.445	7.103	D + Q T + C	D + Q T + C + D + Q	3
H23*	12	2000	472 ± 7	0.572	7.494	D + Q T + C	D + Q + T + C T + C	5
H24*	12	2000	480 ± 5	0.600	7.569	D + Q T + C	D + Q + T + C T + C	12
H17	83	2000	497 ± 5	0.755	8.049	D + Q T + C	D + Q + T + C T + C	10
H35	17	2000	476 ± 6	0.764	8.121	D + Q T + C	D + Q T + C	0
H47	67	2000	470 ± 5	0.787	8.217	D + Q T + C	D + Q T + C + D + Q	8
H48	35	2000	500 ± 5	0.885	8.579	D + Q T + C	D + Q T + C	0
H49	35	2000	522 ± 5	0.918	8.736	D + Q T + C	D + Q T + C	0
H51	34	2000	519 ± 4	0.930	8.826	D + Q T + C	D + Q T + C + D + Q	8

TABLE 2

Notation

Subscripts refer to components. Superscripts refer to phases as abbreviated:

C — calcite
D — dolomite
F — fluid
M — magnesite
P — periclase
T — talc
Q — quartz

Superscript ° refers to standard state, that is, phase consisting of pure component at temperature of interest:

G — μ—Gibbs free energy per mole
V — molar volume
X — mole fraction
f — fugacity
a — activity (defined by $\overline{G} = {}^{\circ}\overline{G} + RT \ln a$)
γ — activity coefficient (defined by $a = \gamma X$)

At the conclusion of a run the fluid is rapidly extracted through a two-stage cold trap into a known volume. Water content is found by weighing the cold trap, and the other gases, principally CO_2, are determined volumetrically. The gas analysis is accurate to ± 0.3 percent (Greenwood, 1967).

Gas chromatography showed no CO or CH_4 at the 0.03 percent detection level. Run products were examined with petrographic and X-ray diffraction techniques. Newly-formed talc and quartz were easily identified optically, but the carbonates could be distinguished only by the appropriate (104) peak on the diffractometer trace.

Not enough dolomite was produced during any run to verify the presence of the superstructure reflections of ordered dolomite. Production of a disordered dolomite and quartz from talc and calcite still represents reversal of the reaction, however, as under the temperatures of the experiments, ordered dolomite and quartz are even more stable than the assemblage containing the disordered carbonate (Graf and Goldsmith, 1956; Goldsmith and Heard, 1961).

The direction of reactions was determined by noting which of the two starting mixtures reacted to form the other two phases. Extent of reaction was estimated by measuring the relative heights of calcite and dolomite peaks on diffractometer traces of each run. Calibration against mounts of known composition shows the lower limit of detection to be approximately 3 percent reaction and the accuracy to vary from about ± 5 percent at 50 percent reaction to ± 3 percent at 5 percent reaction. To this must be added an unknown uncertainty due to differences in X-ray characteristics between the starting materials and phases formed during a run. The extents of reaction given in table 1 represent relative quantities rather than absolute amounts.

The small extents of reaction reported in table 1, although of uncertain magnitude, are none the less real, as the reaction products were not present in the reactants at the beginning of the runs.

EXPERIMENTAL RESULTS

The experimental results are listed in table 1 and shown in figures 1 and 2. Note that Run H22 did not have quartz added to the bomb, and no quartz could be detected in the talc-calcite starting material although dolomite did form. Run H9 is not plotted in figure 1, since it was made at a pressure of 1000 bars. The curve in figure 1 has been calculated assuming ideal mixing of H_2O and CO_2 (Greenwood, 1967), and equilibrium at

$$T = 447°C, X_{CO_2} = 0.4, \text{ and } \frac{\Delta H_R}{RT} = \frac{35{,}000}{T}$$

Figure 2 illustrates the experimental results recalculated to the form of an "equilibrium constant". The fugacity compilation of Skippen (ms), in part based on reduced variable calculations, was used to compute log $(f_{CO_2})^3/f_{H_2O}$ assuming ideal mixing of the fluid phase. Run H9 has been recalculated to a total pressure of 2000 bars and thus appears on this plot.

The plot of log $(f_{CO_2})^3/f_{H_2O}$ versus 1/T is useful, because for small temperature ranges the equilibrium curve is very nearly straight. This permits the use of experiments to bracket the curve even when they are far apart in log $(f_{CO_2})^3/f_{H_2O}$ − 1/T space. The equilibrium constant

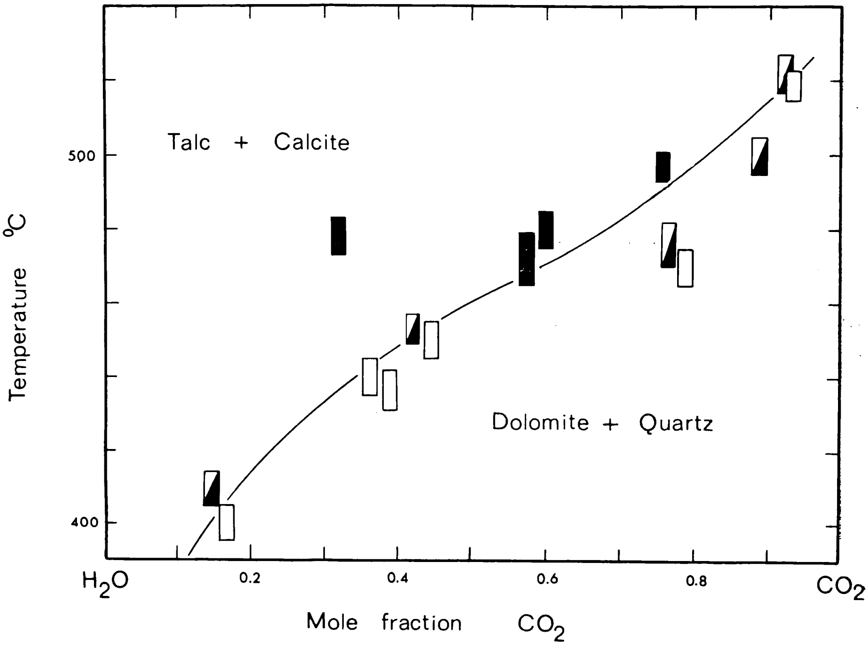

Fig. 1. Experimental results at 2000 bars. Solid symbols: talc and calcite formed. Open symbols: dolomite and quartz formed. Half-shaded symbols: no reaction. Curve calculated assuming ideal mixing of H_2O and CO_2, equilibrium at 447° and X_{CO_2} = 0.4, and ΔHR/RT = 35,000/T.

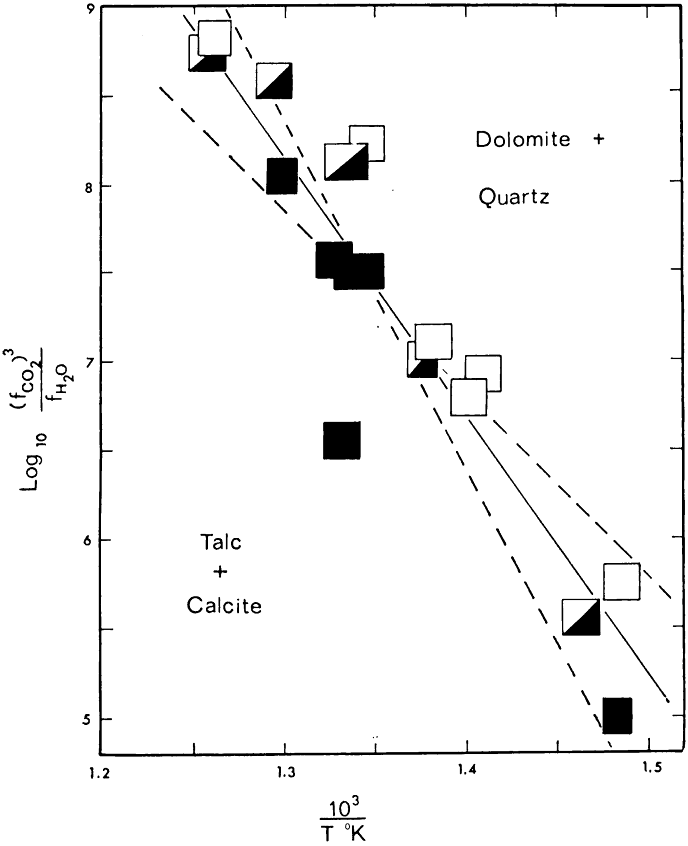

Fig. 2. Experimental results at 2000 bars recalculated to $\log_{10}(f_{CO_2})^3/f_{H_2O}$. Symbols as in figure 1.

for this reaction is not strictly $\log(f_{CO_2})^3/f_{H_2O}$ (see next section), but the remaining terms are also linear in 1/T.

The equation for the line in figure 2 is:

$$\log_{10}\frac{(f_{CO_2})^3}{f_{H_2O}} = \frac{-14{,}490}{T} + 27.00 \text{ (2000 bars)}$$

with a *maximum* uncertainty in slope of ± 30 percent as shown by the dotted lines.

In natural logarithms the equation is:

$$\ln\frac{(f_{CO_2})^3}{f_{H_2O}} = \frac{-33{,}370}{T} + 62.17 \quad \text{(2000 bars)} \qquad (1)$$

Figure 3 shows the data of Metz and Winkler (1963, table 4) and the curve shown in figure 1. The data are in agreement within experimental uncertainties. The success of their technique underlines the fact, also

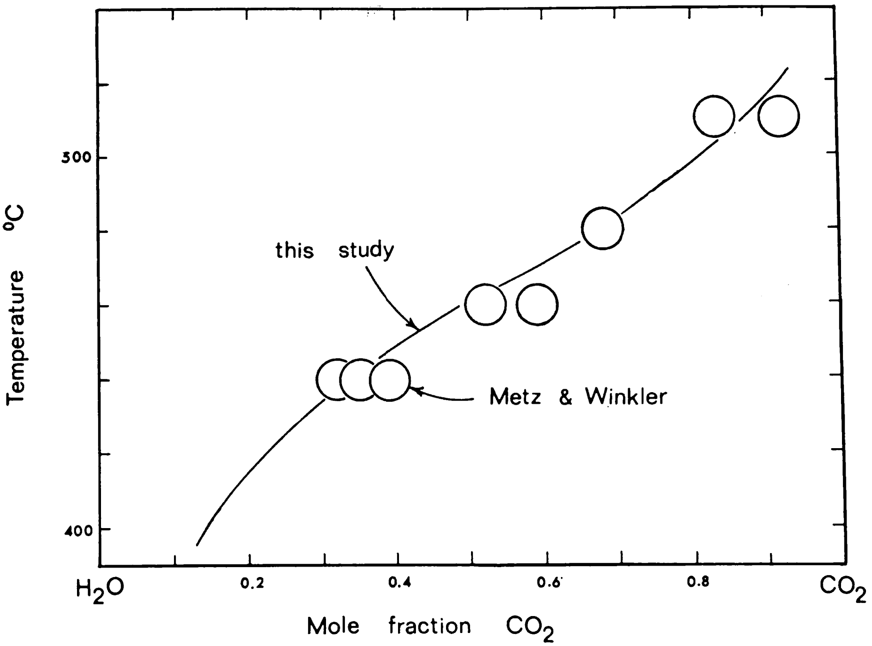

Fig. 3. Experimental results of Metz and Winkler (1963) and curve plotted in figure 1. The symbols represent determinations of the equilibrium curve and are not reversed brackets.

noted in this study, that the reaction of dolomite and quartz to form talc and calcite proceeds at a much faster rate than the reverse reaction.

THERMODYNAMIC CONSIDERATIONS

The equilibrium constant of a reaction involving pure solids and a fluid phase may be expressed as a logarithmic function of the fugacities of the appropriate gas species. This has a nearly linear variation with reciprocal temperature. The relationship of the equilibrium constant to free energy permits use of experimentally determined equilibrium constants in the calculation of other equilibria. Equilibrium constants for reactions involving calcite and dolomite must also take account of the variable activities of $CaCO_3$ and $MgCO_3$ due to solid solution in the carbonates (Skippen, ms). If an isobaric univariant assemblage includes both dolomite and calcite, their compositions are restricted to the calcite-dolomite solvus. If only one carbonate is included in an isobarically univariant assemblage with Ca and Mg bearing silicates, then its composition is also uniquely defined by the temperature. The latter compositions, however, have not been experimentally determined.

There follows an estimate of the activities of the components of magnesian calcite and an application of this estimate to determine the standard free energy change of the reaction under consideration.

THE ACTIVITY OF $MgCO_3$ IN MAGNESIAN CALCITE

The experimental results of Graf and Goldsmith (1955) may be used to estimate the activity of $MgCO_3$ in magnesian calcite. They report the results of a series of synthesis experiments in which magnesian calcites were found to coexist with periclase and carbon dioxide.

The isobarically univariant reaction:

$$MgCO_3 \text{ (solid solution)} = MgO + CO_2$$

has an equilibrium free energy change given by:

$$0 = \bar{G}^{P} + {}^{\circ}\bar{G}_{CO_2} - {}^{\circ}\bar{G}^{c}_{MgCO_3} + RT \ln \frac{f_{CO_2}}{a^{c}_{MgCO_3}} \quad \text{(see table 2 for notation)} \qquad (2)$$

For the breakdown of pure magnesite:

$$0 = \bar{G}^{P} + {}^{\circ}\bar{G}_{CO_2} - {}^{\circ}\bar{G}^{c}_{MgCO_3} + RT \ln f^{*}_{CO_2} \qquad (3)$$

where $f^{*}_{CO_2}$ is the fugacity of CO_2 in equilibrium with magnesite and periclase.

Equating expressions (2) and (3) gives:

$$\ln a^{c}_{MgCO_3} = \ln \frac{f_{CO_2}}{f^{*}_{CO_2}} \quad \text{at constant T.} \qquad (4)$$

Similar formulae have been used to determine the activities of components undergoing oxidation. (Wones and Eugster, 1965; Muan, 1965).

The compositions of magnesian calcites coexisting with periclase at various temperatures and CO_2 pressures were taken from table 2 of Graf and Goldsmith (1955). The $MgCO_3$ contents were reduced to five-sixths of their original values as suggested by Graf and Goldsmith (1958). In their experiments calcareous algal material containing approximately 20 mole percent $MgCO_3$ was held at elevated temperatures and CO_2 pressures for times between 5 and 840 hours. It is assumed in what follows that equilibrium was attained in these runs. If this is not the case, then most probably the calcites contain more $MgCO_3$ than the equilibrium values, and the calculated activity coefficient will be too small.

Additional data were obtained from the compositions of calcites in equilibrium wth dolomite, periclase, and CO_2. This was done using the dolomite decomposition curve of Graf and Goldsmith (1955) and the solvus of Goldsmith and Heard (1961). Although the position of the calcite-dolomite solvus is pressure dependent, no correction was made for this effect since it is small (Goldsmith and Newton, 1969) and within the error of determining compositions from the solvus.

The fugacities of CO_2 at the experimental conditions were determined using the data of Majumdar and Roy (1956) and the compilation of Skippen (ms). These values were then corrected so that the final fugacities refer to a hypothetical equilibrium state in which the pressure on the solid phases equals 1 bar. The correction was made by extending the formula of Eugster and Wones (1962, p. 91) as follows:

For the reaction:

$$MgCO_3 \text{ (solid solution)} = MgO + CO_2$$

At equilibrium and at constant T:

$$
\begin{aligned}
0 &= d\Delta G_R \\
&= (\overline{V}_{MgO} - {}^{o}\overline{V}^{c}_{MgCO_3})\, dP_{total} + RT\left(\frac{\partial \ln f_{CO_2}}{\partial P_{CO_2}}\right) dP_{CO_2} \\
&\qquad - RT\left(\frac{\partial \ln a^{c}_{MgCO_3}}{\partial P_{total}}\right) dP_{total}
\end{aligned}
$$

Now:

$$\frac{\partial \ln a^{c}_{MgCO_3}}{\partial P} = \frac{\overline{V}^{c}_{MgCO_3} - {}^{o}\overline{V}^{c}_{MgCO_3}}{RT}$$

So:

$$\ln \frac{f_{CO_2}(2)}{f_{CO_2}(1)} = \frac{-\overline{V}_{MgO} + \overline{V}^{c}_{MgCO_3}}{RT}\,[P_{total}(2) - P_{total}(1)] \qquad (5)$$

where the compressibilities of the solid phases are considered negligible.

The partial molar volume of $MgCO_3$ in calcite, $\overline{V}^{c}_{MgCO_3}$, was estimated by fitting a least squares quadratic in $X^{c}_{MgCO_3}$ to the deviation from ideality of the volumes of magnesian calcites calculated from the data of Goldsmith, Graf, and Heard (1961). The function reproduces their data to ± 0.09 cm^3/mole.

Applying the formula:

$$\overline{V}^{c}_{MgCO_3} = \overline{V}^{c} + (1 - X^{c}_{MgCO_3})\frac{\partial \overline{V}^{c}}{\partial X^{c}_{MgCO_3}}$$

to the fitted curve gives the expression:

$$\overline{V}^{c}_{MgCO_3} = 27.24 + 1.40\, X^{c}_{MgCO_3} - 0.70\, (X^{c}_{MgCO_3})^2$$

Values of $\overline{V}^{c}_{MgCO_3}$ obtained from this expression were used in equation (5) to evaluate the correction for pressure.

The remaining term, $\ln f^{*}_{CO_2}$, was evaluated from the thermochemical data in table 3. Although this involves the use of C_P data for $MgCO_3$ outside its range of validity, the results are consistent with the experiments of Harker and Tuttle (1955a). Both the calculated curve and the experimental data corrected to 1 bar solid pressure, are shown in figure 4.

TABLE 3

Thermochemical data

Phase	Formula	Molar volume* (cc)	Hf oxides* 298 °K cal/mole	S* 298 °K cal/mole°	$Cp = A + BT - CT^{-2}$** cal/mole° A	B(10^3)	C(10^{-5})
Calcite	$CaCO_3$	36.94	–42242	22.2	24.98	5.24	6.20
Dolomite	$CaMg(CO_3)_2$	64.35	–73869	37.09	sum of calcite & magnesite		
Magnesite	$MgCO_3$	28.02	–28198	15.7	18.62	13.80	4.16
Periclase	MgO	11.25	0	6.44	10.18	1.74	1.48
Carbon dioxide	CO_2	—	0	51.07	10.57	2.10	2.06

Sources of data: (*) Robie, 1966.
(**) Kelley, 1960.

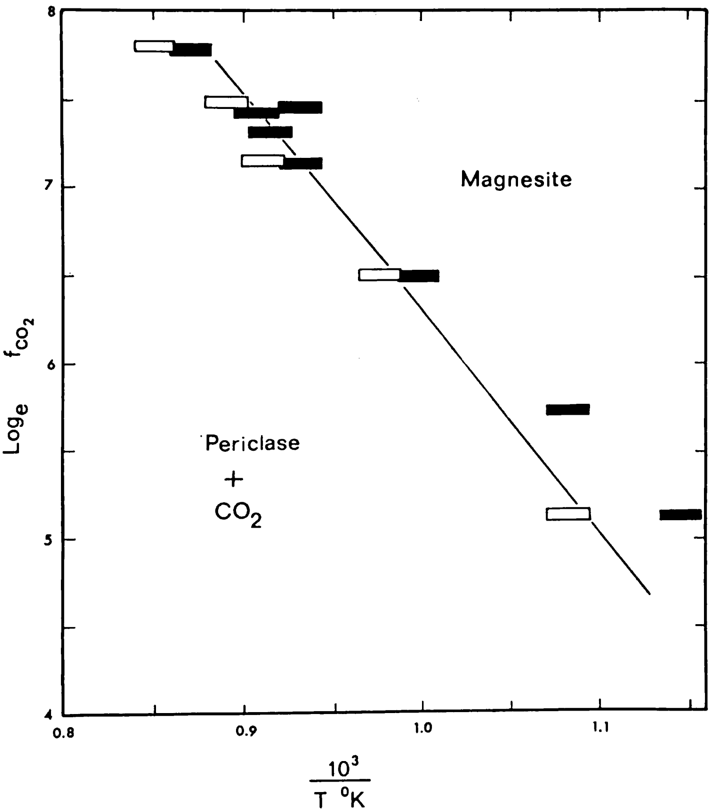

Fig. 4. Experimental results of Harker and Tuttle (1955a) and equilibrium curve calculated from thermochemical data. Solid pressure 1 bar.

The values of ln f_{CO_2} and ln $f^*_{CO_2}$ derived above were substituted into equation (4) to give a set of values of ln $a^c_{MgCO_3}$ each at a particular temperature and composition, but all at a solid pressure of 1 bar. The accumulated uncertainty in ln $a^c_{MgCO_3}$ is difficult to evaluate but is probably about 10 percent. Table 4 summarizes the results.

In theory, iso-compositional plots of ln $a^c_{MgCO_3}$ versus reciprocal temperature should be straight lines, thus permitting simple contouring of the results in table 4. In fact, the number of data points is so small and the uncertainty sufficiently large that this approach is not useful. No temperature dependence of ln $a^c_{MgCO_3}$ can be detected in the data. The assumption was thus made that it is independent of temperature, and all data points were considered together. From the data in table 4 a best fit equation giving ln $\gamma^c_{MgCO_3}$ as a function of $X^c_{MgCO_3}$ was determined. The function was chosen in the form of a Margules expansion (Thompson, 1967).

TABLE 4

Calculation of $a^c_{MgCO_3}$

T°C	$X^c_{MgCO_3}$	P_{CO_2} (psi)	ln f_{CO_2} $Pt = 1$ bar	ln $f^*_{CO_2}$ $Pt = 1$ bar	ln $a^c_{MgCO_3}$	$a^c_{MgCO_3}$ $Pt = 1$ bar
Calcite coexisting with periclase and CO_2						
802	0.006	500	3.5692	7.1848	−3.6156	0.027
700	0.009	285	2.9979	5.9521	−2.9542	0.052
750	0.012	990	4.2544	6.5921	−2.3377	0.097
698	0.013	500	3.5645	5.9249	−2.3604	0.094
807	0.013	3000	5.3629	7.2382	−1.8753	0.153
752	0.024	2000	4.9588	6.6162	−1.6574	0.191
680	0.026	975	4.2340	5.6744	−1.4404	0.237
700	0.026	990	4.2510	5.9521	−1.7011	0.182
801	0.031	5000	5.8646	7.1740	−1.3094	0.270
644	0.033	750	3.9678	5.1399	−1.1721	0.310
853	0.034	8000	6.3245	7.7037	−1.3792	0.252
619	0.038	450	3.4531	4.7400	−1.2869	0.276
725	0.044	3050	5.3669	6.2813	−0.9144	0.401
854	0.050	12,000	6.7111	7.6887	−0.9776	0.376
803	0.077	8000	6.3139	7.1955	−0.8817	0.414
Calcite coexisting with dolomite, periclose, and CO_2						
602	0.070	400	3.3335	4.4535	−1.1200	0.326
637	0.080	900	4.1504	5.0304	−0.8800	0.415
717	0.108	3600	5.5320	6.1780	−0.6460	0.524
792	0.145	10,000	6.5231	7.0761	−0.5530	0.575
857	0.187	20,000	7.1896	7.7420	−0.5524	0.576

The expression is:

$$\ln \gamma^c_{MgCO_3} = (1 - X^c_{MgCO_3})^2 \, (2.1718 - 1.8960 \, X^c_{MgCO_3})$$

$$0 \leqslant X^c_{MgCO_3} \leqslant 0.18 \qquad (6)$$

Activities calculated from the above equation and the data points are shown in figure 5.

The Gibbs-Duhem relationship permits the calculation of the activity coefficient of a component of a binary mixture when the activity coefficient of the other component is known. For calcite the equation is:

$$\ln \gamma^c_{CaCO_3} = (1 - X^c_{CaCO_3})^2 \, (1.2238 + 1.8960 \, X^c_{CaCO_3})$$

This formula was used to compute the activity of component $CaCO_3$ in calcite. The results of this calculation are shown in figure 5 where it may be seen that $a^c_{CaCO_3}$ very closely approximates Raoult's Law. The activities of both components show positive deviation from ideality.

THE ACTIVITY OF $MgCO_3$ IN CALCITE IN EQUILIBRIUM WITH DOLOMITE

The activity of $MgCO_3$ in calcite at equilibrium with dolomite may be approximated by a function of the form:

$$\ln a^c_{MgCO_3} = \frac{A}{T} + B$$

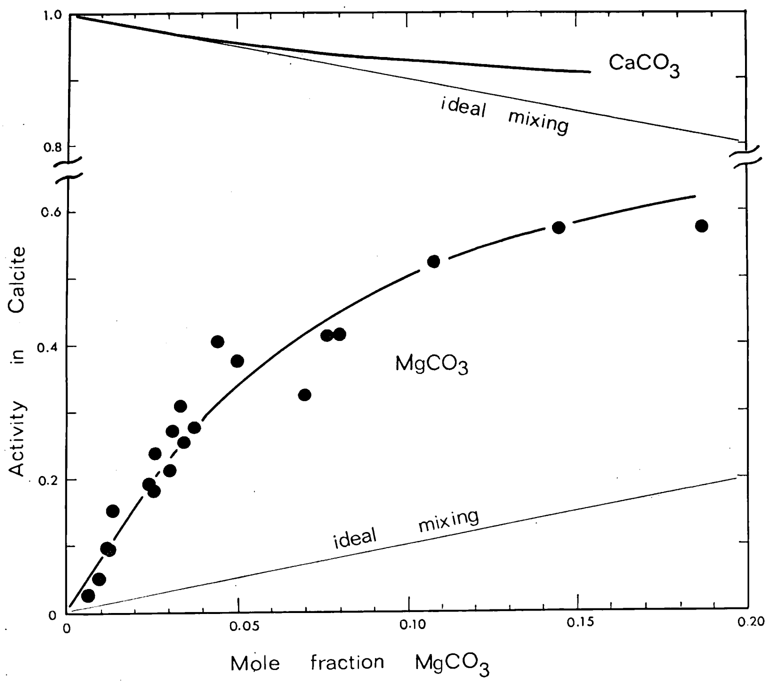

Fig. 5. Activities of $CaCO_3$ and $MgCO_3$ in calcite. Points from table 4. Activity of $MgCO_3$ calculated from equation (6). Activity of $CaCO_3$ determined from Gibbs–Duhem relationship.

A least squares fit of this function to the solvus data of Graf and and Goldsmith (1958) and Harker and Tuttle (1955b) in combination with activities calculated from equation (6) gives:

$$\ln a^c_{MgCO_3} = -\frac{1683}{T} + 1.1177 \tag{7}$$

Equations (6) and (7) may be used to recover the experimental solvus within 0.01 mole fraction $MgCO_3$.

Points used in curve fitting were restricted to temperatures of 704°C and lower since the data of the above investigators and Goldsmith and Heard (1961) are in agreement at these temperatures.

STANDARD FREE ENERGY OF REACTION

The particular reaction under consideration is: dolomite + quartz + water = calcite + talc + carbon dioxide. Taking account of solid solution in the carbonates, this becomes:

$$3\frac{1-b}{1-a-2b}\underset{\text{dolomite}}{[(1+a)CaCO_3\,(1-a)MgCO_3]} + \underset{\text{quartz}}{4SiO_2} + H_2O =$$

$$3\frac{1+a}{1-a-2b}\underset{\text{calcite}}{[(1-b)CaCO_3\,bMgCO_3]} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 3CO_2$$

At equilibrium, because

$$\mu^{D}_{CaCO_3} = \mu^{C}_{CaCO_3}$$

and

$$\mu^{D}_{MgCO_3} = \mu^{C}_{MgCO_3} = {}^{\circ}\mu^{C}_{MgCO_3} + RT \ln a^{C}_{MgCO_3}$$

the Gibbs free energy change for the reaction may be written:

$$\Delta G_R = {}^{\circ}\overline{G}^{T} + 3{}^{\circ}\overline{G}^{F}_{CO_2} - 4{}^{\circ}\overline{G}^{Q} - {}^{\circ}\overline{G}^{F}_{H_2O} - 3{}^{\circ}\overline{G}^{C}_{MgCO_3} + RT \ln \frac{(f_{CO_2})^3}{f_{H_2O}(a^{C}_{MgCO_3})^3}$$

where standard states are defined in table 2.

Note that because component $CaCO_3$ occurs only in coexisting carbonate phases, its free energy does not appear in the equation. At equilibrium:

$$\ln \frac{(f_{CO_2})^3}{f_{H_2O}\,(a^{C}_{MgCO_3})^3} = -\frac{1}{RT}[\overline{G}^{T} + 3{}^{\circ}\overline{G}^{F}_{CO_2} - 4\overline{G}^{Q} - {}^{\circ}\overline{G}^{F}_{H_2O} - 3{}^{\circ}\overline{G}^{C}_{MgCO_3}] \tag{8}$$

Although equation (8) is correct as written, it is useful to have an equation relating f_{CO_2} and f_{H_2O} to a term involving the free energies of pure dolomite and calcite.

Because calcite and magnesite have the same crystal structure, ${}^{\circ}\overline{G}^{C}_{MgCO_3}$ may be taken as equal to ${}^{\circ}\overline{G}^{M}_{MgCO_3}$, and equation (8) may be rewritten:

$$\ln \frac{(f_{CO_2})^3}{f_{H_2O}} - 3 \ln a^{C}_{MgCO_3} + \frac{3}{RT}[{}^{\circ}\overline{G}^{D} - {}^{\circ}\overline{G}^{C} - {}^{\circ}\overline{G}^{M}] = -\frac{1}{RT}[\overline{G}^{T} + 3{}^{\circ}\overline{G}^{F}_{CO_2} + 3{}^{\circ}\overline{G}^{C} - 4\overline{G}^{Q} - 3{}^{\circ}\overline{G}^{D} - {}^{\circ}\overline{G}^{F}_{H_2O}] \tag{9}$$

The first term, $\ln (f_{CO_2})^3/\ln f_{H_2O}$ has been evaluated experimentally at 2000 bars over the temperature range 400° to 520°C and is represented by equation (1). This was corrected to apply at a total pressure of 1 bar using the formula of Eugster and Wones (1962, p. 91) and molar volumes from Robie (1966).

The resulting equation is:

$$\ln \frac{(f_{CO_2})^3}{f_{H_2O}} = -\frac{32{,}400}{T} + 62.17 \qquad (1\ \text{bar}) \tag{10}$$

The second term, $-3 \ln a^{C}_{MgCO_3}$, may be calculated from equation (7) to give:

$$-3 \ln a^{C}_{MgCO_3} = \frac{5049}{T} - 3.3531 \qquad (1\ \text{bar}) \tag{11}$$

The third term, $3/RT\ [{}^{\circ}\overline{G}^{D} - {}^{\circ}\overline{G}^{C} - {}^{\circ}\overline{G}^{M}]$, may be calculated from the thermochemical data in table 3 to give:

$$\frac{3}{RT}[{}^{\circ}\overline{G}^{D} - {}^{\circ}\overline{G}^{C} - {}^{\circ}\overline{G}^{M}] = \frac{-5176}{T} + 1.22 \tag{12}$$

Equations (9), (10), (11), and (12) may be combined to:

$$-\frac{\Delta G_R}{RT} = -\frac{32,576}{T} + 60.04 \qquad (°K, cal) \qquad (13)$$

representing the temperature dependence of the standard free energy of reaction at 1 bar.

Strict accounting of the uncertainties involved in arriving at equation (13) would show, as with most thermochemical calculations, that the maximum possible error completely overshadows the magnitude of the free energy change. Nevertheless, it is felt that the procedures used result

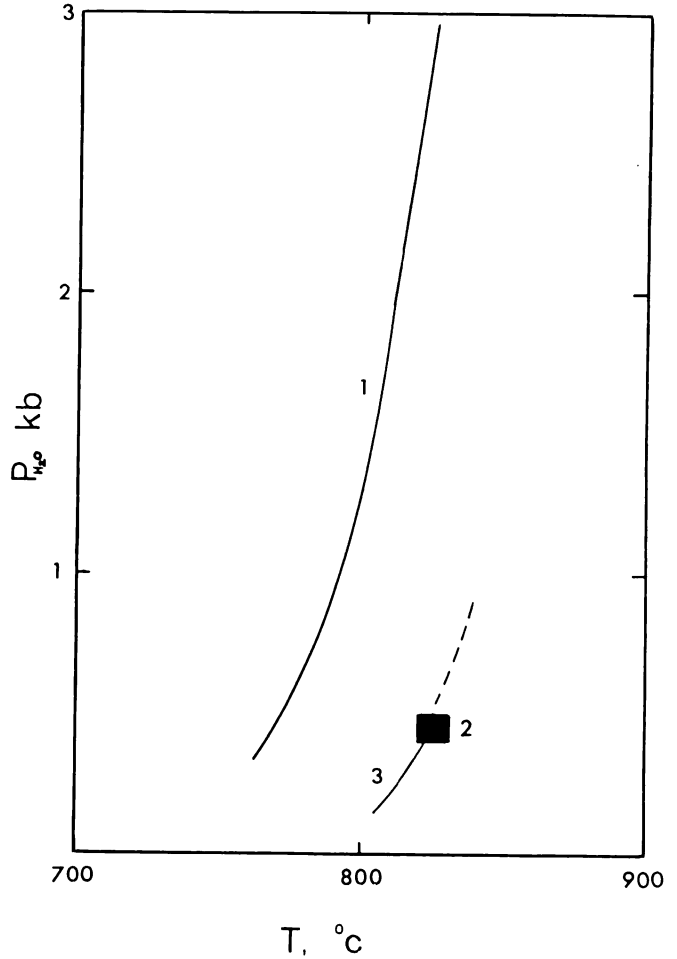

Fig. 6. Experimentally determined equilibria involving phlogopite, potassium feldspar, quartz, enstatite, talc, and water.

Curve 1. Talc = enstatite + quartz + water from Bowen and Tuttle (1949).

Point 2. From Wones and Dodge (1966).

Curve 3. Phlogopite + quartz = enstatite + potassium feldspar + water.

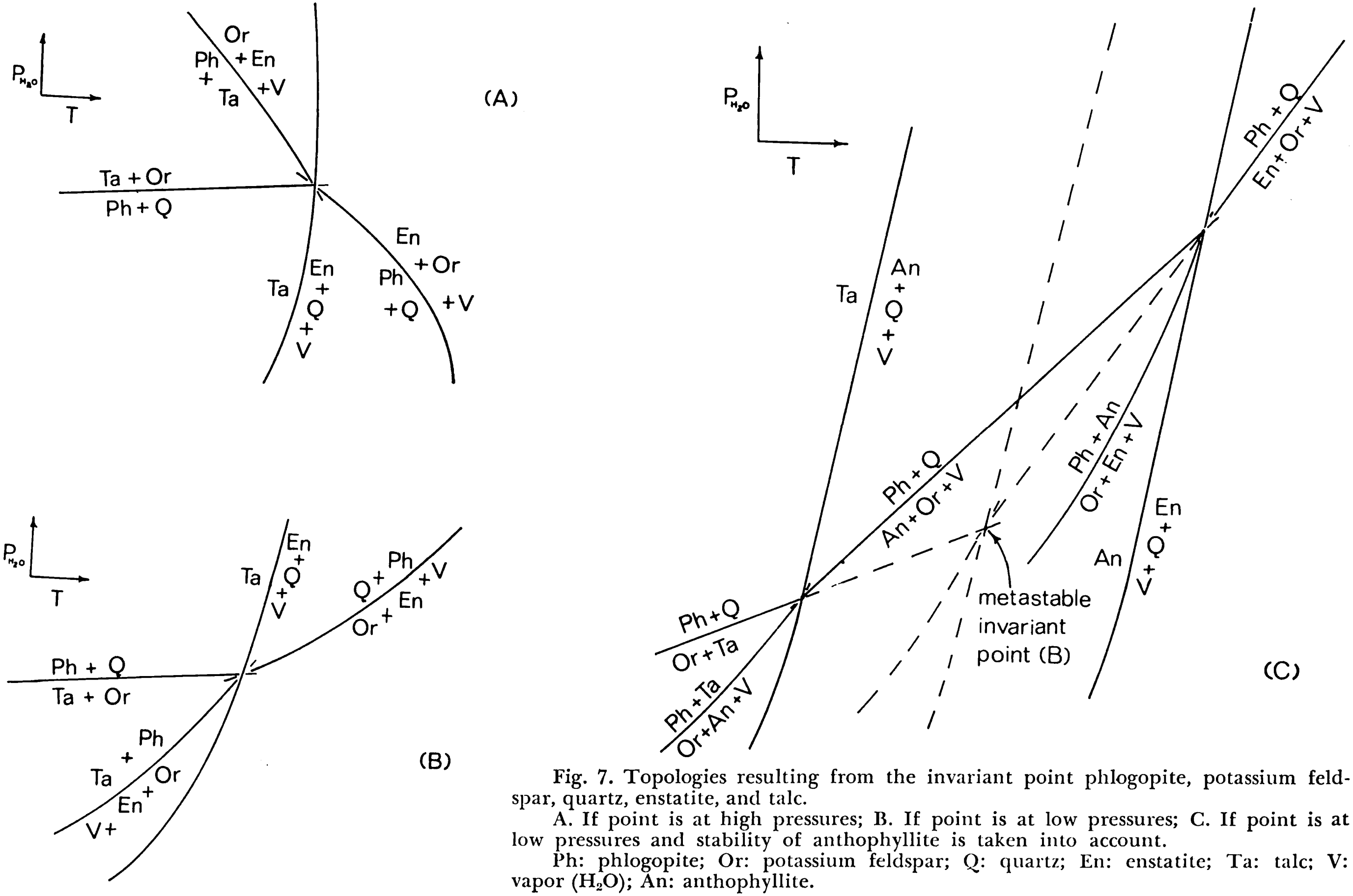

Fig. 7. Topologies resulting from the invariant point phlogopite, potassium feldspar, quartz, enstatite, and talc.

A. If point is at high pressures; B. If point is at low pressures; C. If point is at low pressures and stability of anthophyllite is taken into account.

Ph: phlogopite; Or: potassium feldspar; Q: quartz; En: enstatite; Ta: talc; V: vapor (H_2O); An: anthophyllite.

in a reasonable estimate of the standard free energy change of the reaction.

This may then be used to calculate other equilibria in the CaO–MgO–SiO_2–H_2O–CO_2 system.

ON THE ABSENCE OF TALC IN MANY SILICEOUS DOLOMITES

Despite the fact that, under moderate P-T conditions, talc forms from a mixture of dolomite and quartz, talc is not common in regionally metamorphosed siliceous dolomites. An obvious explanation for this fact is the effect of other components in reducing the stability field of talc.

Fawcett and Yoder (1966) have shown that at 2000 bars P_{H_2O} and temperatures from 425°C to approximately 500°C, the addition of greater than 4 wt percent Al_2O_3 to the talc composition results in the assemblages talc–chlorite–quartz, quartz–chlorite–montmorillonite, or quartz–chlorite.

An alternative explanation for the relative scarcity of talc is suggested by the common occurrence of phlogopite in magnesian marbles. Phlogopite is related to talc by the reaction:

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \underset{\text{potassium feldspar}}{KAlSi_3O_8} = \underset{\text{phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{quartz}}{4SiO_2} \quad (14)$$

Sufficient experimental data are available to show that over a wide range of P-T conditions phlogopite + quartz is the stable assemblage.

Consideration of the phase rule shows that reaction (14) should pass through an invariant point involving the phases phlogopite, potassium feldspar, quartz, enstatite, and talc. Other reactions meeting at this invariant point are:

$$\text{talc} = \text{enstatite} + \text{quartz} + H_2O$$
$$\text{phlogopite} + \text{talc} = \text{potassium feldspar} + \text{enstatite} + H_2O$$
$$\text{phlogopite} + \text{quartz} = \text{potassium feldspar} + \text{enstatite} + H_2O$$

(see fig. 7).

Of these reactions, only the metastable breakdown of talc to enstatite, quartz, and water has been studied over a wide P-T range (Bowen and Tuttle, 1949). Another restriction is available, however, since the reaction of phlogopite and quartz to enstatite, potassium feldspar, and water is known to pass through an invariant point fixed by Wones and Dodge (1966). The univariant curve defined by equation (14) intersects these two curves simultaneously at the invariant point shown schematically in figure 7. The fact of intersection is independent of the stability or metastability of the curves in question.

Figure 7C shows that the low pressure intersection is in fact metastable, since the field of anthophyllite (Greenwood, 1963) prevents the stable coexistence of talc, enstatite, quartz, and water at low pressures. Other equilibria, such as the orthoclase–quartz–vapor eutectic, will similarly make the equilibria shown in figure 7A metastable but will not affect the topology.

Figure 6 shows the experimentally determined equilibria bearing on this question. It is not possible to determine whether the invariant point involving both the curves occurs at very low temperatures and pressures or at very high pressures. Both curves have the same slope within the uncertainties of available thermochemical data.

Consideration of figures 6 and 7 shows, however, that regardless of the location of the invariant point, the assemblage phlogopite + quartz is more stable than the assemblage talc + potassium feldspar over a large range of P-T conditions, including those to be expected in the lower grades of metamorphism.

It is suggested, then, that even small activities of component $KAlSi_3O_8$ are sufficient to eliminate the stability field of talc in favor of phlogopite. This component is available in many rocks and may be derived from detrital illite or muscovite.

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