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THE EXPERIMENTAL CALIBRATION OF CONTINUOUS REACTIONS IN SILICEOUS CARBONATE ROCKS

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ABSTRACT

Phase relations among the minerals quartz-talc-carbonate and quartz-tremolite-carbonate in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2\text{-}H_2O$ are described and related to temperature-gas composition diagrams. Equilibrium surfaces are calculated for $3MgCO_3 + 4SiO_2 + H_2O \rightleftarrows Mg_3Si_4O_{10}(OH)_2 + 3CO_2$, and $2CaCO_3 + 5MgCO_3 + 8SiO_2 + H_2O \rightleftarrows Ca_2Mg_5Si_8O_{22}(OH)_2 + 7CO_2$.

For the three-mineral assemblages, talc-quartz-calcite and tremolite-quartz-calcite, it is possible to calculate equilibrium surfaces as functions of either the activity of $MgCO_3$ or the mole fraction of $MgCO_3$ in calcite. Such surfaces, contoured for mole fraction of $MgCO_3$ in calcite, are useful in field studies since a three-mineral assemblage containing calcite of known composition can be correlated with an isobarically univariant curve on a temperature-gas composition diagram.

INTRODUCTION

The progressive metamorphism of siliceous carbonate rocks is generally calibrated by a series of discontinuous reactions that can be observed in the field (*e.g.* Trommsdorff 1972) and studied experimentally (*e.g.* Skippen 1971). Thompson (1957) has distinguished between *discontinuous* and *continuous* reactions in studies of pelitic schists. The discontinuous reactions, described by Thompson, are comparable to the isograds normally mapped in siliceous marbles where one assemblage of phases is replaced by an alternative assemblage in the prograde sequence. It is also possible to define continuous reactions in siliceous carbonates to describe the changes in mineral composition for a particular assemblage in response to changing conditions of metamorphism. The present paper outlines the method by which existing experimental data can be used to calibrate the continuous change in the composition of magnesian calcite coexisting with talc plus quartz or tremolite plus quartz. If the equilibrium composition of magnesian calcite in either of these assemblages is measured by electron microprobe (Hutcheon & Moore 1973), it is possible to assign the three-mineral assemblage to an isobarically univariant curve.

PHASE RELATIONS AMONG TALC-QUARTZ-CARBONATE

The first appearance of talc in equilibrium with a carbonate mineral in prograde metamorphism is usually governed by the equilibrium:

$$3MgCO_3 + 4SiO_2 + H_2O \leftrightarrows Mg_3Si_4O_{10}(OH)_2 + 3CO_2 \qquad (1)$$

It should be emphasized that each of the terms in equilibria such as (1) refers to a component rather than a phase. Thus, $MgCO_3$ does not imply the presence of the phase, magnesite, but rather the component, $MgCO_3$, which can be dissolved to a significant extent in calcite, dolomite, or magnesite.

The energy balance required for equilibrium (1) is given by,

$$3\mu_{MgCO_3} + 4\mu_{SiO_2} + \mu_{H_2O} \leftrightarrows \mu_{Mg_3Si_4O_{10}(OH)_2} + 3\mu_{CO_2}$$

where μ_i is the chemical potential of component *i*. If the minerals, talc and quartz occur as pure phases, the chemical potentials of $Mg_3Si_4O_{10}(OH)_2$ and SiO_2 are not functions of composition and have a fixed value for specified total pressure and temperature. The chemical potentials of H_2O and CO_2 can vary with changing composition of the fluid phase at a specific temperature and total pressure. Similarly, the chemical potential of $MgCO_3$ can vary with changing composition of the carbonate phase, the highest value being associated with pure magnesite (Fig. 1a). As the carbonate phase dissolves $CaCO_3$ (Fig. 1b), the chemical potential of $MgCO_3$ is lowered until the magnesite-dolomite immiscibility gap is encountered (Fig. 1c). At this point the chemical potential of $MgCO_3$ has the same value in both magnesite and dolomite and the two carbonate minerals can coexist. The chemical potential of $MgCO_3$ is further lowered as $CaCO_3$ is added to dolomite (Fig. 1d) until the chemical potential of $MgCO_3$ has the same value in calcian dolomite as magnesian calcite and the calcite-dolomite immiscibility gap is reached (Fig. 1e). The chemical potential of $MgCO_3$ is further lowered by dilution of $MgCO_3$ with

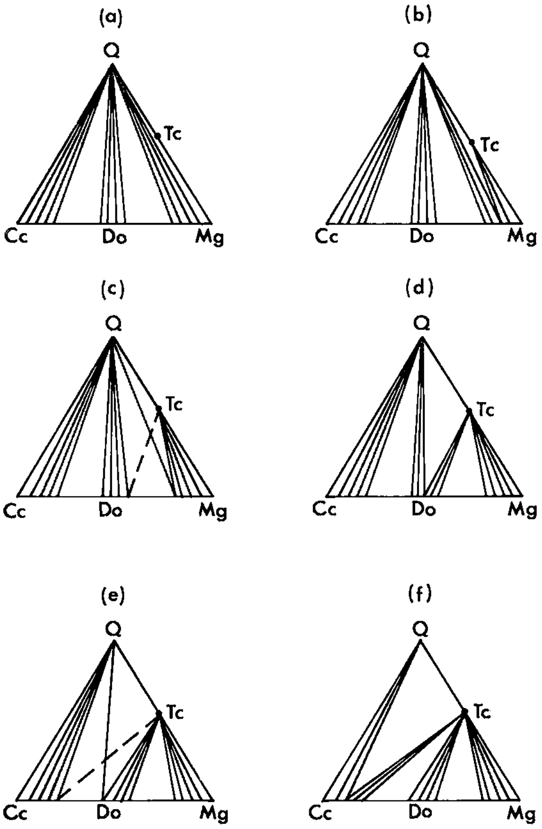

FIG. 1. Phase relations among the minerals talc-quartz-carbonate in the system $CaO-MgO-SiO_2-CO_2-H_2O$, projected onto the triangle $CaO-MgO-SiO_2$. (a) Talc forms first along the join, quartz-magnesite, as studied by Johannes (1969). (b) The reaction moves into the ternary system if the chemical potential of $MgCO_3$ is lowered. (c) The magnesite-dolomite two-phase region is encountered. (d) Only dolomite coexists with talc plus quartz. (e) The calcite-dolomite two-phase region is encountered. (f) Only calcite coexists with talc + quartz. Symbols: Q, quartz; Tc, talc; Cc, calcite; Do, dolomite; Mg. magnesite.

$CaCO_3$ in magnesian-calcite (Fig. 1f) until the talc-bearing assemblage becomes metastable with respect to a tremolite-carbonate assemblage (Skippen 1974). Thus, the chemical potential of $MgCO_3$ in equation 1 can vary at specified total pressure and temperature, from a maximum value given by the free energy of pure magnesite to a value that approaches negative infinity as the composition of the carbonate approaches pure $CaCO_3$.

Existing studies of equilibrium 1 (for example, Gordon & Greenwood 1970) have considered the cases in which $MgCO_3$ exists in pure magnesite (Fig. 1a) and in coexisting calcite-dolomite (Fig. 1e). In this paper, we will extend the use of experimental data to calibrate the conditions at which the three-mineral assemblage, talc-calcite-quartz (Fig. 1f), can exist in siliceous marbles.

PHASE RELATIONS AMONG TREMOLITE-QUARTZ-CARBONATE

The first appearance of tremolite in siliceous carbonates is controlled by the equilibrium:

$$2CaCO_3 + 5MgCO_3 + 8SiO_2 + H_2O \rightleftharpoons Ca_2Mg_5Si_8O_{22}(OH)_2 + 7CO_2 \tag{2}$$

The range of phase relations to which equilibrium (2) can apply is shown on Figure 2. The lower stability of tremolite is indicated on Figure 2a by a discontinuous reaction in which dolomite, magnesite, quartz and fluid react to form tremolite. Since both carbonate components are involved in the left hand side of equilibrium 2, it is possible to extend the stability field of carbonate plus quartz in equilibrium

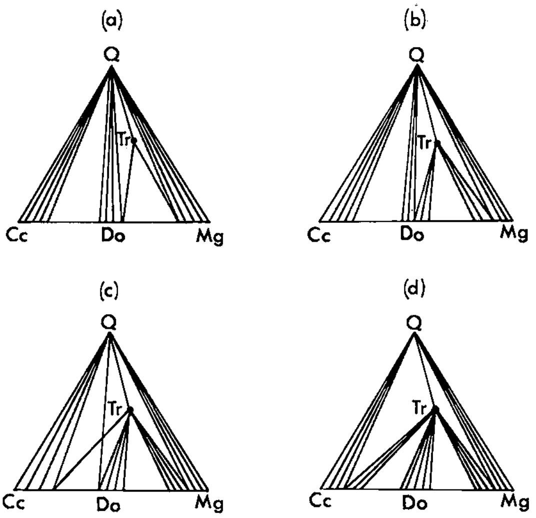

FIG. 2. Phase relations among the minerals tremolite-quartz-carbonate in the system $CaO-MgO-SiO_2-CO_2-H_2O$, projected onto the triangle $CaO-MgO-SiO_2$. (a) Tremolite forms by a discontinuous reaction involving dolomite, magnesite and quartz. (b) As the chemical potential of $CaCO_3$ is lowered, tremolite coexists with quartz plus magnesite. By lowering the chemical potential of $MgCO_3$, tremolite also coexists with dolomite plus quartz. (c) The calcite-dolomite two-phase region is encountered. (d) Tremolite coexists with either magnesite plus quartz or calcite plus quartz. Symbols: Q, quartz; Tr, tremolite; Cc, calcite; Do, dolomite; Mg, magnesite.

with tremolite by allowing the carbonate to become either more calcium- or more magnesium-rich, as shown in Figure 2b. Thus, it is possible for equilibrium to hold at fixed total pressure, temperature and gas composition for 2 different carbonate compositions *i.e.* the assemblages, tremolite-quartz-magnesite and tremolite-quartz-dolomite, as shown on Figure 2b. The bulk composition determines which of the two possible assemblages is present in a rock. With continued dilution of $MgCO_3$ in dolomite, the calcite-dolomite immiscibility gap is encountered in Figure 2c. At this point, both calcite and dolomite coexist in the same assemblage with tremolite plus quartz. This assemblage is frequently used to define an isograd in marbles (Trommsdorff 1972; Hutcheon & Moore 1973). Further dilution of either $CaCO_3$ in magnesite or $MgCO_3$ in calcite is possible with the chemical potential of $MgCO_3$ approaching negative infinity as the carbonate approaches pure calcite and the chemical potential of $CaCO_3$ approaching negative infinity as the carbonate approaches pure magnesite (Fig. 2d).

EXPERIMENTAL DATA

Equilibrium 1 has been studied experimentally in the system CaO-MgO-SiO_2-CO_2-H_2O by Metz *et al.* (1968), Metz & Puhan (1970), Gordon & Greenwood (1970) and Skippen (1971). In all of these experiments the equilibrium was studied for the case in which calcite coexisted with dolomite. (Fig. 1e). Gordon & Greenwood (1970) calculated an equilibrium constant by obtaining an expression for the activity of $MgCO_3$ in coexisting calcite-dolomite and by choosing pure magnesite as the standard state for $MgCO_3$. The same procedure was followed by Skippen (1974) to obtain the following expression, for an equilibrium constant that is consistent with all of the above experimental data:

$$(1)\ \log K = \frac{-11935}{T} + 24.634 + \frac{0.2014(P_{\text{total}}-1)}{T}$$

with temperature, T, in degrees K, and total pressure in bars. The standard states for $Mg_3Si_4O_{10}(OH)_2$, $MgCO_3$, and SiO_2 are taken as pure talc, magnesite, and quartz at 1 bar, and the standard states for CO_2 and H_2O as the ideal gases at 1 bar.

Equilibrium 1 has also been studied by Johannes (1969) for the case in which the carbonate phase is pure magnesite (Fig. 1a). The equilibrium gas compositions reported by Johannes have been used to obtain the data points shown on Figure 3. Fugacities were calculated from gas pressures by assuming ideal mixing in the fluid phase and using fugacity coefficients for H_2O from Burnham *et al.* (1969) and for CO_2 from Skippen (1971). Data points measured by Johannes at 330 bars, 1000 bars, and 2000 bars were adjusted to 1 bar using the equation:

$$(2)\ \log K\ (1\ \text{bar}) = \log K\ (P) - \frac{\Delta Vs\ (1-P)}{2.3026\ RT}$$

Molar volume data used to calculate ΔVs, the volume change of the pure solids in the reaction,

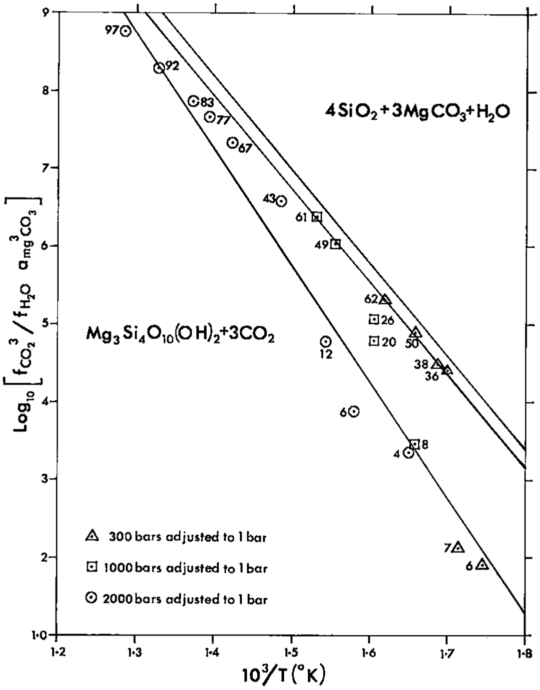

FIG. 3. Experimental measurements of the equilibrium constant for $4SiO_2 + 3MgCO_3 + H_2O = Mg_3Si_4O_{10}(OH)_2 + 3CO_2$. All data are adjusted to a total pressure on the solid phases of one bar. Data points are calculated from experiments reported by Johannes (1969) for the reaction of pure magnesite plus quartz to talc. Triangles were measured at 330 bars, squares at 1000 bars, circles at 2000 bars. Numbers beside data points indicate the per cent CO_2 in the gas phase measured by Johannes. The solid lines indicate the equilibrium constant with upper and lower limits of uncertainty as given by equation (1) from the text. Equation 1 is consistent with all available experimental data in the system CaO-MgO-SiO_2-CO_2-H_2O.

TABLE 1. CALCULATION OF EQUILIBRIUM CONSTANT FOR THE FORMATION OF TALC FROM QUARTZ AND MAGNESITE

Temp. °K	Mole %* CO_2	f_{CO_2}	f_{H_2O}	log $K(P)$	log $K(1)$
total pressure = 330 bars					
300	6	20.10	77.55	2.0197	1.906
310	7	23.47	76.73	2.2266	2.113
315	36	120.8	53.43	4.5186	4.406
320	38	128.2	54.42	4.5873	4.476
330	50	169.8	48.68	5.0024	4.893
345	62	213.8	38.00	5.4103	5.303
total pressure = 1000 bars					
330	8	93.84	133.4	3.792	3.458
350	20	241.4	140.8	5.000	4.677
350	26	313.8	130.2	5.375	5.052
370	49	604.7	106.6	6.317	6.004
380	61	760.1	88.14	6.697	6.389
total pressure = 2000 bars					
350	4	136.8	259.2	3.995	3.348
360	6	206.4	276.4	4.503	3.866
375	12	415.2	293.9	5.387	4.765
400	43	1503	230.3	7.169	6.570
430	67	2360	163.0	7.906	7.334
445	77	2721	124.2	8.210	7.649
455	83	2938	97.24	8.416	7.863
480	92	3275	52.16	8.828	8.294
505	97	3453	22.14	9.270	8.752

*Data from Johannes (1969)

were taken from Robie & Waldbaum (1968). The calculations are summarized in Table 1.

The agreement between equation 1 and the data points shown in Figure 3 from Johannes (1969) is within the limits of experimental uncertainty, except for compositions that are very water-rich or very CO_2-rich. All of the points calculated from gas compositions with less than 12% CO_2 or greater than 92% CO_2 fall outside of the experimental uncertainty in equation 1. Since the assumption of ideal mixing in the fluid phase is likely to hold best in compositions that approach either pure H_2O or pure CO_2, it is likely that the lack of agreement for CO_2-rich and CO_2-poor compositions arises from the experimental difficulty in accurately measuring the fluid composition when one of the components is present in small amounts. The agreement over most of the range of fluid composition is taken to verify the equilibrium constant given by equation 1 and the expression for the activity of $MgCO_3$ in coexisting calcite and dolomite given by Gordon & Greenwood (1970).

The equilibrium constant for equilibrium 2 is given by Skippen (1974) as:

$$(3)\ \log_{10} K = \frac{-29566}{T} + 61.707 + \frac{0.6401(P_{\text{total}} - 1)}{T}$$

with temperature in degrees K and total pressure in bars. The standard states for $Ca_2Mg_5Si_8O_{22}(OH)_2$, SiO_2, $CaCO_3$, and $MgCO_3$ are taken respectively, as pure tremolite, quartz, calcite and magnesite at 1 bar. Standard states for H_2O and CO_2 are the ideal gases at unit pressure.

T-X DIAGRAM FOR TALC-BEARING ASSEMBLAGES

The equilibrium constant for equilibrium 1 can be written:

$$(4)\ K = f_{CO_2}{}^3 \ / \ (a_{MgCO_3}{}^3 \cdot f_{H_2O})$$

where f_i and a_i are the fugacity or activity of component i. Activity terms are not included in 4 for $Mg_3Si_4O_{10}(OH)_2$ and SiO_2 since these components are assumed to occur in pure talc and pure quartz respectively. If the partial pressures, p, of CO_2 and H_2O sum to a specified total pressure (*i.e.*, the fluid phase is assumed to be a binary mixture) then the following equation can be written:

$$P_{\text{total}} = P_{CO_2} + P_{H_2O} \text{ or,}$$

$$(5)\ P_{\text{total}} = (f_{CO_2} \ / \ \gamma_{CO_2}) + (f_{H_2O} \ / \ \gamma_{H_2O})$$

where γ_i is the fugacity coefficient of component i. If numerical values of K in 4 are obtained from equation 1, then it is possible to solve 4 and 5 simultaneously for p_{CO_2} and p_{H_2O} at specified values of the activity of $MgCO_3$ and P_{total}. This procedure has been carried out by computer for a total pressure of 3000 bars at temperature intervals of 5 degrees between 350°C and 650°C. Fugacity coefficients from Burnham *et al.* (1969) and Skippen (1971) were used. The results are plotted on Figure 4 for activities of $MgCO_3$ varying between 1 and 0.1. Figure 4 is a projection of a continuous reaction surface, bounded on the low temperature side by a discontinuous reaction involving talc, quartz, pure magnesite and fluid. The discontinuous reaction bounding the surface on the high temperature side is not shown on Figure 4 but it is usually a reaction involving the formation of tremolite (Skippen 1974).

Of particular interest is the univariant across the surface on Figure 4 along which calcite and dolomite coexist with talc and quartz. This particular path corresponds to a discontinuous reaction which is generally mapped as an isograd in the field (*e.g.*, Trommsdorff 1972; Puhan & Hoffer 1973). This path can be obtained from direct experimental data, or the path can be calculated from the expression given by Gordon & Greenwood (1970) for the activity of $MgCO_3$ in calcite coexisting with dolomite, *i.e.*

$$(6)\ \text{Ln}\ a_{MgCO_3} = \frac{-1683}{T} + 1.1177$$

The line shown on Figure 4 for coexisting calcite and dolomite is the path traced across the contoured activity surface by equation 6.

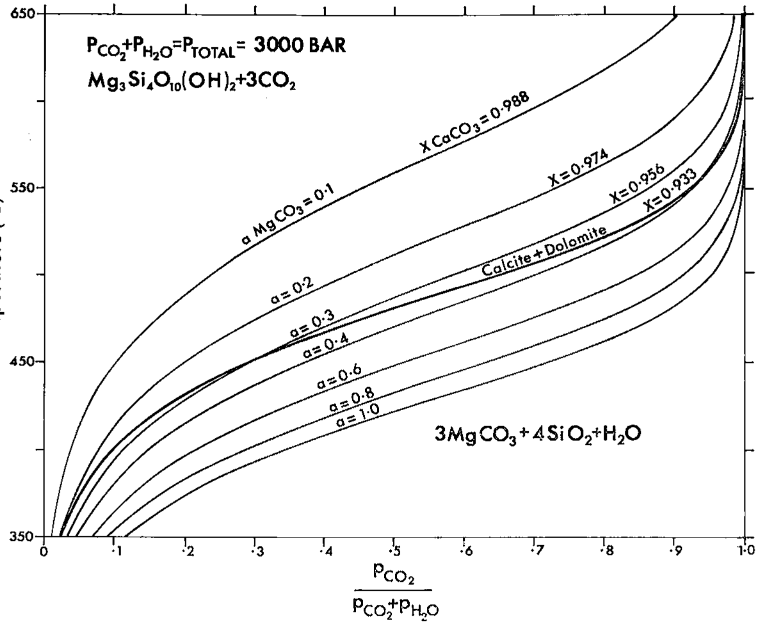

FIG. 4. Temperature-gas composition diagram at a total pressure of 3000 bars for the equilibrium: $3MgCO_3 + 4SiO_2 + H_2O \leftrightharpoons Mg_3Si_4O_{10}(OH)_2 + 3CO_2$. The equilibrium is represented by a surface contoured for the activity of $MgCO_3$ in the carbonate phase. The curve labelled calcite + dolomite indicates the temperatures, gas compositions and carbonate activities for the coexistence of both calcite and dolomite with talc and quartz. Activity coefficients given by Gordon & Greenwood (1970) have been used to convert the activity contours to mole fraction of $CaCO_3$ in calcite for the assemblage, talc-quartz-calcite.

The surface in Figure 4 contoured for the activity of $MgCO_3$ is less useful in practice than a similar surface contoured for the mole fraction of $MgCO_3$. Activity coefficients for $MgCO_3$ in calcite have been published by Gordon & Greenwood (1970, equation 6):

(7) $\text{Ln}\,\gamma_{MgCO_3} = (1 - X_{MgCO_3})^2\,(2.1718 - 1.8960\,X_{MgCO_3})$
$0 \leqslant X_{MgCO_3} \leqslant 0.18$

From the definition of the activity coefficient:

(8) $a_{MgCO_3} = \gamma_{MgCO_3}\,X_{MgCO_3}$

Equations 7 and 8 have been used to correlate activity contours with mole fraction of $MgCO_3$ in calcite. It is not, however, possible to contour the entire surface for composition since activity coefficients for $MgCO_3$ in dolomite and magnesite are not available. For application to siliceous carbonates, that portion of the surface which can presently be contoured is the most important since calcite is the most common carbonate phase in marble.

T-X DIAGRAM FOR TREMOLITE-BEARING ASSEMBLAGES

The calculation of activity contours on a $T - X_{CO_2}$ section is complicated by the presence of both $CaCO_3$ and $MgCO_3$ in equilibrium (2).

The equilibrium constant is given by:

(9) $K = f_{CO_2}{}^7 \,/\, (a_{MgCO_3}{}^5 \cdot a_{CaCO_3}{}^2 \cdot f_{H_2O})$

The Gibbs-Duhem equation indicates that the activities of two components in a binary phase cannot be varied independently, and it is not therefore possible to assign arbitrary values to the activities of both $MgCO_3$ and $CaCO_3$. Gordon & Greenwood (1970) have used the Gibbs-Duhem equation to obtain the following expression for the activity coefficient of $CaCO_3$ in calcite:

(10) $\text{Ln}\,\gamma_{CaCO_3} = (1 - X_{CaCO_3})^2\,(1.2238 + 1.8960\,X_{CaCO_3})$

It is therefore possible to choose arbitrary values of a_{MgCO_3} and to calculate X_{MgCO_3} from equations 7 and 8. X_{CaCO_3} is obtained from the requirement that the mole fraction sum to unity:

$$(11)\ X_{CaCO_3} + X_{MgCO_3} = 1$$

The activity of $CaCO_3$ is then obtained from equations 8 and 10 and substituted into 9 along with the arbitrarily chosen value of a_{MgCO_3}. Numerical values of K were obtained from equation 3 at a total pressure of 3000 bars and activity contours were determined by computer as outlined in the previous section for equilibrium 1. Since the values of Ln γ_{CaCO_3} in equation 10 hold only for $CaCO_3$ dissolved in calcite, it is possible to calculate only that portion of the reaction surface on which calcite is the stable carbonate phase. Results for tremolite coexisting with calcite + quartz are shown on Figure 5.

CONCLUSION

Hutcheon & Moore (1973) have used the $MgCO_3$ content of calcite to determine the temperature at which calcite equilibrated with coexisting dolomite in metamorphosed siliceous marbles. The data given on Figures 4 and 5 provide a basis for extending this approach to marbles in which calcite is the only carbonate phase present. If total pressure is known or can be estimated, then the composition of calcite coexisting with tremolite plus quartz or with talc plus quartz can be used to relate the temperature and fluid composition at which a particular assemblage has equilibrated. This approach can be extended to a number of equilibria commonly observed in siliceous carbonates provided equilibrium constants have been measured experimentally.

REFERENCES

BURNHAM, C. W., HOLLOWAY, J. R. & DAVIS, N. F. (1969): Thermodynamic properties of water to 1000°C and 10,000 bars. *Geol. Soc. Amer. Spec. Paper* **132.**

GORDON, T. M. & GREENWOOD, H. J. (1970): The reaction: dolomite + quartz + water = talc + calcite + carbon dioxide. *Amer. J. Sci.* **268,** 225-242.

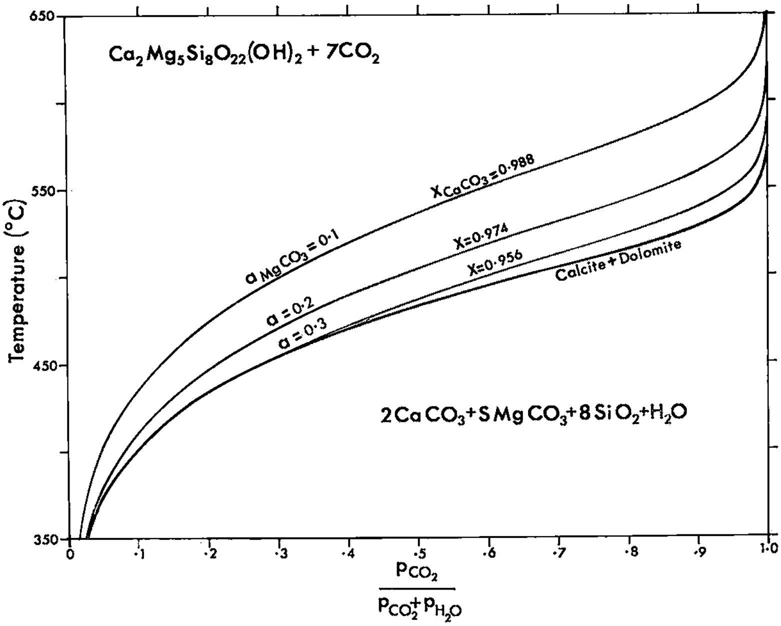

FIG. 5. Temperature-gas composition diagram at a total pressure of 3000 bars for the equilibrium: $2CaCO_3 + 5MgCO_3 + 8SiO_2 + H_2O \leftrightharpoons Ca_2Mg_5Si_8O_{22}(OH)_2 + 7CO_2$. The equilibrium can be represented by a surface contoured for the activity of $MgCO_3$ for that portion of the phase relations in which calcite or calcite + dolomate coexist with tremolite plus quartz. Activity coefficients from Gordon & Greenwood (1970) have been used to convert the activity contours to mole fraction of $CaCO_3$ in calcite.

HUTCHEON, IAN, & MOORE, J. M. (1973): The tremolite isograd near Marble Lake Ontario. *Can. J. Earth Sci.* 10, 936-947.

JOHANNES, W. (1969): An experimental investigation of the system MgO-SiO_2-H_2O-CO_2. *Amer. J. Sci.* 267, 1083-1104.

METZ, P. & PUHAN, D. (1970): Experimentelle Untersuchung der Metamorphose von kieselig dolomitischen sedimenten. *Contr. Mineral. Petrol.* 18, 305-309.

——— . ——— & WINKLER, H. G. F. (1969): Equilibrium reactions on the formation of talc and tremolite by metamorphism of siliceous dolomite. *Naturwiss.* 55, 225-226.

PUHAN, D. & HOFFER, E. (1973): Phase relations of talc and tremolite in metamorphic calcite-dolomite sediments in the southern portion of the Damara Belt (South West Africa). *Contr. Mineral. Petrol.* 40, 207-214.

ROBIE, R. A. & WALDBAUM, D. R. (1968): Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1259.

SKIPPEN, G. B. (1971): Experimental data for reactions in siliceous marbles. *J. Geol.* 79, 451-481.

——— (1974): An experimental model for low pressure metamorphism of siliceous dolomitic marble. *Amer. J. Sci.* 274, 487-509.

THOMPSON, J. B. (1957): The graphical analysis of mineral assemblages in pelitic schists. *Amer. Mineral.* 42, 842-858.

TROMMSDORFF, V. (1972): Change in T - X during metamorphism of siliceous dolomitic rocks of the Central Alps. *Schweiz. Mineral. Petrog. Mitt.* 52, 567-571.

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