

THE STABILITY OF GROSSULARITE IN H₂O-CO₂ MIXTURES

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ABSTRACT

Phase relations in the system CaO-Al₂O₃-SiO₂-H₂O-CO₂ have been calculated on the basis of previous work in the systems CaO-Al₂O₃-SiO₂-H₂O and CaO-SiO₂-H₂O-CO₂.

Experimental determination of the equilibria:

- (1) calcite + anorthite + wollastonite = grossularite + CO₂ and
(2) calcite + anorthite + quartz = grossularite + CO₂

in water-carbon dioxide mixtures verify the calculations. The equilibrium boundary for reaction (1) at 2000 bars passes approximately through the points: $X_{\text{CO}_2}=0.15$, $T=590^\circ\text{C}$; $X_{\text{CO}_2}=0.20$, $T=665^\circ\text{C}$; and $X_{\text{CO}_2}=0.30$, $T=790^\circ\text{C}$. The equilibrium boundary of reaction (2) passes approximately through the points: $X_{\text{CO}_2}=0.10$, $T=550^\circ\text{C}$, and $X_{\text{CO}_2}=0.08$, $T=530^\circ\text{C}$. Grossularite is stable on the water-rich sides of the above boundaries.

Application of the phase equilibria to natural assemblages shows that fluid composition is an important variable in the Nanga Parbat region, and that natural systems may be either "open" or "closed" with respect to H₂O and CO₂.

INTRODUCTION

Garnets of the ugrandite series are common both in regionally metamorphosed and contact metasomatized rocks. As the host rock is often a carbonate, knowledge of the effect of CO₂ on garnet stability is useful in interpreting natural occurrences. This is a report of an experimental study of some equilibria involving the calcium end-member, grossularite, and H₂O-CO₂ fluid phase.

A comprehensive study by Boettcher (1970) reviews and summarizes experimental work in the CO₂-free system CaO-Al₂O₃-SiO₂-H₂O. Papers dealing particularly with grossularite include those of Yoder (1950, 1953), Roy and Roy (1957), Pistorius and Kennedy (1960), Newton (1965, 1966), Hays (1967), Liou (1969), and Storre (1970).

Greenwood (1962, 1967b), Wyllie and Haas (1965, 1966), and Boettcher and Wyllie (1969) have described equilibria in the system CaO-SiO₂-H₂O-CO₂. Their work, and that cited above, permits calculation of several equilibria in the combined system CaO-Al₂O₃-SiO₂-H₂O-CO₂.

THEORETICAL PHASE RELATIONS

This study has been restricted to equilibria at 2000 bars total pressure and temperatures between 400° and 900°C. This eliminates the following phases: lawsonite, laumontite, prehnite, and wairakite (Liou, 1969, 1970); philipsite, scolecite, heulandite, and epistilbite (Koizumi and

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Roy, 1960); pyrophyllite (Kerrick, 1968); and gyrolite, truscottite, and tobermorite (Harker, 1964).

The further restriction that the field of interest lies at higher CO_2 pressures than the calcite-wollastonite-spurrite-vapor equilibrium (Wyllie and Haas, 1966) eliminates from consideration the phases: lime-silicate liquid, calciochondrodite, spurrite, portlandite, larnite, and rankinite. In this paper, as in Wyllie and Haas, tilleyite is neglected. It is rare in nature and has not been synthesized in the absence of fluoride.

In the absence of experimental data, the phase margarite and pure calcium scapolite, meionite, have not been considered. Margarite usually occurs in more aluminous assemblages than those of interest here, while pure meionite has not been found in nature.

The above restrictions, together with the requirement that the solid phases coexist with an $\text{H}_2\text{O}-\text{CO}_2$ fluid, permit the valid projection of mineral compositions onto the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ triangle. Such a projection is shown in Figure 1.

Phase relations of a system in which a binary vapor phase is present are conveniently represented on an isobaric temperature-mol fraction ($T-X$) diagram in which one axis represents the composition of the binary vapor (Greenwood, 1962, 1967a; Wyllie, 1962). The $T-X$ diagram for the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ was constructed by superimposing equilibrium relations from the bounding systems $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (Boettcher, 1970; Liou, 1969) and $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ (Green-

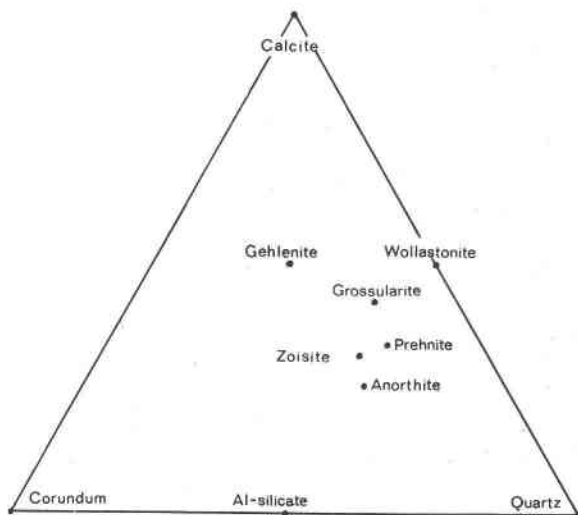


FIG. 1. Projection of mineral compositions in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ onto the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ triangle. Compositions in mol percent.

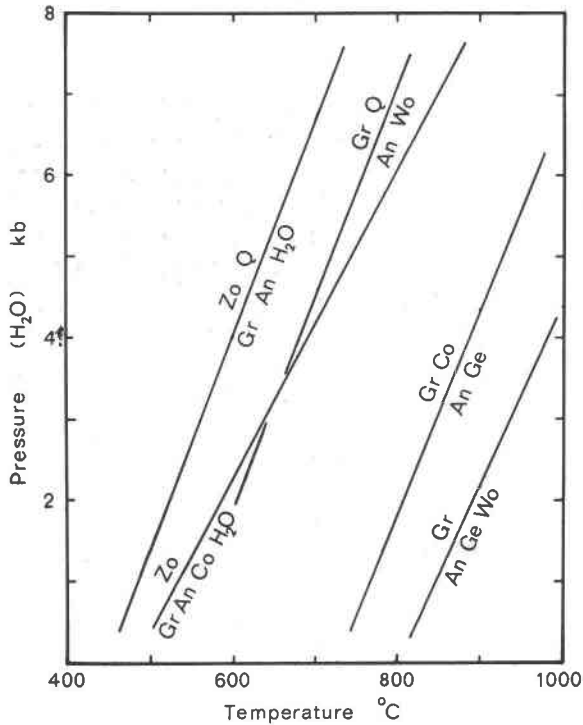
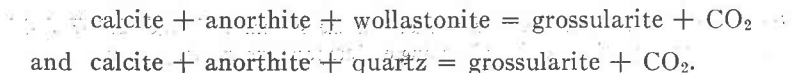


FIG. 2. Subsolidus equilibria in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (after Boettcher, 1970). Abbreviations—as in Figure 3.

wood, 1967b). Relevant subsolidus equilibria in the CO_2 free system are shown in Figure 2 (after Boettcher). The schematic T - X diagram for the five component system at 2000 bars total pressures is shown in Figure 3. Similar diagrams have recently been published by Kerrick (1970) and Store (1970). Both these authors suggest a low temperature termination of the stability field of grossularite+quartz by the reaction: zoisite + wollastonite = grossularite+quartz+ H_2O . This reaction is metastable. The results of Liou (1969) show that grossularite+quartz is a stable assemblage at temperatures where prehnite decomposes to zoisite, grossularite, quartz, and water and this data was used in constructing Figure 3.

The validity of Figure 3 has been tested by an experimental study of the reactions:



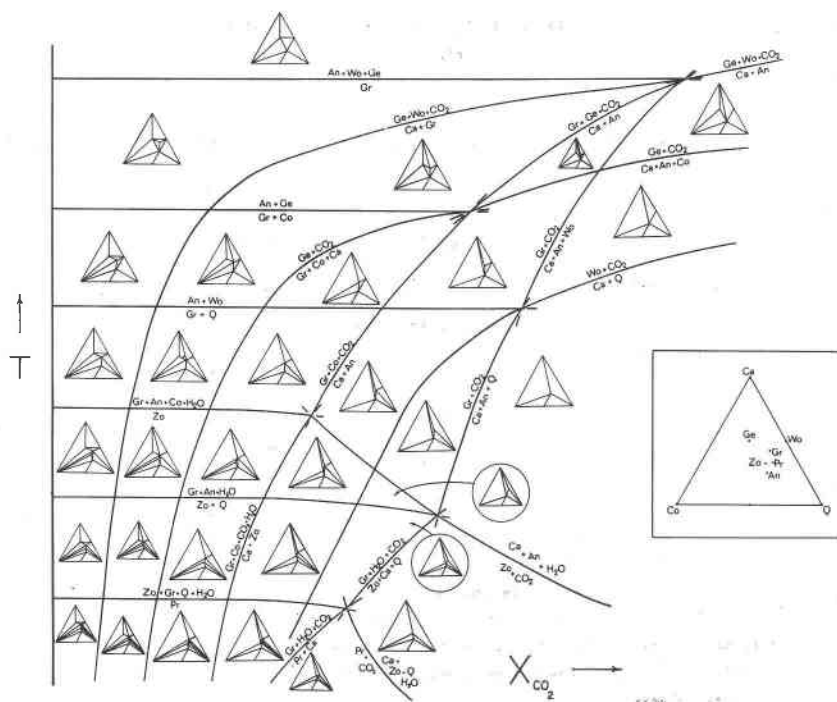


FIG. 3. Schematic temperature-mol fraction CO_2 diagram for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ at a total pressure of 2000 bars. All assemblages coexist with a binary $\text{H}_2\text{O-CO}_2$ fluid phase. Inset shows phases represented on compatibility triangles.

Abbreviations:—Ca—calcite; Ge—gehlinite; Wo—wollastonite; Gr—grossularite; Zo—zoisite; Pr—prehnite; An—anorthite; Co—Corundum; Q—quartz.

EXPERIMENTAL TECHNIQUE

Both natural minerals and synthetic phases were used as starting materials for the experiments.

Two specimens of grossularite with partial chemical analyses were kindly provided by Professor R. C. Newton of the Department of Geophysical Sciences, University of Chicago.

Unzoned anorthite was obtained from an augite-anorthite rock collected and described by Smitheringale (1955). Optical examination showed the anorthite to contain less than 1 percent of inclusions. Three separate glasses prepared from this anorthite had indices of refraction of $1.5725 \pm .001$, corresponding to composition An_{97} (Schaier *et al.*, 1956)

Wollastonite from Willsboro, New York was obtained from the collection of the University of British Columbia.

Calcite was obtained as Baker and Adamson Reagent Grade CaCO_3 .

Natural quartz from Lisbon, Maryland, containing less than 0.03 weight percent impurities was used after crushing and washing.

A glass of grossularite composition was prepared from the natural quartz, Baker and Adamson CaCO_3 , and gamma alumina prepared from Baker and Adamson Reagent Grade aluminum hydroxide.

Table 1. Analyses Of Starting Materials
Weight Percent

	Grossularite 1 (a)	Grossularite 2 (b)	Anorthite (c)	Wollastonite (c)
SiO ₂	-	41.0	40.86	50.12
TiO ₂	-	0.25	.02	.002
Al ₂ O ₃	-	23.2	36.62	.04
Fe ₂ O ₃	} 1.0	} 1.71	} 0.80 (as Fe ₂ O ₃)	} 0.90 (as Fe ₂ O ₃)
FeO				
MnO	0.6	0.67	.01	.06
MgO	0.23	0.24	.62	.17
CaO	-	36.2	20.75	47.24
Na ₂ O	-	0	.4	ND
K ₂ O	-	0	ND	ND
H ₂ O ⁺	-	0.19	-	-
Ni	-	-	.1	ND
Sr	-	-	.03	.007

^aAnalyst N. Suhr 1964, R. C. Newton pers. comm. 1968.

^bAnalyst E. Olsen 1958, R. C. Newton pers. comm. 1968.

^cAnalyzed by Coast Eldridge Ltd., Vancouver, 1968.

Ti, Mn, Na, K, Ni, Sr determined spectrographically.

ND - not detected.

Table 1 lists analyses of the natural starting materials. The iron and magnesium in the anorthite analysis are probably due to a small amount of augite in the specimen.

Equimolar mixtures of calcite, wollastonite, and anorthite; and calcite, wollastonite, and quartz were weighed and ground together under acetone. These mixtures, and 50-50 combinations of these mixtures with "grossularite 2" (see Table 1) were used as starting materials.

Distilled water and Canadian Liquid Carbonic "Hi-Dry" 99.95 percent carbon dioxide made up the fluid phase in runs in Morey bombs. Distilled water and Reagent Grade oxalic acid were used in some experiments.

Most experiments were made using the technique of Greenwood (1961, 1967a). Starting materials are supported in open platinum capsules in 25 cc Morey bombs. After the bombs are placed in the furnaces, sufficient CO₂ is added to keep the calcite stable until the bomb reaches the desired temperature. When the bomb reaches the temperature of the run, the CO₂ pressure is adjusted and water pumped in to bring the fluid to the desired composition and pressure.

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 CO₂, are determined volumetrically. Gas chromatography was not used to check the gas composition in these experiments, but a number of runs under similar conditions have shown negligible CO and CH₄ (Greenwood, 1967a, 1967b; Gordon and Greenwood, 1970).

The technique described by Holloway *et al.* (1968) was used in several experiments. Known amounts of water and oxalic acid were weighed into a 5-mm Pt capsule. The oxalic

acid was not dried or stored in a desiccator, but stored in and used directly from a tightly sealed bottle as suggested by Holloway (personal communication, 1969). Starting materials, in crimped 3-mm Pt capsules were added, and the large capsule was welded shut. Runs were made in Morey bombs and standard cold-seal apparatus. Under conditions of the experiments, the oxalic acid decomposes to CO_2 , H_2O , and H_2 . The excess hydrogen diffuses out of the capsule as the pressure medium, water, is at an oxygen potential approximately the Ni-NiO buffer.

Gas compositions are known to ± 3 percent in the Morey bomb experiments (Greenwood, 1967a) and to ± 1 percent in the oxalic acid experiments (weighing error).

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 the melting points of National Bureau of Standards zinc (m.p. 419.5°C), lead (m.p. 327.4°C), and aluminum (m.p. 660.2°C). Reagent NaCl (m.p. 800.4°C) was also used. Temperatures were uniform to 1°C over the three inch depth of the Morey bomb cavities and one inch at the specimen and of the cold seal bombs.

A Leeds and Northrup 16-point recorder was used to monitor each bomb temperature and periodic checks were made with a Leeds and Northrup K-3 potentiometer. Temperatures were controlled by Barber-Coleman on-off type controllers, solid-state proportional controllers (modified from Hadadiacos, 1969), and by limiting power to the furnaces with variable transformers. Maximum temperature uncertainties, including calibration, thermal gradient, and one-half of control fluctuation are listed in Table 2.

Run products were examined by optical and X-ray diffraction techniques. Run materials were very fine-grained, and identification of phases was made chiefly on the basis of X-ray diffractometer traces. Where possible, the refractive index of newly-formed grossularite was determined.

The direction of reaction was decided by noting which of the starting materials reacted to form the other phase or phases. If the starting material contained both reactants and products, direction of reaction was determined from the ratios of peak heights on diffractometer traces of the run products. The ratios of intensities of the grossularite (420) peak with the calcite (104) peak and the anorthite (204) peak were used in these determinations.

Calibration curves were prepared based on three oscillations of three separate mounts of known mixtures of run products and reactants. The maximum uncertainty in percent grossularite, based on the grossularite: calcite intensity ratio was ± 6 percent. The maximum uncertainty in percent grossularite from the grossularite: anorthite intensity ratio was ± 12 percent.

The direction of reaction of four-phase starting materials was not considered to be demonstrated unless determinations of percent grossularite from both calibration curves were consistent and amounted to at least 50 percent reaction.

Extents of reaction reported in Table 2 are subject to an unknown uncertainty due to differences between X-ray characteristics of calibration materials and run products.

The grossularites in the experiments have indices of refraction of $1.730 \pm .002$, indicating a small amount of hydrogrossular component. The runs nevertheless indicate the direction of the equilibrium curve. Roy and Roy (1957) have indicated that anhydrous grossularite is more stable than hydrogrossularite at temperatures as low as 400°C.

EXPERIMENTAL RESULTS

Experimental results are listed in Table 2 and shown in Figures 4 and 5. Fugacities were calculated using Skippen's (1967) compilation.

Figure 4 is a \ln fugacity CO_2 vs $1/T$ plot for a total pressure of 2000

Table 2. Experimental Results At 2000 Bars

Run	Temperature °C	Duration days	X _{CO₂}	ln(f _{CO₂})	Starting material	Products (Gr RI)	Percent reaction
39D	542±5	24	.008	3.355	Ca+An+Wo	Gr (1.730)	100
53E7 -4	540±6	97	.100*	5.881	Ca+An+Q Gr 1	Ca+An+Q Gr+Ca+An+Q	10
37E	543±6	64	.127	6.120	Gr 1	Gr+Ca+An+Q	95
43D	570±7	24	.026	4.539	Ca+An+Wo	Gr+An+Ca (1.730)	80
54G7	572±8	97	.126*	6.117	Ca+An+Q Gr 1	Ca+An+Q Gr+Ca+An+Q	20
6	699±4	15	.003	2.374	Ca+An+Wo	Gr+An+Wo	50
7	704±4	18	.108	5.957	Ca+An+Wo	Gr+An+Wo (1.731)	60
22-1 -2 -3 -4	700±11	15	.176	6.446	Gr 2 Ca+An+Wo 50:50 mix Gr glass	Gr Ca+An+Wo Gr increase Gr+Ca+An+Wo	80
27-A -B -C -D	706±4	15	.236	6.739	Ca+An+Wo Gr 1 50:50 mix Gr glass	Ca+An+Wo Gr+An+Wo+Ca less than 50% Ca+An+Wo+Gr	20
57	698±3	13	.347*	7.125	Gr 1	Gr+Ca+An+Wo	15
4	749±3	6	.149	6.274	Ca+An+Wo	Gr+Ca+An+Wo (1.729)	30
20-1 -2 -3 -4	750±6	10	.233	6.721	Gr 2 Ca+An+Wo 50:50 mix Gr glass	Gr Ca+An+Wo Gr increase Gr+Ca+An+Wo	50
25-A -B -C -D	755±4	7	.242	6.759	Ca+An+Wo Gr 1 50:50 mix Gr glass	Ca+An+Wo Gr Gr increase Gr+Ca+An+Wo	50
33-A -B -C -D	751±10	7	.567	7.610	Ca+An+Wo Gr 1 50:50 mix Gr glass	Ca+An+Wo Gr+Ca+An+Wo less than 50% Ca+An+Wo+Gr	30
46-A -B	848±2	7	.298*	6.956	Gr 1 50:50 mix	Gr Gr increase	60
48-A -B	849±3	7	.400*	7.250	Gr 1 50:50 mix	Gr+Ca+An+Wo less than 50%	10

*Runs using technique of Holloway *et al.* (1968). All other runs in Morey bombs using technique of Greenwood (1967).

bars. The results of the experiments reported here are shown along with Greenwood's (1967b) determination of the calcite+quartz=wollastonite+CO₂ equilibrium and Boettcher's (1970) and Newton's (1966) determination of the grossularite+quartz=wollastonite+anorthite equilibrium.

The slopes shown for the reactions determined in this study were cal-

culated from data in Robie and Waldbaum (1968), with the added information that ΔH_R (2000 bars) = 22.9 kcal for the reaction calcite + quartz = wollastonite + CO_2 (Greenwood, 1967b).

Note that the starting material for runs 39 and 43 were Ca + An + Wo and hence these runs do not strictly bracket the calcite + anorthite + quartz = grossularite CO_2 curve. The locus of this equilibrium is however strongly restricted by the calcite + quartz = wollastonite CO_2 curve and by runs 53E4, 37E, and 43D.

The four isobarically univariant equilibrium curves shown in Figure 4 must intersect at an isobaric invariant point. The area of intersection is within experimental error. No further refinement of available thermochemical data can be made on the basis of the data presented here.

Figure 5 is a T - X_{CO_2} diagram for a total pressure of 2000 bars showing the same data as Figure 4. Other equilibria have been calculated as

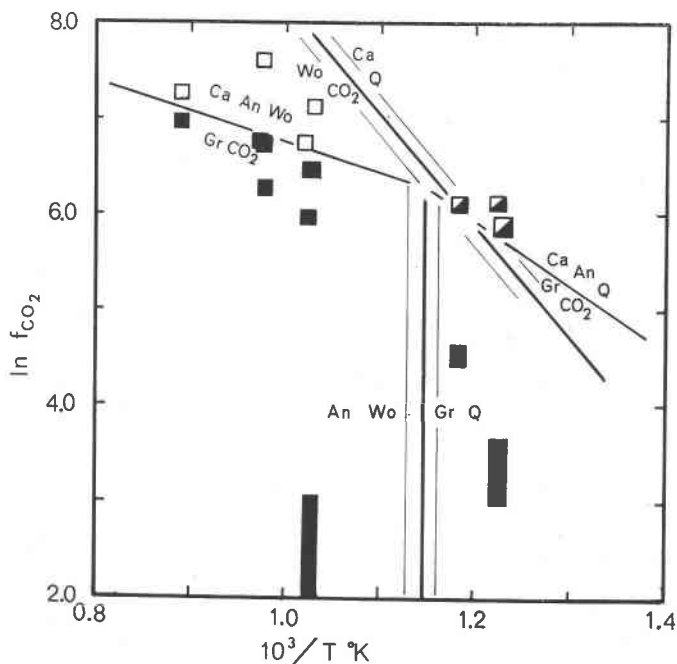


FIG. 4. Experimental results at 2000 bars. Calcite + quartz = wollastonite + CO_2 curve from Greenwood (1967b), grossularite + quartz = wollastonite + anorthite curve from Boettcher (1970) and Newton (1966). Heavy lines indicate experimentally determined boundaries, light lines, experimental uncertainties. Solid symbols—grossularite grew at the expense of calcite, wollastonite, and anorthite. Open symbols—calcite, wollastonite, and anorthite grew from grossularite. Half-shaded symbols—calcite, anorthite, and quartz grew from grossularite.

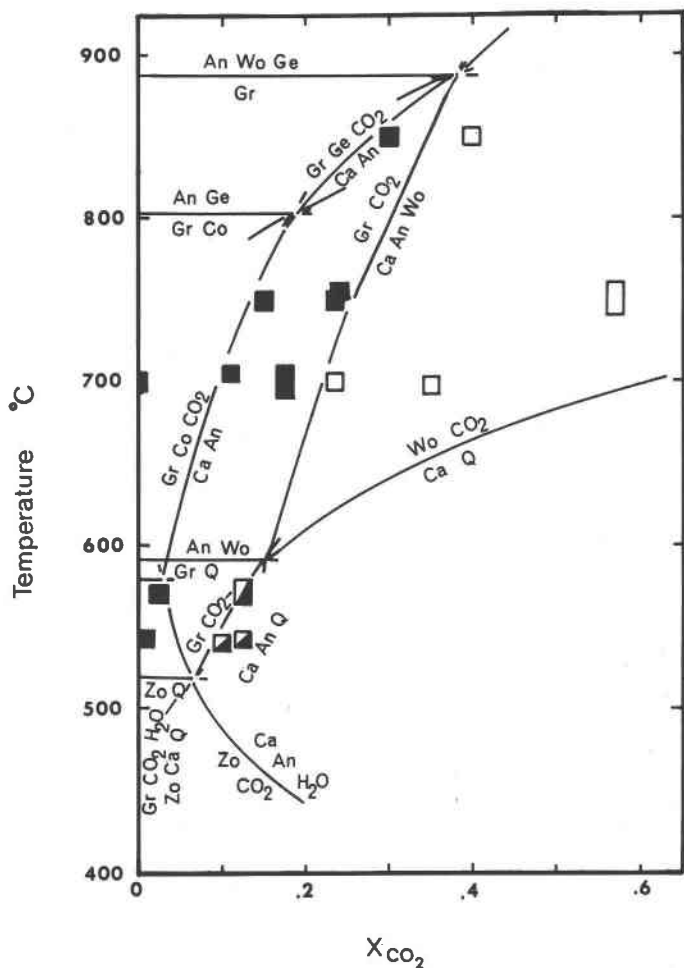


FIG. 5. Experimental results and calculated equilibria for a total pressure of 2000 bars. Symbols as in Figure 4. Some equilibria have been omitted for clarity.

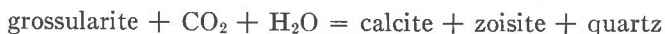
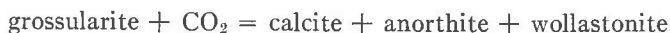
described below. Figure 5 may be compared with Figure 3, which shows schematically the same phase relations.

The reactions shown in Figure 5 were calculated using the relationships derived by Greenwood (1962, 1967a), the thermochemical data mentioned above, and dP/dT of 26.7 bars/degree for zoisite+quartz = anorthite+grossularite+ H_2O from the data of Boettcher (1970). The position of the isobaric invariant point of Figure 4 was taken as 590° , $X_{CO_2}=0.15$.

Calculations were facilitated by assuming that water and carbon dioxide mix ideally at these temperatures and pressures. As yet no equilibrium determined in H₂O-CO₂ mixtures invalidates this hypothesis.

It must be emphasized that other equilibria in this system occur in water-rich compositions at the edge of Figure 5. (Wyllie and Haas, 1966). Although they do not affect the equilibria shown here, they should be considered in any attempt to apply the phase diagram to natural assemblages.

The reactions restricting the grossularite field are, from high to low temperatures:



These reactions place strict limits on the conditions of formation of grossularites believed to have grown in equilibrium with a fluid phase.

The calculated equilibria also show that, at 2000 bars, zoisite is restricted to temperatures below 500 degrees in fluids containing more than 10 mole percent CO₂. The thermochemical data for zoisite is limited and the calculated reaction should be considered as a first approximation only.

A recent study by Storre (1970) redetermines the equilibrium: grossularite+quartz=anorthite+wollastonite, placing the equilibrium at 630° at 2 kilobars. Although Storre's runs agree with Newton's within their stated experimental uncertainties, references to our Figures 4 and 5 shows the 630° mid-point of Storre's reversals to be incompatible with both of our experimentally determined reactions limiting the stability of grossularite in H₂O-CO₂ mixtures. All three studies used reversed reactions, but different starting materials, but this difference seems inadequate to explain the discrepancy. In view of our agreement with Newton (1966), Boettcher (1970), and Greenwood (1976b), we prefer to leave the invariant point at the position shown in Figure 5.

APPLICATION TO NATURAL ASSEMBLAGES

Kerrick (1970) has published an analysis of mineral assemblages in contact metamorphosed calcareous rocks in the Sierra Nevada. He discusses particularly the effects of plagioclase composition and the addition of ferric iron to the simple system described here. Further refinement of the phase relations must await additional experimental studies.

It is of interest, however, to compare the calc-silicate rocks of Nanga Parbat (Misch, 1964) with those predicted from experimental work. The

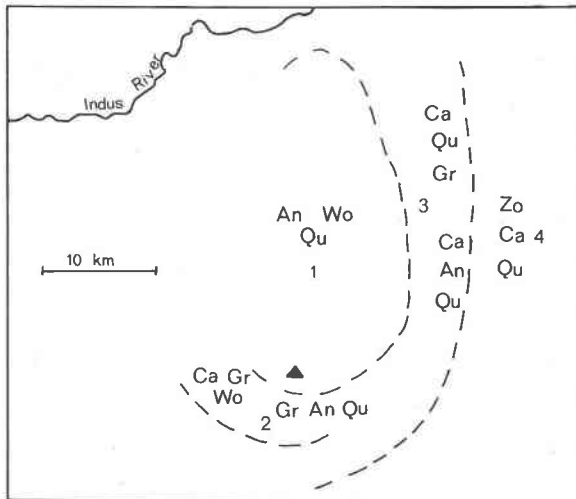


FIG. 6. Three phase calc-silicate assemblages of the Nanga Parbat region as reported by Misch (1964). Numbers refer to metamorphic zones described by Misch.

rocks described by Misch include the assemblages: anorthite-wollastonite-quartz; calcite-grossularite-wollastonite; grossularite-anorthite-quartz; calcite-quartz-grossularite; calcite-anorthite-quartz; and zoisite-calcite-quartz.

The assemblages reported indicate that CO_2 pressures were high enough that the liquidus relationships described by Wyllie and Haas (1966) can be safely neglected. Plagioclase compositions are all extremely calcic, hence anorthite may be considered as a reasonable approximation to the actual feldspar. No data are available on the iron content of the garnets, so it is assumed in the following discussion that the phase equilibria are not seriously affected by the addition of some ferric iron.

A minimum total pressure of 5.5. kbar is indicated by presence of kyanite and sillimanite to the exclusion of andalusite (Richardson *et al.*, 1969). Water pressure must have been close to total pressure as muscovite and quartz are stable in all but the highest grade rocks in the core of the massif. If a total pressure of 6kb is assumed, with $P_{\text{fluid}} = P_{\text{total}}$, then an approximate T - X diagram for $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ can be constructed.

Relevant three-phase assemblages, as reported by Misch, are shown in Figure 6. Sillimanite or fibrolite occur in the inner two zones, while kyanite is the stable polymorph in the outer zones.

Figure 7 illustrates the relative stability fields of the calc-silicate as-

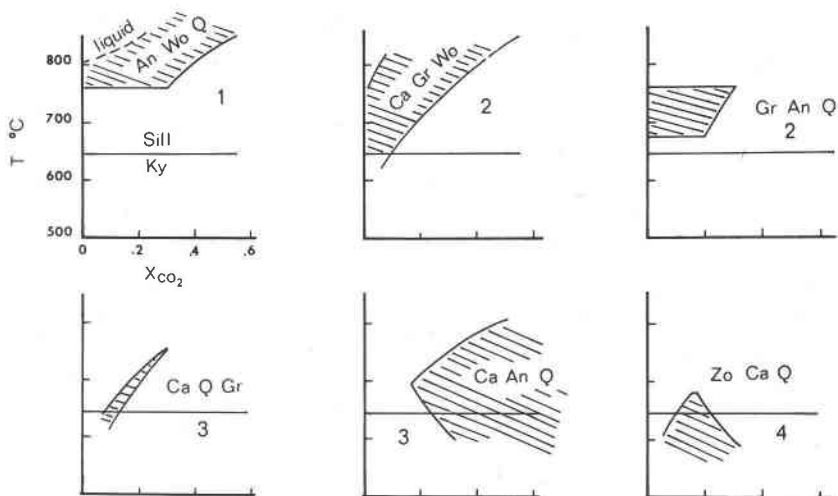


FIG. 7. Approximate stability fields of some assemblages in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ at a total pressure of 6 kbar. Numbers indicate the equivalent zone on Misch's map.

semblages. The diagrams are based on Boettcher's (1970) work and an extrapolation of Harker and Tuttle's (1956) calcite+quartz=wollastonite+ CO_2 curve. The calculated fluid compositions are sensitive to small changes in temperature, but the relative positions of the three-phase fields are correct.

Figures 6 and 7 show several interesting features. Temperatures in the inner An-Wo-Q zone are bracketed by the grossularite+quartz=wollastonite+anorthite reaction and by the An-Wo-Q-liquid-vapor eutectic (Boettcher, 1970). In Misch's Zone 2, the Gr-An-Q assemblage provides a much tighter temperature calibration than the Ca-Gr-Wo assemblage, although both fields overlap in fluid composition. The Ca-Q-Gr and Ca-An-Q fields also overlap, but at temperatures where kyanite is the stable aluminosilicate, the fields are distinct, supporting Misch's suggestion that P_{CO_2} varied throughout the area. Finally, the Zo-Ca-Q assemblage of the outer zone indicates comparatively water-rich fluids, verifying Misch's conclusion based on muscovite stability.

The mineral assemblages of Nanga Parbat discussed above indicate that the local assemblages were effectively 'open' to H_2O and CO_2 although there were apparently variations in proportions from place to place. A somewhat similar situation apparently existed during the metamorphism of the rocks of the Whetstone Lake area, Ontario, described

by Carmichael (1970), in which the pore fluids in adjacent pelitic and carbonate-rich beds had very similar H_2O/CO_2 ratios and where regional gradients in this ratio must have also existed. A further example of a carbonate-rich system that was apparently open to CO_2 and H_2O has been described by Greenwood (1967b), from Salmo, British Columbia. There wollastonite occurs close to the contact of a quartz diorite pluton and quartz+calcite farther away. The three minerals were not found together suggesting that the system was open to CO_2 in this contact metamorphic aureole.

Many metamorphosed carbonate-bearing rocks however give evidence having been closed to variations in the H_2O/CO_2 ratio during metamorphism, and even closed to exchange of H_2O and CO_2 between adjacent beds of differing initial composition. Kerrick (1970, pp 2931) shows that during contact metamorphism in the Standard area, California, "the fluid-phase composition of mappable calc-silicate units was controlled by local domains rather than by an external source. . .". Melson (1966) shows in his study of a calc-silicate hornfels in Montana that H_2O and CO_2 cannot be regarded as perfectly mobile components but must be considered as having been controlled by the local assemblage. Trommsdorff (1966, and personal comm., 1970) describes from the Bergell Alps in Switzerland the assemblage diopside+wollastonite+quartz+calcite+grossularite in the high grade part of a regionally metamorphosed terrain. In this assemblage the $CO_2:H_2O$ ratio must be buffered, at any temperature and total pressure, by the coexistence of calcite, quartz, and wollastonite, while the presence of grossularite with quartz requires that the temperature must have been less than the equilibrium temperature for the reaction grossularite+quartz=anorthite+wollastonite. These restrictions, together with the observation that the pelitic rocks are progressively metamorphosed at pressures above the Al_2SiO_5 triple point make Figure 7 appropriate for discussion of these rocks. At an inferred pressure of approximately 6 Kb the temperature must have been less than about $700^\circ C$ (in agreement with Trommsdorff, *op. cit.*) and the mole fraction of CO_2 must have been less than about 0.20 and buffered by calcite+quartz+wollastonite.

It seems clear in the light of the above observations that the natural metamorphism of carbonate-bearing rocks may take place either under open or closed conditions with respect to H_2O and CO_2 . Both contact and regional environments can exhibit both kinds of behavior and it is therefore unsafe to apply any rule of thumb to this problem. Each natural occurrence must be carefully judged on the basis of its own characteristics and a decision reached, if possible, as to whether the

system was perfectly open, completely closed, or buffered by local domains such as original sedimentary layers.

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