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High-temperature contact metamorphism of carbonate rocks in a shallow crustal environment, Christmas Mountains, Big Bend region, Texas

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Abstract

Emplacement of a composite stock of alkali gabbro and syenite into limestone in the Christmas Mountains produced a narrow reaction zone at the contact, consisting of wollastonite-nepheline pyroxenite and a mineralogically-zoned calc-silicate skarn. The sequence of prograde mineral assemblages across skarn and contiguous marble is melilite + wollastonite, melilite + rankinite + spurrite, melilite + spurrite, and melilite + spurrite + calcite ± merwinite, and defines a mineral facies in $P\text{-}T\text{-}X_{CO_2}$.

Lithostatic pressure at the time of gabbro emplacement varied with position in the aureole from 325 to 355 bars. In the presence of pure fluid CO_2 critical assemblages in skarn, marble, and calc-silicate nodules that define maximum temperatures in the aureole are

calcite + melilite + merwinite	1035°C	1.4 m
rankinite + spurrite	1030°C	7.5 m
rankinite + tilleyite	990°C	16 m
wollastonite + tilleyite	930°C	31 m
wollastonite + calcite	600°C	100 m

At maximum dilution of the fluid, $X_{CO_2} = 0.6$ in nodules, $X_{CO_2} = 0.2$ in skarn, and temperatures are lower by 40 to 100°C.

Introduction

Emplacement of a composite stock of alkali gabbro and syenite into Lower Cretaceous limestone in the Christmas Mountains (lat. 29°26′N; long. 103°27′W) produced a narrow reaction zone at the contact and an extensive marble aureole. The reaction zone consists of wollastonite-nepheline pyroxenite formed by contamination of gabbroic magma and a mineralogically zoned calc-silicate skarn, formed by diffusive exchange of material between feldspathic magma and carbonate wallrock (Joesten, 1974a). Mineral assemblages in skarn and adjacent calc-silicate marble at the intrusive contact and in xenoliths enveloped by gabbro record temperatures in excess of 1000°C, and assemblages of calc-silicate nodules in marble record temperatures exceeding 900°C within 40 m of the intrusive contact (Joesten, 1974b). The establishment of temperatures in the aureole that approach that of the magma solidus implies that magmatic convection was the dominant mode of energy transport within the intrusion, heat conduction was the dominant mode of energy transport within the aureole, and that the convective cycling of meteoric-hydrothermal water through the aureole (Taylor, 1974) did not occur, at least during the peak of metamorphism.

Mineral facies of skarn

Skarn occurs in a band, 0.1 to 1 m thick, that separates pyroxenite and marble along the intrusive contact and forms a rim on marble xenoliths in gabbro. Mineral assemblages in skarn and calc-silicate marble are listed in Table 1. A generalized sequence of prograde mineral zones developed across skarn and marble is:

idocrase + wollastonite

melilite + wollastonite

TABLE 1. Mineral assemblages in skarn and marble, Christmas Mountains, Texas

Assemblage No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Calcite	.	.	.	.	.	.	.	.	.	.	.	.	X	X	X
Tilleyite	.	.	.	.	.	.	.	.	.	.	X	X	.	.	.
Spurrite	.	.	.	.	X	.	X	X	X	X	X	.	X	X	.
Larnite	.	.	.	.	.	X	X	.	.	.	.	.	.	.	.
Rankinite	.	.	.	.	X	X	.	X	.	.	.	.	.	.	.
Wollastonite	X	X	X	X	X	.	.	.	.	.	.	.	.	.	.
Bredigite	.	.	.	.	.	X	X	.	.	.	.	.	.	.	.
Merwinite	.	.	.	.	.	.	.	.	.	X	.	.	.	.	X
Monticellite	.	.	.	.	.	.	.	.	.	X	.	.	.	X	.
Melilite	.	.	.	X	X	X	X	X	X	X	.	.	X	X	X
Idocrase	X	X	X	*	.	.	.	.	.	.	X	X	.	.	.
Grossular	X	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Ti-Zr Garnet	.	X	X	X	X	.	.	X	X	.	X	X	X	X	X
Perovskite	.	.	X	X	X	X	X	X	X	X	X	.	X	X	X
Magnetite	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

* Idocrase, pseudomorphous after melilite, may occur in any melilite-bearing assemblage.

melilite + rankinite + spurrite ± wollastonite

melilite + spurrite

melilite + spurrite + calcite ± merwinite

Titanian-zirconian andradite, perovskite, and magnetite are accessory phases in most skarn assemblages. The composition of melilite ranges from $AK_{12}FeAK_{20}GE_{68}$ in wollastonite skarn to $AK_{38}FeAK_{07}GE_{55}$ in marble. Assemblages in Table 1 involving monticellite (10, 14) are interpreted as being retrograde in origin, and those assemblages with larnite (6, 7), which occur only in rocks of a septum between two gabbro bodies, result from polymetamorphism. Idocrase, pseudomorphous after melilite, occurs locally in all skarn assemblages, and is the result of low temperature (T <600°C) hydrothermal activity (Joesten, 1974c).

To a first approximation, the mineral assemblages in skarn and marble can be described by phases in the system CaO–MgO–FeO–Al_2O_3–SiO_2–CO_2. The ubiquitous accessory phases—garnet, perovskite, and magnetite—which contain Fe_2O_3, TiO_2, and ZrO_2, rarely exceed 3 volume percent and are not included in the graphical presentation. If it is assumed that each assemblage equilibrated with a fluid in which the chemical potential of CO_2 (μ_{CO_2}) was controlled externally, CO_2 may be treated as an environmental rather than compositional variable, and the number of graphical components can be reduced to five. MgO and FeO can be combined as a single component for the purpose of graphical portrayal of the five-component system on a tetrahedron without loss of generality, because in most assemblages melilite is the only phase in which they occur. In those assemblages in which melilite coexists with monticellite and/or merwinite, no crossing tie-line relationships arise that are attributable to this simplification.

Although assemblage zoning is the result of diffusional exchange of Ca, Fe, Al, and Si between magma and wallrock, the set of all prograde assemblages that comprise skarn and contiguous marble defines a mineral facies in the system CaO–(MgO + FeO)–Al_2O_3–SiO_2–CO_2 (Fig. 1). To the extent that mineral assemblages representing the bulk compositions of the skarn zones are sensitive to variation in P, T, and μ_{CO_2}, conditions of skarn growth were identical at the intrusive contact and within xenoliths enveloped by gabbro.

Estimate of P, T, and X_{CO_2}

Stratigraphic estimate of lithostatic pressure

Cross-cutting relations indicate that the rocks of the gabbro complex are the oldest of a series of intrusive and extrusive igneous rocks in the western part of the Christmas Mountains (Bloomer, 1949; Swadley, 1958; Jenkins, 1959). Folding and uplift of the range predated gabbro emplacement or was synchronous with it. Sedimentary and volcanic rocks of early Tertiary age accumulated in a basin bounded on the west by the Christmas Mountains uplift (Maxwell *et al.*, 1967, p. 300). It is thus likely that the maximum thickness of strata overlying the contact aureole at the time of gabbro emplacement was that of the Cretaceous section. The total thickness of Cretaceous strata in the Christmas Mountains, from the base of the Sue Peaks Formation to the top of the Javelina

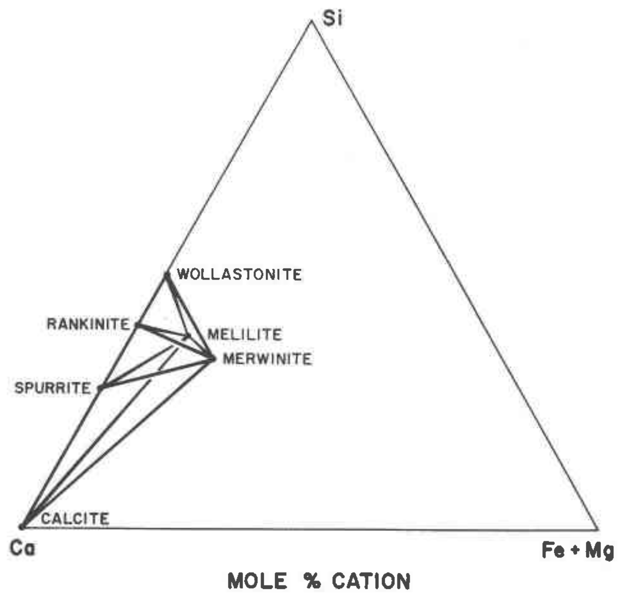

FIG. 1. Mineral facies defined by prograde assemblages in skarn and marble. Composition of melilite (AK + $FeAK_{40}GE_{60}$) is projected from Al onto the Ca–(Fe + Mg)–Si face of the Ca–(Fe + Mg)–Al–Si tetrahedron. Tie lines to melilite are shown vanishing to a point to aid in the visualization of the four-phase volumes.

Formation, is 1345 m. This is based on unfaulted segments of the sections measured by Bloomer (1949) and extrapolations of sections measured to the south and east of the range by Maxwell et al. (1967). Using a rock density of 2.7 g/cm^3, the lithostatic pressure at the base of the Sue Peaks Formation was 355 bars. Upper and lower limits to the estimated lithostatic pressure, corresponding to the maximum and minimum total stratigraphic thicknesses in the Big Bend region (Maxwell *et al.*, 1967), are 390 and 250 bars, respectively. Skarn was sampled from the base of the Sue Peaks Formation (location $^{32}57^{390}$N/$^{06}50^{460}$E 1000-m Universal Transverse Mercator Grid, Christmas Mountains (7½′) quadrangle) and from a xenolith of Santa Elena (?) Limestone in gabbro, 75 m stratigraphically above the base of the Sue Peaks Formation (location $^{32}56^{270}$N/$^{06}50^{000}$E). Lithostatic pressure acting on the xenolith was 335 bars. The calc-silicate nodules (Joesten, 1974b) were collected from Santa Elena Limestone, 115 m stratigraphically above the base of the Sue Peaks Formation. The corresponding lithostatic pressure was 325 bars.

Estimate of P, T *and* X_{CO_2} *for system* $CaO–SiO_2CO_2$

Correlation of mineral facies of skarn and of the calc-silicate nodules with phase equilibrium data for the system $CaO–SiO_2–CO_2$ (Zharikov and Shmulovich, 1969; Joesten, 1974b) places narrow limits on *P*, *T*, and fluid composition during skarn and nodule growth. In the presence of pure fluid CO_2, the coexistence of rankinite + spurrite in skarn indicates a maximum lithostatic pressure of 500 bars, confirming the stratigraphic estimate, and at pressures of 325 to 355 bars limits the temperature of skarn growth to a range of 995 to 1030°C (Fig. 2). The inferred coexistence of rankinite + tilleyite in calc-silicate nodules in the aureole within 16 m of the intrusive contact (Joesten, 1974b, p. 884) imposes a lower limit of 140 bars lithostatic pressure in presence of pure fluid CO_2, restricts the composition of the fluid in the vicinity of a growing nodule to one in which X_{CO_2} was greater than 0.6 at 325 bars, and places a lower limit of 920°C for metamorphism within 16 m of the gabbro contact (Joesten, 1974b, Fig. 5). At 920°C and 325 to 350 bars, the stability of rankinite + spurrite relative to larnite requires X_{CO_2} in fluid in skarn to have been greater than 0.2. The lack of evidence for melting of calcite places a similar lower limit on X_{CO_2} (Wyllie and Haas, 1966, p. 528). In the presence of pure fluid CO_2 at 325 bars, the coexistence of wollastonite + tilleyite in a calc-silicate nodule 31 m from the contact indicates a temperature of 930°C, and the coexistence of wollastonite + calcite in nodules indicates a temperature of 600°C was attained 100 m from the contact (Joesten, 1974b).

Equilibria involving merwinite

The assemblage spurrite + calcite + melilite + merwinite of calc-silicate marble in contact with skarn confirms the high temperature of skarn growth. The presence of merwinite as inclusions in melilite suggests that merwinite was formed in marble by a reaction similar to

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{akermanite}}{Ca_2MgSi_2O_7} = \underset{\text{merwinite}}{Ca_3MgSi_2O_8} + CO_2. \quad (1)$$

Although merwinite coexists with spurrite in marble, the experimentally determined *P-T* curve for this reaction (Shmulovich, 1969) lies within the tilleyite field (Fig. 2). Although the assemblage spurrite + calcite + merwinite + melilite occurs in marble of the Sue Peaks Formation only within 1.4 m of the pyroxenite-skarn contact, calc-silicate layers with the assemblage rankinite + spurrite + melilite occur in Sue Peaks marble to a distance of 7.5 m from the contact. These observations require that the merwinite-producing reaction lie near the high temperature limit of the coexistence of rankinite + spurrite.

Electron microprobe analyses of coexisting melilite

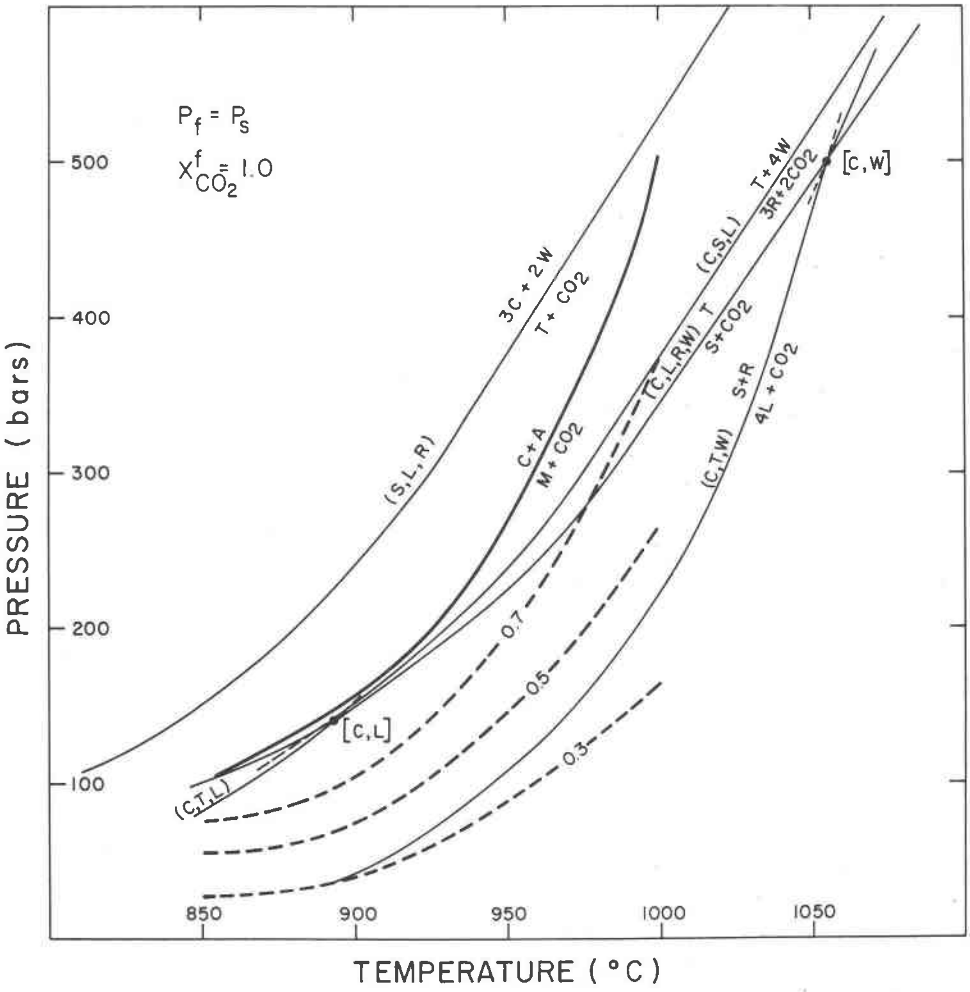

FIG. 2. *P-T* diagram for system CaO–SiO_2–CO_2 at $X_{CO_2} = 1$ (from Zharikov and Shmulovich, 1969, and Joesten, 1974b). Curves for univariant reaction (1) (heavy solid line) and divariant reaction (2) (heavy dashed line, number gives mole fraction $Ca_2MgSi_2O_7$ in melilite) are superimposed. Mineral names: W = wollastonite ($CaSiO_3$), R = rankinite ($Ca_3Si_2O_7$), L = larnite (Ca_2SiO_4), S = spurrite ($Ca_5Si_2O_8CO_3$), T = tilleyite ($Ca_5Si_2O_7(CO_3)_2$), C = calcite ($CaCO_3$), A = akermanite ($Ca_2MgSi_2O_7$), M = merwinite ($Ca_3MgSi_2O_8$).

and merwinite (Table 2, analyses by method described in Joesten, 1974c, p. 696) show that neither phase has the Mg end-member composition. The coexistence of calcite + melilite + merwinite may result from reaction of calcite with a melilite solid solution to form merwinite + gehlenite,

$$\underset{\text{calcite}}{X\,CaCO_3} + \underset{\text{melilite } AK_xGE_{1-x}}{Ca_2Mg_xAl_{2-2x}Si_{1+x}O_7} = \underset{\text{merwinite}}{X\,Ca_3MgSi_2O_8} + \underset{\text{gehlenite}}{(1-X)Ca_2Al_2SiO_7} + X\,CO_2, \quad (2)$$

or by a similar reaction involving exchange of Fe and Mg between melilite and merwinite to produce melilite enriched in Al and Fe. Solid solution in melilite on the left-hand side of reaction (2) shifts the equilibrium to higher *T* or lower *P*. An estimate of the shift of the *P-T* coordinates of reaction (2) due to ideal solid solution in melilite can be obtained by solving the equilibrium constant expression for the fugacity of CO_2 necessary for equilibration with melilite of a specified mole fraction AK at a given *T* (Fig. 2). Melilite coexisting with merwinite + calcite (Table 2, samples 8-7A and 108) has a composition of $AK_{30}FeAK_{08}GE_{62}$. At 350 bars, merwinite is stable relative to calcite + melilite (AK_{30}) at approximately 1060°C (Fig. 2). The effect of solution of Fe in merwinite (Mg/(Mg + Fe) = 0.9) coexisting with melilite

(AK_{30}) is to lower the equilibration temperature to 1035°C at 350 bars.

In Santa Elena (?) marble from the core of a xenolith from gabbro (Sample 108, Table 2), merwinite is separated from calcite by an optically-continuous rim of either spurrite or monticellite. Vermicular intergrowths of spurrite and monticellite enveloped by an optically-continuous rim of spurrite also occur. The textural incompatibility of calcite and merwinite and the vermicular intergrowths of spurrite and monticellite suggest that these four phases are related by the reaction defining the low-temperature limit of coexistence of calcite + merwinite,

$$\underset{\text{monticellite}}{2\,CaMgSiO_4} + \underset{\text{spurrite}}{Ca_5Si_2O_8CO_3} = \underset{\text{merwinite}}{2\,Ca_3MgSi_2O_8} + \underset{\text{calcite}}{CaCO_3}, \quad (3)$$

which runs to the right at 820°C and 60 bars and has a slope of about 90 bars/°C (Walter, 1965). Although the inferred four-phase assemblages in marble, spurrite + calcite + monticellite + melilite and spurrite + monticellite + melilite + merwinite, are stable on the low-temperature side of reaction (3), their probable derivation from the prograde assemblage spurrite + calcite + melilite + merwinite rigorously indicates that the temperature in the core of the xenolith exceeded 820°C regardless of the fluid composition.

Summary of maximum temperatures attained in the aureole

In the presence of pure fluid CO_2 at 325 to 355 bars lithostatic pressure, assemblages defining maximum temperatures in the aureole are

calcite + melilite + merwinite	1035°C	1.4 m
rankinite + spurrite	1030°C	7.5 m
rankinite + tilleyite	990°C	16 m
wollastonite + tilleyite	930°C	31 m
wollastonite + calcite	600°C	100 m

At maximum dilution of the fluid, $X_{CO_2} = 0.6$ in nodules, $X_{CO_2} = 0.2$ in skarn, and temperatures are lowered by 40 to 100°C.

Heat transfer in the marble aureole

Assuming similar fluid composition, the temperature of skarn growth was essentially the same at the intrusive contact and in xenoliths enveloped by gabbroic magma, and was in the range 920 to 1035°C.

TABLE 2. Electron microprobe analyses of calc-silicate minerals from marble

Sample	8-7A		91		108		
Mineral*	MEL	MER	MEL	MER	MEL	MER	MO
Assemblage†	15		15		10		
	Weight % oxide						
SiO_2	31.29	36.65	29.07	37.47	32.98	37.16	37.20
TiO_2	0.0	0.0	0.01	0.0	0.01	0.0	0.0
Al_2O_3	22.06	0.0	23.55	0.04	19.92	0.01	0.0
FeO	2.13	1.54	2.09	1.81	1.78	1.88	11.80
MnO	..	0.0	0.02	0.07	0.01	0.03	0.44
MgO	4.84	11.28	3.94	11.33	5.48	11.07	16.20
CaO	39.08	49.84	40.69	49.86	39.69	50.63	36.04
Na_2O	0.52	0.11	0.22	0.10	0.65	0.14	0.01
Σ	99.92	99.42	99.62	100.68	100.54	100.93	101.69
	Mineral formulae						
Cation sum	5.0	3.0	5.0	3.0	5.0	3.0	3.0
Si 4+	1.43	1.01	1.34	1.02	1.50	1.02	1.01
Al 3+	1.19	0.0	1.28	0.0	1.07	0.0	0.0
Fe 2+	0.08	0.04	0.08	0.04	0.07	0.04	0.27
Mn 2+	..	0.0	0.0	0.0	0.0	0.0	0.01
Mg 2+	0.33	0.46	0.27	0.46	0.37	0.45	0.66
Ca 2+	1.92	1.48	2.01	1.46	1.93	1.48	1.05
Na +	0.05	0.01	0.02	0.01	0.06	0.01	0.0
O 2-	7.01	4.01	6.97	4.02	7.00	4.01	4.01

* Mineral names: MEL = melilite, MER = merwinite, MO = monticellite.
† Assemblages listed in Table 1.

The temperature in the core of a 2 m thick marble xenolith, heated by conduction, will approach that of the surrounding magma within a few weeks of immersion (Lovering, 1938; Carslaw and Jaeger, 1959, p. 102). Thus, the temperature of skarn growth was essentially the same as that of the magma.

Where heat conduction is the sole mechanism of energy transport within an intrusion and its aureole, the maximum temperature in the wallrock, attained at the intrusive contact, is equal to about two-thirds of the solidus temperature of the magma (Carslaw and Jaeger, 1959, p. 288–289; Jaeger, 1968, p. 520–523). However, convection in a narrow boundary layer along a vertical contact between basaltic magma and wallrock will maintain the contact temperature at or slightly above that of the basalt solidus during the early stages of solidification (Shaw, 1974, p. 157–162). Duration of the boundary layer regime in the solidification of the Christmas Mountains complex probably was in the range 500 to 5000 years. In addition to accounting for the ususually high temperatures recorded by mineral assemblages from the contact aureole, convection in a thermal boundary layer greatly increases the effectiveness of diffusional exchange of material between magma and wallrock as required for the development of pyroxenite and skarn.

In contrast to the high temperatures attained in the marble aureole of the Christmas Mountains gabbro, contact temperatures of nearby sills of chemically similar alkali gabbro did not exceed 500°C, as calcite + quartz coexist in baked sandstone in contact with chilled gabbro. Intrusion of gabbroic magma into permeable clastic sedimentary rocks of the Aguja Formation of Late Cretaceous age probably initiated convective cycling of water through the magma and aureole which rapidly cooled the intrusion and provided an efficient mechanism for the transport of heat away from the contact. The low permeability of marble precluded establishment of a meteoric-hydrothermal convection system in the Christmas Mountains aureole.

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