Pseudomorphic Replacement of Melilite by Idocrase in a Zoned Calc-Silicate Skarn, Christmas Mountains, Big Bend Region, Texas[1]

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Abstract

Intrusion of alkali gabbro into Lower Cretaceous limestone in the Christmas Mountains, Big Bend Region, Texas, produced a narrow reaction zone at the contact comprised of nepheline pyroxenite and a mineralogically zoned calc-silicate skarn. From pyroxenite to marble, the skarn zones are defined by idocrase + wollastonite, melilite + wollastonite, melilite + rankinite, melilite + spurrite ± calcite. The contact between the idocrase + wollastonite and the melilite + wollastonite zones is sharp and planar at most localities. However, replacement of melilite by idocrase along zones adjacent to fractures suggests that the contact between the idocrase and melilite zones did not propagate through the skarn as a planar front. Idocrase, pseudomorphic after melilite, accurately preserves the grain habit and internal cleavage of melilite. Ca, Mg, Fe, Al, and Si are equally partitioned between coexisting melilite and idocrase, but Na is depleted by a factor of 2 to 50 in idocrase. Analyses of both phases approximately fit the formula

$$Ca_{2-x}Na_x (Mg, Fe)_y Al_{2-x-2y} Si_{1+x+y} (O, OH)_7$$

with $0.0 \leq x \leq 0.12$ and $0.17 \leq y \leq 0.57$.

An aqueous fluid flowed along fractures in the melilite skarn to hydrate the melilite adjacent to the fracture. Diffusion of H_2O down the chemical potential gradient established across the idocrase zone and reaction with melilite at the zone boundary caused the zone to grow outward, perpendicular to the fracture. Complete replacement of melilite skarn results from the coalescence of idocrase veinlets developed along a network of intersecting fractures. The presence of idocrase in skarn is not related to the primary compositional zonation developed during diffusional growth of the skarn but is the result of a lower temperature, hydrothermal replacement of melilite.

Introduction

A composite stock of alkali gabbro and syenite, intrusive into limestone of the Lower Cretaceous Commanche Series in the Christmas Mountains in the Big Bend Region of Texas, produced a mineralogically varied suite of rocks at its contact. Gabbro and marble are everywhere separated by a narrow reaction zone consisting of nepheline pyroxenite and a mineralogically zoned calc-silicate skarn, 0.1 to 1 m in width. The sequence of mineral zones across the skarn, from pyroxenite to marble, is:

idocrase + wollastonite
melilite + wollastonite
melilite + wollastonite + rankinite
melilite + rankinite + spurrite
melilite + spurrite
melilite + spurrite + calcite ± merwinite.

Titanian-zirconian garnet, perovskite, and magnetite are accessory phases in all assemblages. Veinlets of idocrase, developed along fractures, may occur in each of the assemblages containing melilite. The set of melilite-bearing assemblages constitutes a facies type, trivariant in P-T-X_{CO_2} space. Different mineral assemblages reflect differences in the bulk composition of the individual skarn zones. The origin of the metasomatic zoning in the skarn is discussed elsewhere (Joesten, 1974a). This note describes the field, textural, and chemical relationships leading to the conclusion that the presence of idocrase in skarn is not related to the primary compositional zonation developed during diffusional growth of
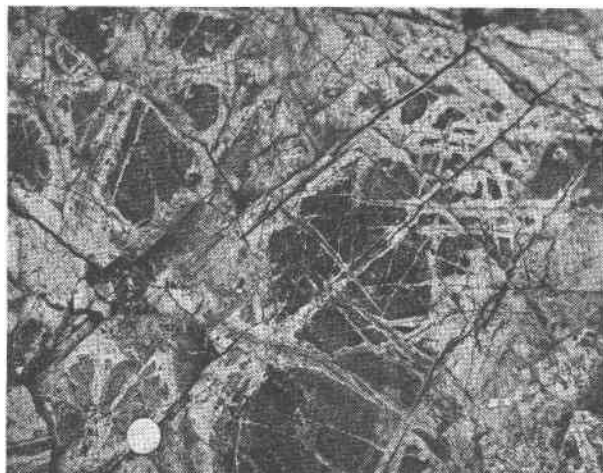
FIG. 1. Latticework of idocrase veinlets in melilite skarn, surrounded by idocrase skarn in the core of a xenolith in gabbro. The contact between idocrase skarn and melilite skarn propagated toward the center of the xenolith by coalescence of idocrase veinlets growing outward from intersecting fractures. Penny, diameter 18 mm, gives scale.

the skarn, but is the result of a lower temperature, hydrothermal replacement of melilite.

Field Relationships

The contact between the zone of green idocrase-rich skarn and brown melilite-rich skarn is sharp and generally planar at most localities. Outside the green skarn zone, idocrase is localized along fractures that cut the melilite skarn (Fig. 1). These fractures can usually be traced back into the zone of green skarn. The vein-like replacement of melilite by idocrase suggests that the idocrase-melilite zone boundary did not propagate through the rock as a planar front but developed by the coalescence of a network of idocrase veinlets.

The gradational contact between green skarn and brown skarn in the core of a large skarn xenolith in gabbro (Fig. 1) clearly shows the progressive replacement of melilite by idocrase. Idocrase developed along intersecting fractures to form a latticework of veinlets which enclose polygonal areas of melilite skarn. Wide idocrase veinlets overlap at points of intersection and round off the corners of the enclosed melilite polygons. As the contact with the main mass of green skarn is approached, the residual "eyes" of melilite become smaller until they are completely engulfed by idocrase.

The spatial relationships between the green and the brown skarn zones at gradational contacts clearly

indicate an origin for idocrase through reaction of melilite with fluid flowing along fractures in brown skarn.

Textural Relationships

Textural evidence in thin section suggests that idocrase formed by pseudomorphic replacement of melilite. Where melilite and idocrase occur in the same thin section, their grain habits are identical, but they may be distinguished by birefringence and appearance in plane light. Melilite is first-order gray to yellow, in contrast with idocrase which may be anomalous blue, brown, brilliant purple, or isotropic. In contrast to melilite, which is colorless and transparent in plane light, idocrase usually has a dusty brown appearance (Fig. 2, 3a). Its sweeping extinc-
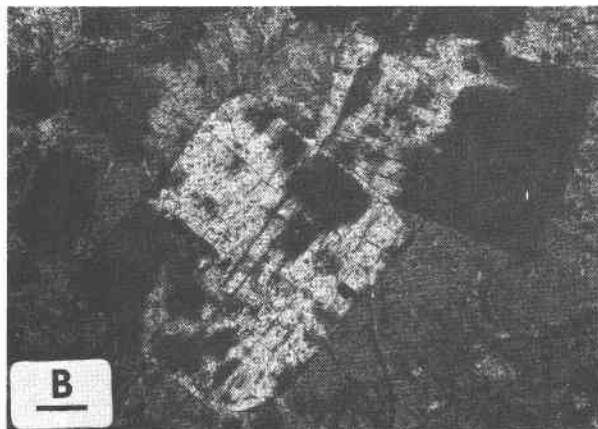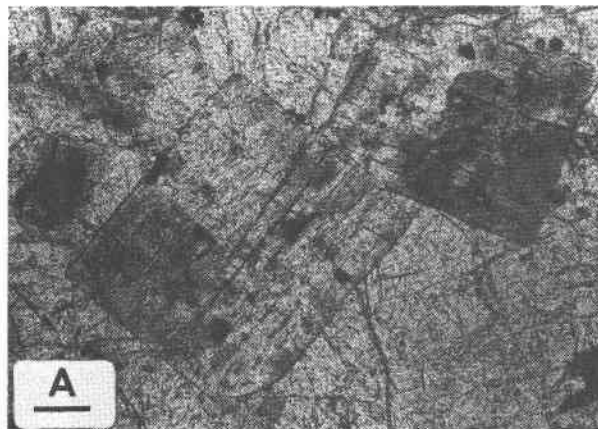

FIG. 2. Partial and complete pseudomorphs of fibrous idocrase after euhedral crystals of melilite in calcite-spurrite-melilite skarn. A. Plane light. B. Same field as A, crossed polars. Idocrase is in extinction. Scale bar is 0.1 mm.
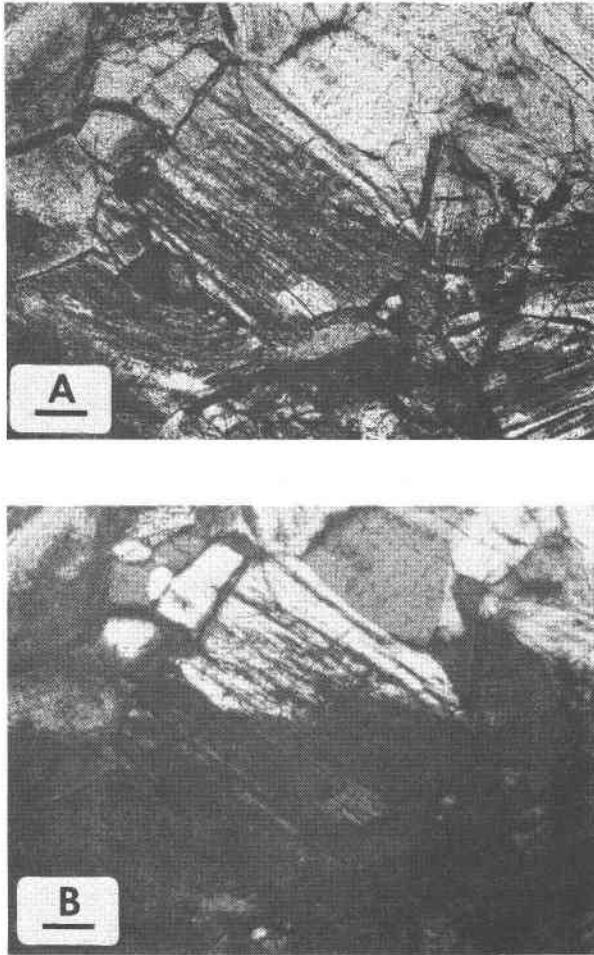
FIG. 3. Replacement of melilite along a planar front parallel to a fracture in melilite skarn. Contact between the melilite zone (above) and idocrase zone (below) bisects field from right to left. **A.** Plane light. **B.** Same field as **A,** polars inclined at 80°. Idocrase is in extinction. Scale bar is 0.1 mm.

tion and lack of well-defined interference figures suggest that idocrase forms a polycrystalline or fibrous replacement of individual melilite grains. Peaks on diffractometer tracings of both clear and fibrous idocrase match those for idocrase on A.S.T.M. X-ray Powder Data File pattern 11-145.

Unequivocal petrographic evidence for pseudomorphism of melilite by idocrase is shown by partial and complete replacement of euhedral prisms of melilite by fibrous idocrase in melilite-spurrite-calcite skarn (Fig. 2). Incipient development of idocrase takes place along the (001) cleavage planes of melilite (Fig. 2, 3a), which are preserved as relicts within grains completely converted to idocrase (Fig.

3a). In all samples in which both idocrase and melilite occur, idocrase pseudomorphs accurately preserve the crystal habit of melilite characteristic of the rock. The habit of idocrase in melilite-free rocks is identical to that of melilite in rocks from the same skarn zone. On the basis of the textural evidence presented, it is suggested that all idocrase in the skarn is pseudomorphous after melilite and that melilite was a primary phase in all idocrase-bearing assemblages examined.

Chemical Relationships

In order to characterize the reaction leading to pseudomorphic replacement, coexisting melilite and idocrase in polished thin sections from 16 skarn samples were analyzed with the electron microprobe. Analyses were performed with a Materials Analysis Company Model 5-SA3 electron microprobe, interfaced to a DEC PDP-8/L computer. Data collection and reduction was done on-line using FOCAL programs based on those developed by Chodos and Albee (1971). X-ray peak and background intensities for all elements analyzed were measured before moving the sample from the point of analysis. Oxide concentrations were computed from background and dead-time corrected X-ray intensity ratios by the method of Ziebold and Ogilvie (1964) using binary oxide correction factors computed by Albee and Ray (1970). Primary standards used were oxides, synthetic silicates, and well-characterized natural minerals. Operating conditions were 15 kV accelerating potential 0.05 μ amp sample current measured on brass and a beam diameter of 2–20 μm. Beam-current drift was compensated by using the ratio of X-ray counts to aperture current averaged over a fixed counting time in all intensity computations.

Analytical results, cast into mineral formulae based on five cations, are listed in Table 1. The original analyses, as weight percent oxide, are listed in Joesten (1974a, p. 380–384). Each analysis represents the mean of 3 to 8 point analyses. Within a single thin section, concentrations of the major elements vary between 0.5 and 5 percent of the amount present, both in melilite and in idocrase. There is no consistent pattern of chemical zonation within single grains of either mineral.

As shown in Table 1 and Figure 4, there is a close and consistent correspondence between the proportion of each element in coexisting melilite and idocrase. Sodium is a notable exception, being depleted by a factor of 2 to 50 in idocrase relative to melilite.

The equal partitioning of Ca, Mg, Fe, Al, and Si between coexisting melilite and idocrase over the full range of solid solution represented clearly shows that the reaction leading to replacement of melilite by idocrase involves simple hydration and removal of Na. Analyses of both melilite and idocrase approximately fit the formula

$$Ca_{2-x}Na_x(Mg, Fe)_y Al_{2-x-2y} Si_{1+x+y}(O, OH)_7$$

with $0.0 \leq x \leq 0.12$ and $0.17 \leq y \leq 0.57$.

Phase Relationships

Reconnaissance hydrothermal experiments outlining the P-T stability fields of melilite (Christie, 1961) and of idocrase (Ito and Arem, 1970) support the possibility of producing idocrase by the hydration of melilite. Christie (1961, p. 257–258) found that melilite ranging in composition from akermanite$_{70}$ gehlenite$_{30}$ to gehlenite$_{100}$ formed a mixture of idocrase and hydrogarnet when heated with water to 450–600°C at 4.8–6.7 kbar. Using gels of a composition corresponding to stoichiometric idocrase, Ito and Arem (1970, p. 884–887) established a P-T boundary separating the stability field of idocrase from that of melilite + H$_2$O. The P-T coordinates of the dehydration reaction are sensitive to gel composition and range from 600 to 700°C over the pressure interval 0.5 to 2.5 kbar. Ito and Arem (1970, p. 885) produced idocrase by heating synthetic melilite with water within the idocrase field of their P-T diagram. Their experiments did not confirm the presence of hydrogarnet as a hydration product of melilite.

Petrogenetic Model

The progressive development of idocrase skarn by the hydration of melilite is a natural analogue of progressive dehydration of hydrohalite in the open system discussed by Thompson (1970, p. 539) and may be modeled as follows. Flow of an aqueous fluid along fractures in the melilite skarn hydrates the melilite adjacent to the fracture. The chemical potential of H$_2$O is buffered by the coexistence of melilite + idocrase at the zone boundary and of idocrase + fluid at the fracture. Because a zone of idocrase skarn everywhere separates melilite skarn from gabbro and its contaminated derivative, pyroxenite, the fluid probably was magmatic. Diffusion of water across the idocrase zone and reaction with melilite at the zone boundary cause the zone to grow outward, perpendicular to the fracture. The

TABLE 1. Formulae of Coexisting Melilite and Idocrase*

	Ca	Na	Mg	Fe	Al	Si	O
M**	Ca$_{1.87}$	Na$_{0.08}$	Mg$_{0.12}$	Fe$_{0.19}$	Al$_{1.32}$	Si$_{1.40}$	O$_{7.02}$
I**	Ca$_{1.91}$	Na$_{0.00}$	Mg$_{0.11}$	Fe$_{0.19}$	Al$_{1.31}$	Si$_{1.46}$	(O,OH)$_{7.12}$
M	Ca$_{1.89}$	Na$_{0.07}$	Mg$_{0.19}$	Fe$_{0.17}$	Al$_{1.25}$	Si$_{1.42}$	O$_{7.01}$
I	Ca$_{1.92}$	Na$_{0.02}$	Mg$_{0.19}$	Fe$_{0.18}$	Al$_{1.25}$	Si$_{1.44}$	(O,OH)$_{7.06}$
M	Ca$_{1.91}$	Na$_{0.07}$	Mg$_{0.20}$	Fe$_{0.16}$	Al$_{1.26}$	Si$_{1.40}$	O$_{6.99}$
I	Ca$_{1.88}$	Na$_{0.01}$	Mg$_{0.17}$	Fe$_{0.17}$	Al$_{1.34}$	Si$_{1.42}$	(O,OH)$_{7.09}$
M	Ca$_{1.92}$	Na$_{0.07}$	Mg$_{0.19}$	Fe$_{0.17}$	Al$_{1.22}$	Si$_{1.42}$	O$_{7.00}$
I	Ca$_{1.93}$	Na$_{0.03}$	Mg$_{0.21}$	Fe$_{0.20}$	Al$_{1.14}$	Si$_{1.47}$	(O,OH)$_{7.02}$
M	Ca$_{1.94}$	Na$_{0.07}$	Mg$_{0.20}$	Fe$_{0.19}$	Al$_{1.16}$	Si$_{1.44}$	O$_{6.99}$
I	Ca$_{2.02}$	Na$_{0.01}$	Mg$_{0.18}$	Fe$_{0.16}$	Al$_{1.14}$	Si$_{1.48}$	(O,OH)$_{7.05}$
M	Ca$_{1.89}$	Na$_{0.07}$	Mg$_{0.22}$	Fe$_{0.17}$	Al$_{1.21}$	Si$_{1.43}$	O$_{6.99}$
I	Ca$_{1.93}$	Na$_{0.01}$	Mg$_{0.21}$	Fe$_{0.15}$	Al$_{1.22}$	Si$_{1.46}$	(O,OH)$_{7.06}$
M	Ca$_{1.92}$	Na$_{0.05}$	Mg$_{0.33}$	Fe$_{0.08}$	Al$_{1.19}$	Si$_{1.43}$	O$_{7.01}$
I	Ca$_{1.96}$	Na$_{0.01}$	Mg$_{0.38}$	Fe$_{0.08}$	Al$_{1.09}$	Si$_{1.49}$	(O,OH)$_{7.03}$
M	Ca$_{1.89}$	Na$_{0.09}$	Mg$_{0.22}$	Fe$_{0.15}$	Al$_{1.19}$	Si$_{1.44}$	O$_{7.00}$
I	Ca$_{1.89}$	Na$_{0.04}$	Mg$_{0.23}$	Fe$_{0.15}$	Al$_{1.23}$	Si$_{1.46}$	(O,OH)$_{7.05}$
M	Ca$_{1.88}$	Na$_{0.12}$	Mg$_{0.20}$	Fe$_{0.15}$	Al$_{1.22}$	Si$_{1.44}$	O$_{7.00}$
I	Ca$_{1.90}$	Na$_{0.04}$	Mg$_{0.21}$	Fe$_{0.14}$	Al$_{1.22}$	Si$_{1.50}$	(O,OH)$_{7.09}$
M	Ca$_{1.96}$	Na$_{0.05}$	Mg$_{0.26}$	Fe$_{0.17}$	Al$_{1.05}$	Si$_{1.50}$	O$_{7.00}$
I	Ca$_{1.96}$	Na$_{0.00}$	Mg$_{0.27}$	Fe$_{0.18}$	Al$_{1.08}$	Si$_{1.51}$	(O,OH)$_{7.05}$
M	Ca$_{2.00}$	Na$_{0.02}$	Mg$_{0.25}$	Fe$_{0.18}$	Al$_{1.12}$	Si$_{1.44}$	O$_{6.99}$
I	Ca$_{2.02}$	Na$_{0.00}$	Mg$_{0.20}$	Fe$_{0.16}$	Al$_{1.18}$	Si$_{1.44}$	(O,OH)$_{7.03}$
M	Ca$_{2.03}$	Na$_{0.02}$	Mg$_{0.22}$	Fe$_{0.16}$	Al$_{1.20}$	Si$_{1.37}$	O$_{6.96}$
I	Ca$_{1.97}$	Na$_{0.01}$	Mg$_{0.23}$	Fe$_{0.16}$	Al$_{1.24}$	Si$_{1.40}$	(O,OH)$_{7.02}$
M	Ca$_{2.02}$	Na$_{0.01}$	Mg$_{0.17}$	Fe$_{0.13}$	Al$_{1.38}$	Si$_{1.28}$	O$_{6.97}$
I	Ca$_{2.03}$	Na$_{0.00}$	Mg$_{0.15}$	Fe$_{0.17}$	Al$_{1.29}$	Si$_{1.35}$	(O,OH)$_{7.00}$
M	Ca$_{2.00}$	Na$_{0.02}$	Mg$_{0.28}$	Fe$_{0.08}$	Al$_{1.25}$	Si$_{1.37}$	O$_{6.98}$
I	Ca$_{1.97}$	Na$_{0.00}$	Mg$_{0.31}$	Fe$_{0.09}$	Al$_{1.24}$	Si$_{1.37}$	(O,OH)$_{6.99}$
M	Ca$_{1.92}$	Na$_{0.04}$	Mg$_{0.38}$	Fe$_{0.19}$	Al$_{0.88}$	Si$_{1.58}$	O$_{7.00}$
I	Ca$_{1.92}$	Na$_{0.00}$	Mg$_{0.37}$	Fe$_{0.16}$	Al$_{0.91}$	Si$_{1.63}$	(O,OH)$_{7.08}$
M	Ca$_{1.90}$	Na$_{0.08}$	Mg$_{0.19}$	Fe$_{0.13}$	Al$_{1.31}$	Si$_{1.38}$	O$_{7.00}$
I	Ca$_{2.07}$	Na$_{0.02}$	Mg$_{0.17}$	Fe$_{0.11}$	Al$_{1.21}$	Si$_{1.42}$	(O.OH)$_{7.02}$

*Formulae based on cation sum equal to 5.0
**M = melilite, I = idocrase

idocrase zone will continue to widen as long as melilite is available for reaction and fluid is flowing in the fracture. The replacement front cuts across individual grains of melilite (Fig. 3), indicating that water diffuses through the idocrase lattice as readily
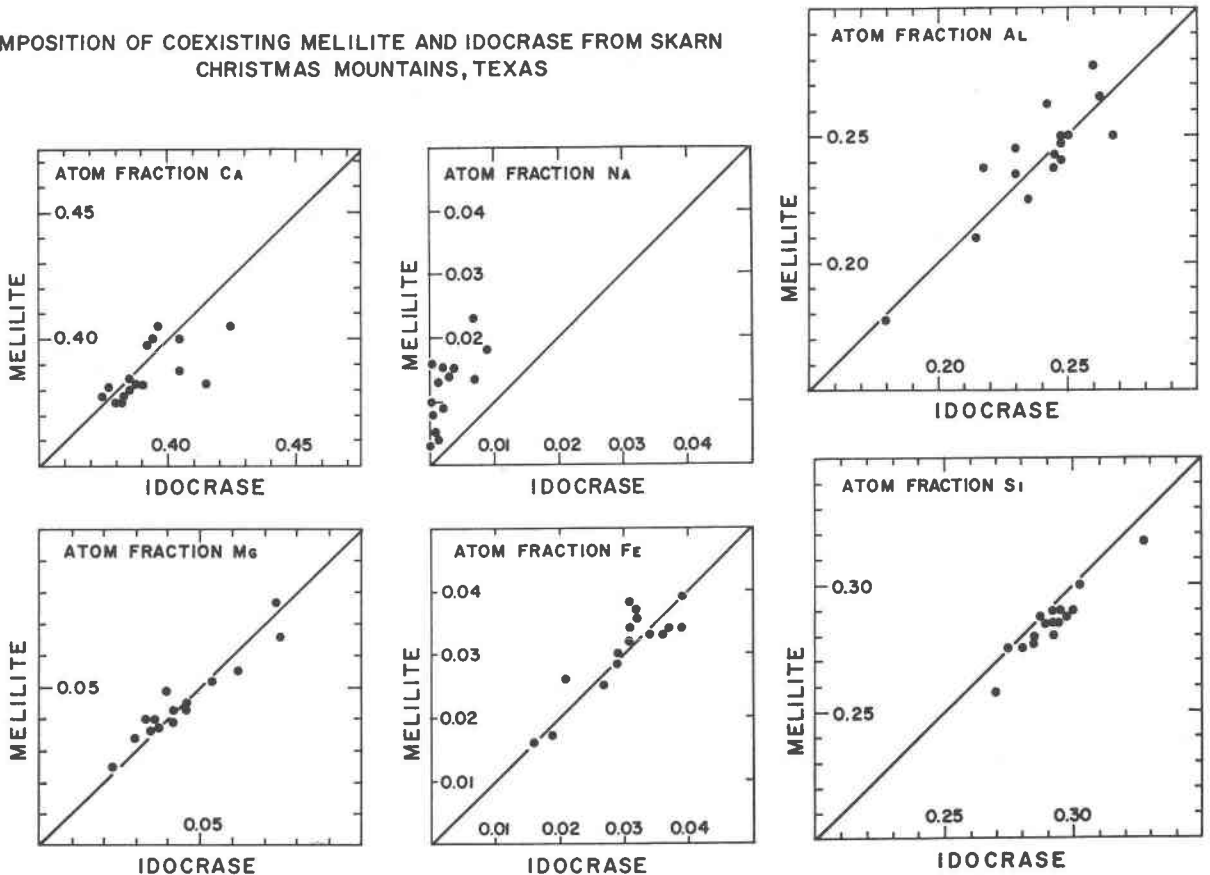
COMPOSITION OF COEXISTING MELILITE AND IDOCRASE FROM SKARN
CHRISTMAS MOUNTAINS, TEXAS

FIG. 4. Atom fraction of each of six major cations in coexisting melilite and idocrase from skarn. Line of slope = 1.0 represents equal partitioning of the cation between the two phases.

as along grain boundaries and cleavage planes. Because there is no systematic enrichment of Na in melilite adjacent to an idocrase zone, Na must diffuse outward through the product idocrase layer and be carried away by the fluid. Complete replacement of melilite skarn by idocrase results from the coalescense of idocrase veinlets developed along a network of intersecting fractures. The faithful preservation of the external habit and internal cleavage of melilite by idocrase and the lack of disruption of the original skarn fabric indicate that metasomatic replacement took place without significant change in volume.

Mineral assemblages in the zoned skarn and in zoned calc-silicate nodules distributed across the contact aureole indicate that the primary mineralogical zoning of the skarn was developed at 925-1025°C at about 0.3 kbar in the presence of a fluid phase with $X_{CO_2} > 0.6$ (Joesten, 1974b). Hydration of melilite with an H_2O-rich fluid records a change in the fluid composition on cooling.

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