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BREDIGITE, LARNITE AND γ DICALCIUM SILICATES FROM MARBLE CANYON

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ABSTRACT

The α' (bredigite), β (larnite) and γ (unnamed) forms of dicalcium silicate (Ca_2SiO_4) occur together in the contact zone around a syenite-monzonite intrusion in Marble Canyon. Bredigite, larnite and γ have consistant crystallographic orientations when they occur together. These relationships reflect the crystallographic direction in which the reorganization occurs when transformation from one form to another takes place.

INTRODUCTION

Two polymorphic forms of dicalcium silicate (Ca_2SiO_4) have been described as naturally occurring minerals by Tilley (1929) and Tilley and Vincent (1948). The minerals were found in a contact zone in Larne, Ireland and given the names larnite and bredigite.

Until 1964, no natural occurrences of these minerals had been reported from any locality in the United States. In 1963, three polymorphic forms of Ca_2SiO_4 were found in the contact zone around a syenite-monzonite intrusion in Marble Cayon.

LOCATION AND SETTING

Marble Canyon is in the east rim of the Diablo Plateau in Culberson County, Trans-Pecos Texas, 30 miles north of the town of Van Horn and 2 miles west of State Highway 54. The canyon is about a mile long and terminates upstream in an elongate amphitheater roughly a mile and a half long and half a mile wide. In the center of this elongate amphitheater is an elliptical outcrop of five different types of igneous rock that are arranged in a concentric pattern. From the center out they are:

(1) a coarse-grained syenite; (2) a coarse-grained green monzonite; (3) a medium-grained gray monzonite; (4) a discontinuous narrow border of olivine gabbro; and (5) small rhyolite dikes which cut the other rock types.

The boundaries of these rock types are not exposed in all parts of the intrusion. In some places the syenite is separated from the green monzonite by a well defined contact; in other places it is not well defined. The gray monzonite forms a resistant ridge around most of the intrusion, and talus on the inner slope of this ridge covers the contact between the green monzonite and gray monzonites. The contact between the green and gray monzonites is probably gradational. Near the sedimen-

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tary-igneous contact, the gray monzonite contains many knots and stringers of the gabbro border facies. The rhyolite occurs as small dikes of a few inches to several feet wide, and may represent a late stage injection into tension fractures of the previously solidified monzonite and syenite.

The intrusion is surrounded by a bleached contact zone ranging in width from 150 to 300 feet. The exposed contact zone includes the Permian Hueco and Bone Spring formations.

The dicalcium silicate occurs in localized zones in the Bone Spring formation, at the metasedimentary-igneous contact, and in one locality was found in the metasediments at a distance of 38 feet from the contact.

The Bone Spring formation is 1270 feet thick (King, 1962) and consists of lenticular massive beds of dolomitic limestone interfingering with thin cherty beds of fossiliferous limestone. The thin platy cherty carbonates range in composition from a dolomitic limestone to an almost pure calcium limestone. The platy limestone is locally interbedded with thin shale partings.

PREVIOUS WORK IN MARBLE CANYON

Richardson (1914) mentioned Marble Canyon in relation to the limestones and marble. In the early 1940's Ingerson (pers. comm.) visited Marble Canyon and collected samples. Ingerson's thin-section studies of samples from Marble Canyon revealed that the contact zone was rich in calcium-magnesium silicates. During the war Ingerson's efforts were redirected, and nothing was published on this work.

King and Knight (1944) prepared a preliminary map of the area that shows sedimentary formations and structure; the text mentions contact metamorphic rocks. King's (1949) more detailed geologic map of the Marble Canyon and associated intrusions, placed on open file by the U. S. Geological Survey, was available to the writer during this investigation.

Holser (1959) mentioned Marble Canyon in relation to the occurrence of non-pegmatitic beryllium in the United States, and described other intrusions in the area. He stated that Earl Ingerson, Charles Milton and others studied samples collected by King, and that the minerals found in the area were brucite, spurrite, merwinite, periclase, grossularite, idocrase, wollastonite, radiophyllite, diopside, melilite, serpentine and plagioclase.

King (1962) published a measured reaction of Permian strata in Marble Canyon, and Dunbar (1953) and Dunbar and Skinner (1937) studied fusulinids from the Marble Canyon area.

PREVIOUS WORK ON DICALCIUM SILICATE

The designations for the polymorphic forms of dicalcium silicates by Bredig (1950) are given below:

$\alpha =$ hexagonal (glaserite type)—not present.
$\alpha' =$ orthorhombic (B-K_2SO_4 type) (bredigite)—present.
$\beta =$ monoclinic (type unknown) (larnite)—present.
$\gamma =$ orthorhombic (olivine type) (unnamed)—present.

The polymorphic forms of the dicalcium silicate have been recognized as constituents in Portland cement for almost a century. The relationships between these polymorphic forms and the structural nature of the transformations involved have only recently been determined. The following is a brief sketch of the history of research on the dicalcium silicate and its polymorphic forms.

In 1882 Le Chatelier, according to Bogue (1947), described some of the polymorphic forms of the dicalcium silicate Ca_2SiO_4 in Portland cement clinker and discussed the transformations that occur. Bogue also stated that in 1897 Tornebohm described two clinker constituents to which he gave the names "belite" and "felite."According to Bredig (1950), belite and felite were β Ca_2SiO_4. Wright (Day *et al.*, 1906) described three polymorphic forms and discussed their temperature relationships.

None of the polymorphic forms of Ca_2SiO_4 had been described as a naturally occurring mineral until Tilley (1929) found the β polymorphic form (larnite) in the contact zone of Chalk and Tertiary dolerite at Scawt Hill, Co. Antrim, Ireland. Tilley named the mineral after Larne, which is near the locality where the mineral occurs. He noted the instability of the mineral and also noted the similarity between the optical properties of the transformation product and the low temperature artificial Ca_2SiO_4.

O'Daniel and Tscheischwili (1942) determined the structure of the low temperature form by analogy with Na_2BeF_4 to be the orthorhombic olivine type.

Tilley and Vincent (1948) described another form (α') of Ca_2SiO_4 from Scawt Hill which they designated as bredigite after Bredig, whose work on the problem of calcium silicate polymorphism (1942, 1943) made an important contribution to its solution.

Bredig (1950) presented a theoretical model for the structure and structural transformations of the polymorphic forms of calcium orthosilicate. Midgley (1952) determined the crystal structure of β dicalcium silicate and, to some extent, substantiated Bredig's speculation.

Bredig suggests that the transformation from the α' to γ may be a change from a coordination of 9 and 10, a packing of 9 and 10 oxygen atoms around one calcium atom, to a coordination of 6 in the γ phase (olivine structure). According to his calculations, this would cause an increase in volume of around 12%. Such an increase in volume is known from the β to γ inversion. He suggests that α' converts to β with a 1% increase in volume and a change to light fold coordination of oxygen around calcium.

Table 1 is a summary of the dicalcium silicate polymorphic forms and corresponding names and physical properties.

MARBLE CANYON DICALCIUM SILICATES

The dicalcium silicate occurs as rounded crystals that cut across boundaries of associated crystals of merwinite, rankinite, and melilite. This relationship suggests that calcite produced by the reaction, spurrite = calcite + calcium orthosilicate, has reacted with surrounding minerals. Some of the above named minerals remain as remnants between the grains of orthosilicate.

Electron probe analysis shows a small amount of iron, less than 1%, is present in some of the bredigite. The bredigite shows varying degrees of stability with some of it transforming rapidly as soon as it has been distrubed or exposed on a freshly cut surface, while other samples transform slowly. The difference in the stabilities observed in different samples of bredigite may be due to the substitution of iron for calcium in the crystal lattice.

Bredigite (α') from Marble Canyon has the following properties:

Shows clevage intersection at about 60° on sections cut normal to the acute bisectrix.

$+2V = 34°$.

The indices of refraction for this mineral are in the range given in Table 1 for bredigite.

This mineral is unstable and undergoes transformation similar to larnite.

Larnite (β) from Marble Canyon has the following properties:

Color—gray to colorless; translucent.

Form—round grains, irregular interlocking grains, and as myrmekitic intergrowth in merwinite, rankinite, and melilite.

Interference colors—up to second order blue.

Indices of refraction as determined by oil immersion are in the range given in Table 1.

$(+)2V = 63°$.

This mineral is unstable at atmospheric temperatures and pressures, especially when disturbed mechanically as by scratching, or when struck with a hammer, and it undergoes a transformation to the γ form of Ca_2SiO_4. This transformation probably proceeds along microfractures produced by the blow of the hammer. The mineral also undergoes transformation when heated. Transformation along cleavage planes can be seen in sections cut normal to the acute bisectrix.

(γ) (unnamed)

Luster—dull to vitreous.

Hardness—5 to 6.

Specific gravity—about 3.0 (meas.).

TABLE 1. POLYMORPHIC FORMS OF DICALCIUM SILICATE AND THEIR PHYSICAL PROPERTIES

Form	Physical Properties	Material	Source of Data
High temperature	Trigonal	Synthetic	Douglas (1952)
α Stable between 2130°–1438° or 1456° C. Has not been described as a naturally occurring mineral and was not observed in the Marble Canyon contact zone.	$\omega=1.724$ $\epsilon=1.738$ Cell dimension (Å) $a=5.46$ $c=6.76$	Data obtained from $(Ca_{1.58}, Mg_{0.32}, Fe_{0.10})SiO_4$	(Used data reported by Beliankin and Lapin, 1946.)
α' Bredigite	Orthorhombic $\alpha=1.713$ $\beta=1.717$ $\gamma=1.732$ (+) 2V 30° (Tilley and Vincent, 1948) Cell dimensions (Å) $a=10.91$ $b=18.41$ $c=6.76$ Contents of unit cell 16 Ca_2SiO_4 Volume $=4$ (339) Å^3 Calculated density $=3.38$ Optic axial plane (010) Cleavage prismatic (130) Twinning (110)	Natural mineral Scawt Hill, County Antrim	Douglas (1952)
β Larnite	Monoclinic $\alpha=1.715$ $\gamma=1.740$ $+$ 2V $=62°$ Cell dimension (Å) $a=5.48$ $b=6.76$ $c=9.28$ $\beta=94°33'$ $b/c=0.729$ Contents of unit cell 4 Ca_2SiO_4 Volume $=344$ Å^3 Calculated density $=3.31$	Synthetic crystals stabilized with 0.5% B_2O_3	Midgley (1952)
	$\alpha=1.707$ $\beta=1.715$ $\gamma=1.730$	Natural mineral from Scawt Hill, County Antrim	Tilley (1929)

TABLE 1—(*Continued*)

Form	Physical Properties	Material	Source of Data
γ (unnamed)	Orthorhombic $\alpha=1.640$ $\beta=1.645$ $\gamma=1.654$ $(-)$ $2V=60°$	Synthetic	Day *et al.* (1906)
	Cell dimensions (Å) $a=5.06$ $b=11.28$ $c=6.78$ Contents of unit cell 4 Ca_2SiO_4 Volume in $=387$ Å^3 Calculated density $=2.97$	Synthetic	O'Daniel and Tscheischwili (1942)

Orthorhombic—appears fibrous in thin section. These fibers appear to have cleavage perpendicular to their length.
Optical properties—optic plane normal to length of fibers.
$-2V=57°\pm3°$.
Parallel extinction.
In a thin section of bredigite with two optic planes oriented vertically, the associated γ comes to extinction with the bredigite.
Indices of refraction ($\pm.003$) $\alpha=1.633$; $\beta=1.640$; $\gamma=1.645$.

The only untransformed crystals of larnite and bredigite remaining in a thin section are usually those crystals bounded on all sides by other minerals, and cut perpendicular to the cleavage and acute bisectrix. The cleavages are usually well defined and contain some of the γ Ca_2SiO_4 form. When a portion of these untransformed crystals is removed from the slide, the remaining crystal will undergo transformation parallel with these cleavage planes until the entire crystal transforms to the γ form.

The diagram in Fig. 1 shows all three minerals in their relative orientation to each other. This diagram was made from a thin section photomicrograph. The crystallographic orientations given in this diagram are those given by Tilley (1929) and Midgley (1952) for larnite, Douglas (1952) for bredigite, Day *et al.* (1906) and Tilley (1929) for the γ form. The optical orientations are those of the minerals in the thin section used on the universal stage.

The *x*-ray diffraction patterns of these minerals and their products of transformation are given in Table 2.

The transformation product is a mixture of bredigite, larnite and γ.

The dicalcium silicate Ca_2SiO_4 is usually associated with merwinite.

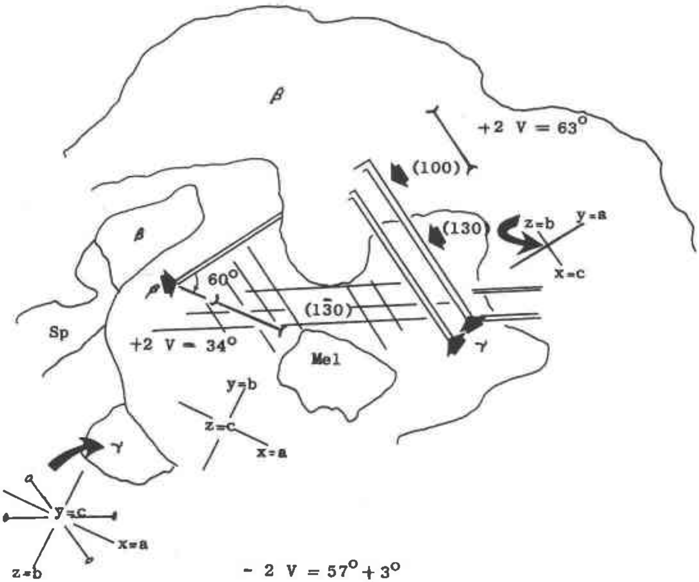

Fig. 1. Diagrams showing the orientation and crystallographic relationships between, bredigite, larnite, and γ in a thin section from near the contact (α' = bredigite, β = larnite, γ, Sp = spurrite, and Mel = melilite). Bredigite is oriented on the acute bisectrix. The cleavage on bredigite intersects at about 60°. All patches of larnite shown on the diagram have the same orientation and are 3° off center counter-clockwise in the optic plane from the acute bisectrix. The optic plane of γ is perpendicular to the optic plane of bredigite. Small amounts of the γ are present along cleavage traces in bredigite and have the orientation described above.

Table 2. Transformation Product of Bredigite (α'); Larnite (β); and Unnamed (γ) Calcium Orthosilicate

d Å	I				d Å	I				d Å	I			
5.60	2			γ	2.57	1	α'		γ	1.92	1	α'	β	
4.31	2			γ	2.54	1		β	γ	1.89	1	α'		γ
4.00	2			γ	2.49	1	α'		γ	1.84	1	α'	β	
3.75	2			γ	2.44	1		β	γ	1.83	1		β	
3.46	1	α'			2.42	1	α'	β		1.79	1	α'	β	γ
3.00	2			γ	2.34	1	α'		γ	1.78	1		β	
2.98	3	α'			2.28	1	α'	β		1.74	1	α'	β	γ
2.87	4	α'	β	γ	2.22	1		β		1.67	1	α'	β	
2.82	1		β	γ	2.20	2		β		1.66	1	α'	β	
2.74	2		β	γ	2.16	1	α'	β		1.62	1	α'	β	
2.72	8		β	γ	2.06	1	α'			1.55	1	α'	β	
2.69	6		β		2.02	1		β	γ					
2.66	10	α'			1.99	1		β						

No substitution of magnesium for calcium in the dicalcium silicate was detected.

Tobermorite and xonotlite occur in and adjacent to fractures in the inner and intermediate contact zones. They are associated with bredigite, larnite and the γ calcium orthosilicate, and are alteration products of these minerals. The calcium orthosilicate is more subject to alteration along fractures than are the other minerals. The alteration probably began at temperatures above 300° C. (McConnell, 1954) for xonotlite, and at progressively lower temperatures for the 9 Å, 11 Å, and 14 Å tobermorites, respectively. The formation of these minerals resulted from the reaction of anhydrous calcium silicates, with ground water and hydrothermal solution introduced along the fractures in the contact rocks.

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