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METAMORPHIC ARAGONITE IN THE GLAUCOPHANE SCHISTS OF CAZADERO, CALIFORNIA

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ABSTRACT. Metamorphic aragonite is the dominant polymorph of $CaCO_3$ within concordant and discordant carbonate-rich lenses and veins in the glaucophane schist belt exposed along Ward Creek, Cazadero, California. This schist sequence is part of a larger metamorphic belt within the Franciscan formation of Jurassic and Cretaceous age. Petrofabric study shows that the fabric element of the aragonite marbles is compatible with the lineation of the enclosing schists. A careful chemical, optical, and X-ray study of four purified aragonite specimens shows that this metamorphic aragonite conforms in every respect with the physical properties recorded for aragonite. The mineral is biaxial negative, 2V approximately 18°, alpha = 1.530 ± .001, beta = 1.680 ± .002, and gamma = 1.685 ± .001. A maximum of 1.26 molecular percent $SrCO_3$ was found by chemical analysis.

The presence of aragonite as a metamorphic mineral within these glaucophane schists suggests that the pressure and temperature conditions for this facies may be unique. Experimental work on the inversion of calcite to aragonite has shown that aragonite is the stable high pressure polymorph of $CaCO_3$; the formation of aragonite in the glaucophane schists indicates that pressures greater than 4000 bars prevailed during metamorphism. Tectonic stresses developed during the formation of the glaucophane schists may have increased the pressure considerably above the lithostatic load pressure and promoted the stable formation of aragonite marbles.

INTRODUCTION

Metamorphic aragonite is of widespread occurrence in the glaucophane schist terrain near Cazadero, California. This unusual occurrence of aragonite as an integral part of the metamorphic sequence raised the question as to its origin and relationships to the host glaucophane schists. This paper describes the aragonite, demonstrates it was formed during metamorphism, and discusses its significance.

Aragonites found prior to this discovery were all formed at or near the Earth's surface at low temperatures (Palache, Berman, and Frondel, 1951; Graf and Lamar, 1955; Graf, 1960a, p. 12) and have been deposited as the metastable form of $CaCO_3$ in these pressure and temperature environments. Experiments by Backstrom (1925) on the transition of aragonite to calcite at 25°C and one atmosphere show that $\Delta F_{298}{}^{\circ}{}_{K} = -190$ cal, with $\Delta V = -2.75$ cc per mole. He concluded that the pressure necessary to allow the stable formation of aragonite was not attainable under geological conditions. Earlier Johnston, Merwin, and Williamson (1916) demonstrated that at one atmosphere and temperatures ranging from 0° to 970°C aragonite is unstable with respect to calcite, but that aragonite may have a stability field at temperatures below −100°C. Aragonite under conditions normally found at the surface of the Earth thus tends to invert to calcite; the rate of this conversion, however, is determined by temperature and/or the presence of water. In a dry environment, aragonite may persist indefinitely, but an increase in temperature or a wet environment promotes the conversion to calcite. For instance, Stehli (1956) found Pennsylvanian fossils sealed in asphalt had not inverted from aragonite to calcite. Johnston and others (1916) suggested that the solid solution of Sr or Pb in aragonite would stabilize it, but MacDonald (1956) has shown that excessive amounts (30 mole percent) of components other than

$CaCO_3$ would be required to "stabilize" aragonite. The more recent works on the aragonite-calcite stability fields at high pressures and temperatures by Jamieson (1953), MacDonald (1956), and Clark (1957) are concordant and clearly demonstrate that aragonite is the high pressure dimorph of calcite, thus confirming Backstrom's earlier conclusions.

It is interesting to note the speculations of these experimentalists regarding the possibility of metamorphic aragonite. Jamieson (1953, p. 1389) states that:

> " . . . except for peculiar local conditions of high hydrostatic pressure and moderate temperatures, the only known form of $CaCO_3$ which is stable under natural geologic conditions is that of calcite."

MacDonald (1956, p. 755) concludes that the equilibrium curve

> " . . . could be interpreted as fixing the maximum pressure to which pure calcite marbles could have been subjected in regional metamorphism. Greater pressures than those given by the equilibrium curve would have resulted in aragonite. However, any aragonite that might have formed could have inverted to calcite at some later time in the history of the marble erasing in such a process evidence of the original aragonite. The absence of aragonite in metamorphic rocks suggests that these may have formed at pressures lower than those of the equilibrium curve, but certainly nothing more definite can be said."

We will return to the implications of this experimental work in the geological interpretation on the significance of aragonite in the glaucophane schist terrain near Cazadero, California.

OCCURRENCE

Aragonite-bearing glaucophane schists are well exposed in Ward Creek canyon about 1¼ miles above its confluence with Austin Creek. This schist sequence is in the SW¼ NE¼, sec. 18, T. 8 N., R. 11 W., Mount Diablo Meridian (38° 32′ N Lat, 123° 06′ W Long) and can be readily located on the 7½-minute topographic map of the Cazadero Quadrangle, Sonoma County, California. The schists are metamorphosed pillow-basalts, cherts, and interbedded shales of the Franciscan formation of Jurassic and Cretaceous ages, and they are part of the Franciscan belt of Northern California recently defined by Bailey and Irwin (1959). The metamorphism probably took place somewhere within the post Upper Jurassic (Tithonian) to pre-middle Cretaceous (Albian) time (Edgar Bailey, written communication, 1960).

Good exposures of the aragonite-bearing schists are restricted to the bottom of the Ward Creek canyon where the rocks are scoured clean during the rainy season. The slopes of the canyon are covered with either a dense redwood forest or a thick mantle of slope debris.

The schist sequence may be divided into two original rock types on the basis of preserved structures and metamorphic mineral assemblages: (1) pillow basalts that have recrystallized to form glaucophane-lawsonite-muscovite-sphene schists containing pumpellyite, clinozoisite, garnet, chlorite, and carbonate in varying amounts; and (2) cherts and shales that have recrystallized to form quartz-stilpnomelane-crossite schists with accessory amounts of garnet, muscovite, epidote, pyrite, and carbonate. The metasediments form thin interbeds (5 to 20 feet) between the thicker metabasalts (several hundreds of feet).

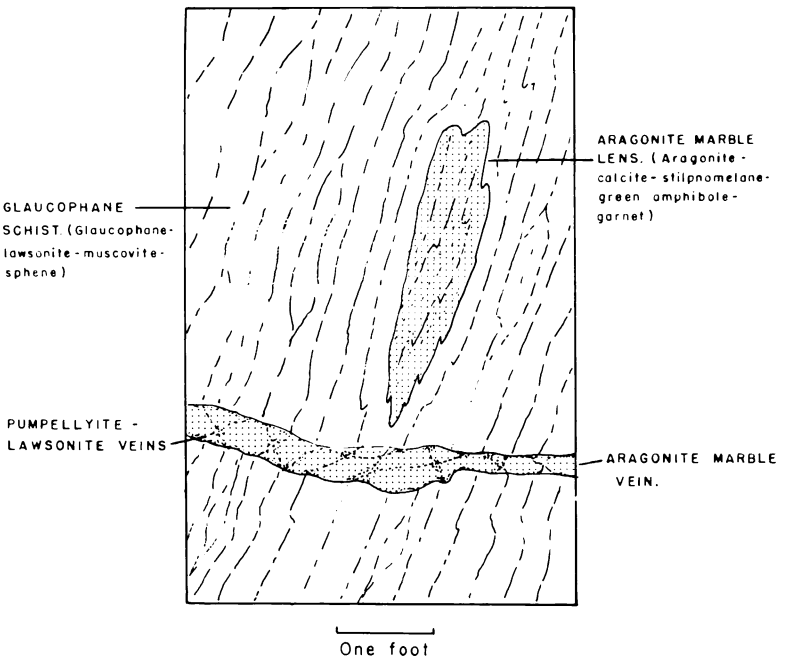

Fig. 1. Sketch illustrating relationships between the lens and vein aragonite within the metamorphosed basalts.

Aragonite occurs within this schist sequence as beds, lenses, and veins and is generally more abundant in the metabasalt types. Elongate carbonate lenses up to 5 feet in length and 3 to 4 inches thick are intercalated with the glaucophane-lawsonite-muscovite-sphene schists (fig. 1). These carbonate lenses may be isolated or clustered. In general, they are tabular parallel to the plane of foliation, with the longest dimension parallel to the other linear elements in the rock. Distinct carbonate beds as much as 2 inches thick are common in the central part of the Ward Creek exposure, where these beds may be continuous for 15 to 20 feet. In most exposures these beds are seen to pinch out. Like the carbonate lenses, the beds also lie in the plane of foliation. Both the carbonate lenses and beds contain as much as 30 or 40 percent of metamorphic silicate minerals (fig. 2).

The most striking occurrence of carbonate within the exposed sequence is as nearly pure veins. They generally cut both the foliation and lineation, for they fill joints normal to the lineation or follow shear zones showing little or no relation to the existing metamorphic structures (fig. 1). These carbonate veins are 3 to 4 inches wide and extend for several hundred feet, but the narrow exposure within the canyon bottom does not allow one to trace them continuously from one exposure to the next. The internal lineation of the veins parallels that of the surrounding schists.

In unmetamorphosed pillow lava sequences of the Franciscan formation in central California, carbonate occurs most commonly as veins but also as

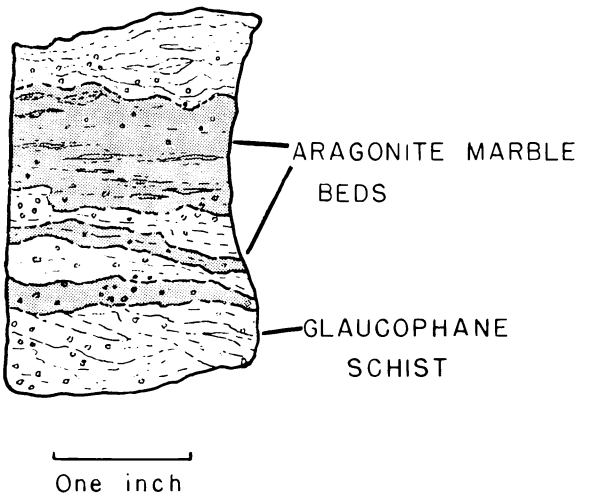

Fig. 2. Scale drawing illustrating relations between carbonate beds and schist. Schist mineral assemblage is: Glaucophane-muscovite-lawsonite-garnet-sphene, and the mineral assemblage for the carbonate bed is: Aragonite-calcite-glaucophane-garnet-quartz-clinozoisite-pyrite.

lenses or discontinuous limestone beds. Even though some of the carbonate in these unmetamorphosed equivalents of the glaucophane schists may have been introduced after the extrusion of the volcanics, its abundance eliminates any need to appeal to the introduction of carbonate during metamorphism to explain the presence of aragonite in the Ward Creek schists.

The discovery of aragonite in the Ward Creek metamorphic sequence led to a random check of carbonate-bearing schists from the Franciscan formation and specimens from other glaucophane schist terrains. Aragonite was identified as a metamorphic mineral from specimens collected from the following areas:

Aragonite Localities

Rock type	Location
Franciscan formation	
1. Jadeite mass in serpentine	Clear Creek, San Benito County, California.
2. Metabasalt	San Benito River, San Benito County, California.
3. Metabasalt Jadeite-bearing metagraywacke Glaucophane-garnet schist	Pacheco Pass, California. (Bates McKee, oral communication, 1960).
4. Metagraywacke	Lick Observatory, Mount Hamilton, California.
5. Metagraywacke Phyllite	SE¼, sec. 4, R. 4 E., T. 7 S., Isabel Valley Quadrangle, California.

6.	Metagraywacke	NW¼, sec. 3, T. 6 S., R. 4 E., Eylar Mountain Quadrangle, California.
7.	Jadeite-bearing metagraywacke	Angel Island, San Francisco Bay, California.
	Catalina schist	
8.	Glaucophane-lawsonite schist	Basement complex, Playa del Rey oil field, Los Angeles Basin, California (specimen obtained from J. E. Schoellhamer, U. S. Geologicial Survey.
	Other specimens	
9.	Metagabbro	Glaucophane schist belt, Roseburg, Oregon.
10.	Glaucophane-lawsonite schist	San Reinigio, Antique, Philippines (collected by J. E. Harrington, U. S. Geological Survey).
11.	Glaucophane schist	Jetty quarry, Bandon, Oregon

The metamorphic aragonite occurs as veins, knots, or lenses within very dense rocks, but not as single crystals or as crystal aggregates lining cavities or veins. In hand specimens, it has a snow-white, dense fine-grained appearance. Aragonite may be the more common polymorphic form of $CaCO_3$ within the metamorphic rocks of the Franciscan formation that are in place, but further intensive studies of distribution are needed to confirm this.

Except perhaps for the Clear Creek material, all the aragonite identified from Franciscan schists comes from rocks that are mappable metamorphic units and in place. These units are characterized by schists with a moderate to weakly developed metamorphic fabric that in many places retain pre-metamorphic igneous and sedimentary structures. A second type of glaucophane schist common to the metamorphic belts of the Franciscan is more restricted in areal extent. These schists occur as isolated coarsely crystalline tectonic blocks having a well developed metamorphic fabric but never forming a continuous mappable unit (Brothers, 1954; Borg, 1956; Switzer, 1945, 1951; Bloxam, 1959). No aragonite has yet been identified from these isolated schist blocks. Without pursuing the ultimate origin of these two distinct types here, suffice it to say that for the remainder of the discussion we are concerned only with the occurrence of aragonite in the metamorphic rocks of the first type, as represented by the Ward Creek schist sequence.

PETROGRAPHY

The aragonite marbles are very dense and fine grained. Where the carbonate phase is dominant the rock is nearly white, but with increasing content of silicate minerals it approaches the color of the host schist. Cleavage faces

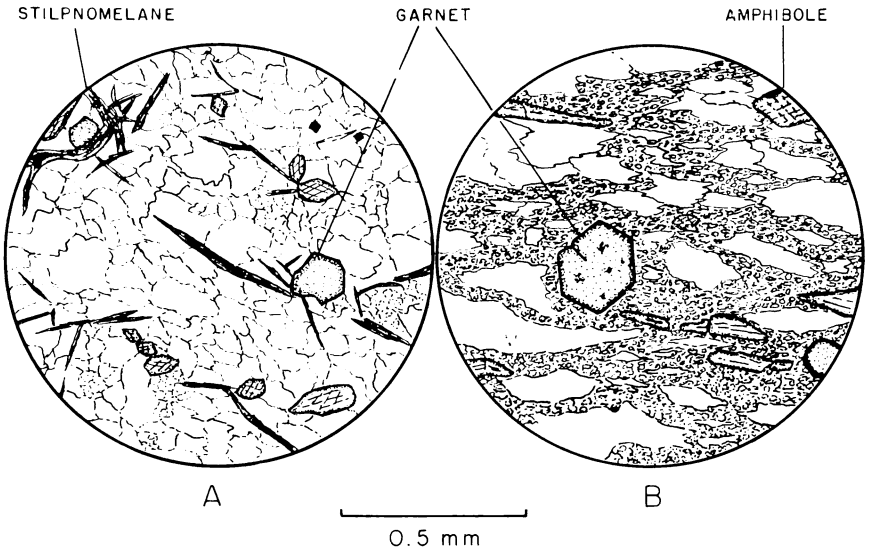

Fig. 3. Aragonite marbles. (A) Aragonite-stilpnomelane-green amphibole-garnet-pyrite schist cut normal to the lineation exhibiting nearly equigranular carbonate groundmass. (B) Aragonite-green amphibole-garnet schist cut parallel to the lineation. The groundmass consists of carbonate elongated along the c-axis set in a finer granulated matrix of carbonate.

cannot be discerned by hand lens inspection, except where late calcite has invaded the aragonite. Because the density of calcite is 2.74 and that of aragonite is 2.94, a small jar of an organic heavy liquid adjusted to a density of 2.76 affords a rapid and reliable field check where hefting the carbonate suggests aragonite. Thus the only two field criteria that seem useful to distinguish calcite marbles from aragonite marbles are (1) density, and (2) presence of the characteristic rhombohedral cleavage of calcite.

The true metamorphic character of the aragonite is revealed by microscopic examination. The texture is controlled largely by the individual aragonite grains, which show a strong elongation in the plane of foliation and characteristically have irregular and interlocking boundaries (fig. 3). Granulation by shearing of the aragonite must have occurred during deformation as the larger porphyroblasts show strain, and extremely fine-grained aragonite is found interstitial to the larger grains. Elongation of the aragonite grains is parallel to that of the amphiboles. The range in dimension of the average aragonite grain in the direction of elongation is 0.2 to 0.3 mm with the larger grains extending almost 4.0 mm. In the short or flattened direction, these dimensions are 0.05 to 0.2 mm for the aragonite lying within the plane of foliation. Universal stage studies revealed that in general this direction of elongation is nearly parallel to the c-axis of aragonite. Characteristic of the metamorphic aragonites is the general lack of cleavage traces, which contrasts with the rhombohedral cleavages universally developed in calcite. In section cut normal to the direction of lineation, a lamellar twinning was commonly observed in those planes normal to the c-axis. A universal stage plot of this

twinning reveals that the twin and composition plane is {110}, similar to that recorded for aragonite (Palache, Berman, and Frondel, 1951, p. 184).

Calcite has also been recognized in most of the aragonite marbles studied, and staining by cobalt nitrate solutions has allowed us to determine the macroscopic relations between these polymorphs. Invariably the calcite is the late carbonate phase, either as veins cutting the aragonite or as irregular patches replacing the aragonite (fig. 4). Microscopically the calcite is seen as an equigranular mosaic with little or no elongation in the grains, and apparently the calcite did not inherit the fabric of the original aragonite. None of this calcite is abnormally biaxial, nor does it show any evidence of strain. The ratio of calcite to aragonite is difficult to estimate in thin section because of the fine-grained texture. After bulk densities of pure carbonate fragments are determined, calculations may be made by assuming an ideal density of 2.74 for calcite and 2.94 for aragonite. In this manner, a range of 55 to 68 percent aragonite was determined for the vein carbonate, and 32 to 95 percent aragonite for the carbonate beds and lenses. As mentioned earlier in this paragraph, the textural relations show that the calcite present is the younger mineral, and not pre-metamorphic calcite that failed to invert to aragonite during metamorphism.

Within the carbonate lenses and beds a characteristic suite of metamorphic minerals prevails. Textural relations reveal that these minerals have formed contemporaneously in stable equilibrium with the aragonite. A pale blue glaucophane is common in the bedded carbonates as nematoblastic subhedral grains. Properties of this glaucophane: alpha = 1.621, beta = 1.641, gamma = 1.646, birefringence 0.025, $Z \wedge C = 5°\text{-}6°$, $2V = 32°$, Z-pale blue = Y-pale violet > X-colorless, and density 3.1-3.19. In contrast, a pale green amphibole, with alpha = 1.646, beta = 1.658, gamma = 1.663, birefringence 0.017, $Z \wedge C = 20\text{-}22°$, 2V = large, X-colorless < Y-light green = Z-light green, and density 3.14-3.21, is predominant within the lenses. Euhedral porphyroblasts of pale pink to colorless garnet are commonly present with the

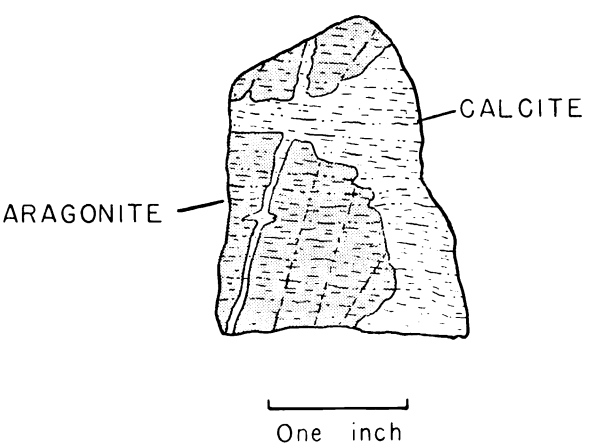

Fig. 4. Scale drawing illustrating the relations between the metamorphic aragonite and late calcite (Aragonite-calcite-green amphibole-stilpnomelane-garnet lens).

TABLE 1

Properties of garnets associated with aragonite

Sample Number	n ± .002	Sp. Gr. ± .02	Cell Size ± .002 A	MnO Weight Percent
18-CZ-59	1.796	4.02	11.662	No data
50-CZ-59	1.791	3.99	11.653	No data
201-RGC-59L	1.798	4.06	11.640	13.0 ± 2.0

beds and lenses. The MnO content of the garnet (table 1) determined by X-ray spectrochemical methods is equivalent to about 30 molecular percent spessartite, which is surprisingly high for garnet formed in a carbonate environment. A comparison of the physical properties of the three garnets indicates that the first two also may contain large amounts of the spessartite molecule. Additional chemical data for many of the garnets from the Ward Creek schist sequence are being obtained, and the subject will not be further pursued here.

Pumpellyite (beta = 1.682. 2V small (+), v>r. X = colorless < Y = blue green > Z = colorless). clinozoisite (gamma = 1.73, 2V = 90°. X = Y = Z colorless) and lawsonite are particularly common in the vein-type carbonates. Lepidoblastic brown stilpnomelane is a minor but persistent constituent of the beds and lenses of carbonate; it was not found in the veins. Stringers and mosaic patches of recrystallized quartz are common in all occurrences, and no indication of reaction between the carbonate and quartz was observed. Euhedral porphyroblastic crystals of pyrite are common in the beds and lenses but lacking in the veins. Small (0.3 mm) grains of a light-brown tourmaline occur in the bedded carbonates.

To summarize, in the carbonate lenses and beds, the minerals are, in decreasing abundance, aragonite (+ calcite), amphibole, garnet, and stilpnomelane; in the veins, the minerals are aragonite (+ calcite), pumpellyite, lawsonite, and clinozoisite. The carbonate lenses and beds, which contain as much as 30 percent silicates, must have been derived from shaley limestones; the vein carbonates, on the other hand, seldom contain as much as 10 percent silicates and must have been derived from relatively pure carbonate veins. As mentioned above, the carbonate beds, stringers, and veins all contain aragonite in apparent stable equilibrium with these silicates, which, as a group, are characteristic of the glaucophane schist facies (Fyfe, Turner, and Verhoogen, 1958).

STRUCTURE AND PETROFABRICS

Conclusive evidence of the metamorphic origin of the Ward Creek aragonite was obtained by establishing the relationship of its fabric to the lineation and foliation of the host schists. The premise here is: If the crystallographic orientation of the aragonite is compatible with the metamorphic structures mapped in the field, then the aragonite must have crystallized during the metamorphism that produced these structures. In general, the foliation and schistosity of these metamorphics conform to the original bedding planes of the lavas and chert-shales. These rocks are folded into an anticline whose axis strikes N 85° W and plunges 42° W. A plot of the linear features (elon-

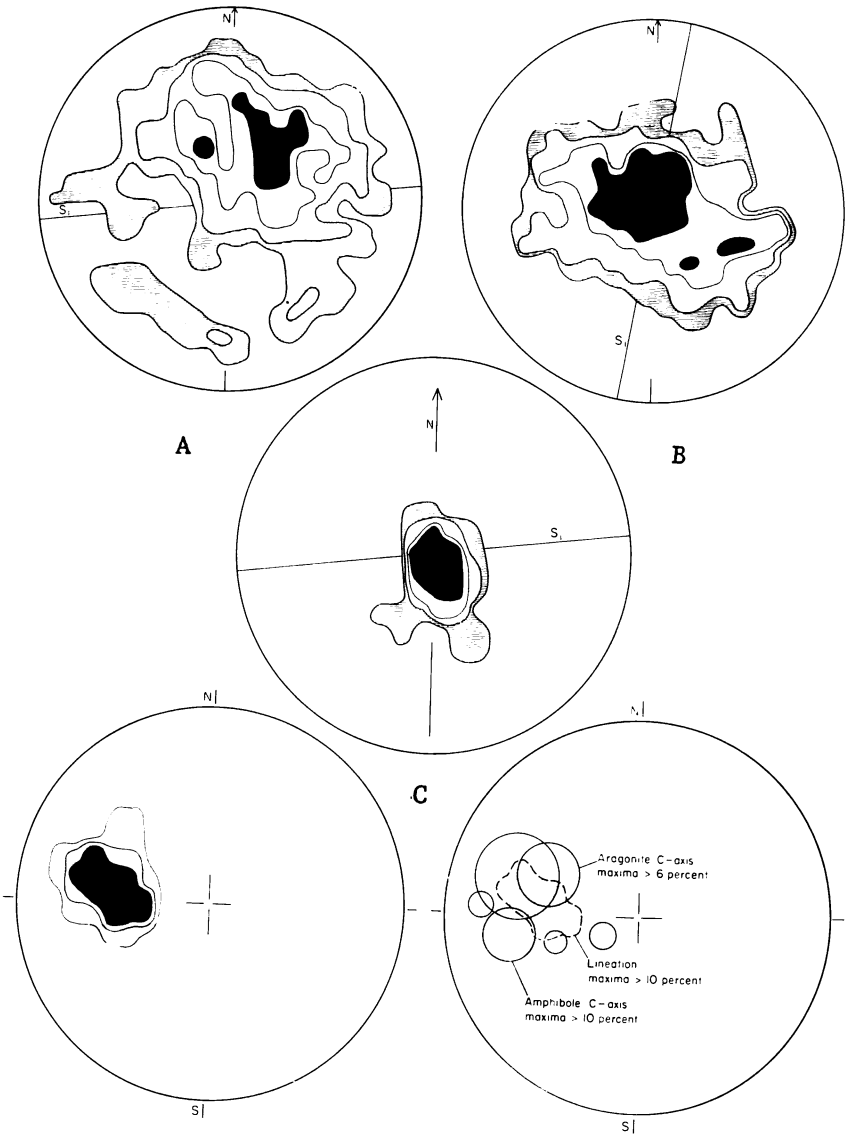

Fig. 5. Fabric of metamorphic aragonite and its relations to the lineations in the host schist. A—Section cut normal to lineation in carbonate lens, c-axis in 150 grains of aragonite. Contours 1, 2, 4, and 6 percent per 1 percent area. S_1—foliation. B—Section cut normal to lineation in carbonate bed, c-axis in 150 grains of aragonite. Contours 1, 2, 4, and 6 percent per 1 percent area. S_1—foliation. C—Section cut normal to lineation, c-axis in 60 amphibole grains from same section as A. Contours 3, 6, 8, and 10 percent per 1 percent area. S_1—foliation. D—Plot of lineations at 40 points within the Ward Creek schists. Contours 0, 4, 6, and 10 percent. Average trend of lineations is N 85° W, plunging 42° W. E—Combined plot of aragonite c-axis maxima, amphibole c-axis maxima, and lineations demonstrating concordancy between local lineations and the microscopic fabric of the aragonite. (Aragonite and amphibole maxima rotated onto horizontal geographic circle).

gated minerals, minor fold axes, mineral streaks, and crenulations) shows an average value nearly identical to the attitude of the anticlinal fold axis (fig. 5-D). To outline briefly the broader field setting, this fold axis parallels the gradational northern contact of the schists with a larger metabasalt mass that contains the schists. The metabasalt mass is bounded on the north by a nearly east-west contact with graywacke, forming a local westerly trend which is oblique to the general N 67° W trend of the major schist belt in this area (Edgar Bailey, written communication, 1960).

Two oriented specimens of the aragonite marbles were selected in order to investigate the relation between the orientation of the aragonite crystals and the linear features of the schist. One aragonite specimen was taken from a lens and the other was from a bed. Petrofabric analyses were made from sections cut normal to the direction of lineation, a direction established easily by visual observation of the elongated amphiboles. Only the porphyroblastic grains of aragonite were included in the analysis, as the tiny (< 0.01 mm) intergranular fragments were too small for universal stage observation. The c-axis of the aragonite was selected as the best crystallographic direction to use, since it is easily identified optically. Both the cleavage and twinning were too erratically developed to yield a good statistical plot.

Figure 5-A and B presents the results of plots which were prepared using methods recommended by Fairbairn (1949). The aragonite c-axis maxima, in both diagrams, are aligned around the tectonic b-axis (lineation). Within the lens (fig. 5-A) the c-axis assumes a rough monoclinic microscopic fabric symmetry, whereas the pattern developed within the bedded carbonates (fig. 5-B) is more nearly an axial symmetry. For comparison, a plot of the amphibole (fig. 5-C) from the lens carbonate is included to show the axial symmetry parallel to lineation. By superimposing the rotated aragonite and amphibole maxima from their individual diagrams to a horizontal geographic circle containing the observed maxima for the macroscopic lineations, a convincing correlation between the lineation and the aragonite orientation is revealed (fig. 5-E). Compatibility of the aragonite fabric element with lineation of the schists leads to the conclusion that the aragonite developed during metamorphism.

MINERALOGY OF THE ARAGONITE

Four aragonite marbles were selected for mineralogical study in order to determine whether or not this metamorphic aragonite corresponds chemically and structurally to metastable aragonites from near-surface deposits.

TABLE 2

Rocks from which the analyzed metamorphic aragonite was obtained

Sample No.	Rock type	Density	Mineralogy
31-CZ-59	Vein	2.86	Aragonite-calcite-lawsonite-green amphibole
45-CZ-59	Vein	2.89	Aragonite-calcite-pumpellyite
50-CZ-59	Carbonate bed	2.94	Aragonite-calcite-glaucophane-garnet-quartz-clinozoisite-pyrite
51-CZ-59	Carbonate bed	2.90	Aragonite-calcite-glaucophane-garnet-quartz-muscovite-tourmaline

A summary description of these rocks is given in table 2. The aragonite was carefully separated from these specimens after crushing and sizing the material. Size fractions between 150 to 200 mesh were centrifuged in bromoform-methylene iodide mixtures. The resultant fractions after repeated centrifuging had a density range between 2.93 to 2.96, i.e., all the material sinks in a liquid of 2.93 and floats in a liquid of 2.96. The average density for each of these samples can then be given as 2.95 ± .03.

Chemical and spectrographic analyses of the purified fractions are presented in table 3. Recalculation of the analyses, assuming the cell contents to be 4 [$CaCO_3$], agrees well with the theoretical formula for aragonite. It is well known that Sr^{++} will substitute for Ca^{++} in the aragonite structure, whereas only minor amounts may enter the calcite structure (Graf, 1960b, p. 32-37). For these metamorphic aragonites the Sr:Ca ratio ranges from 1:62 to 1:39, which is below the maximum reported substitution in natural material, 1:25 (Hutton, 1936). MacDonald (1956), on the basis of thermodynamic reasoning, has pointed out that at least 30 molecular percent of cations other than Ca^{++} would be needed to stabilize aragonite relative to calcite at the pressure and temperature conditions prevailing on the surface of the Earth. The four analyses of Ward Creek aragonite show a maximum of 1.26 molecular percent $SrCO_3$, and satisfy the chemical formula given for aragonite except for this minor solid solution of $SrCO_3$.

Splits of the powdered material used for chemical analysis were X-rayed by the diffractometer, using CuK alpha radiation and alumina as an internal standard. The prominent peaks of aragonite were scanned at speeds of ¼° per minute (table 4). A comparison between each sample and that of the National Bureau of Standards (Swanson, Fuyat, and Ugrinic, 1954) standard spacings for aragonite reveal excellent agreement. Complete scanning of the samples from 5° to 60° 2 θ produced no lines that could not be indexed on the basis of the aragonite space group. The optical constants of the Ward Creek aragonite (table 3) agree well with those listed for aragonite by Palache, Berman, and Frondel (1951).

GEOLOGIC IMPLICATIONS

The crystallization and preservation of aragonite in metamorphic rocks have not been reported previously, although studies concerning the metamorphic petrology of calcite marbles from a wide range of geologic environments are numerous. Aragonite may have been overlooked because its polymorph calcite is sometimes abnormally biaxial, with 2V commonly between 5° to 10°, and exceptionally 30° (see, for example, Palache, Berman, and Frondel, 1951, p. 150). In contact metamorphic rocks biaxial calcite is not uncommon, apparently the result of strain (Gillson, 1927; Walker and Parsons, 1925). As aragonite is not stable in the high temperature environment of contact zones, misidentification of the carbonate phase based on optical determinations is unlikely. In dynamothermal metamorphic rocks, however, biaxial carbonates may be either strained calcite or aragonite, and verification of their identity by X-ray techniques is warranted. This is especially true of carbonates occurring in glaucophane schist terrains where heretofore only calcite has been reported (van der Plas, 1959; Borg, 1956; Bloxam, 1959).

TABLE 3

Chemical and physical properties of the Cazadero aragonites
(Analyses by U. S. Geological Survey)

	31-CZ-59		45-CZ-59		50-CZ-59		51-CZ-59	
	Weight Percent	Metal[1] Atoms	Weight Percent	Metal Atoms	Weight Percent	Metal Atoms	Weight Percent	Metal Atoms
Chemical Analysis by L. E. Reichen								
CaO	54.40	3.99 } 4.04	54.83	3.99 } 4.03	55.26	4.03 } 4.06	55.03	4.02 } 4.06
SrO[2]	1.18	.05 }	1.11	.04 }	0.76	.03 }	1.09	.04 }
CO_2	42.70	3.98	43.02	3.99	42.70	3.97	42.68	3.97
Insol.	1.62		.92		1.30		.92	
Total	99.90		99.88		100.02		99.72	
CaSr/ ratio	39:1		42:1		62:1		43:1	
Spectrographic Analysis by Harry Bastron								
Sr	0.10		0.094		0.064		0.092	
Mg	0.019		0.008		0.035		0.034	
Fe	0.061		0.026		0.081		0.070	
Mn	0 0036		0.0040		0.0048		0.0026	
Density[3]	2.93-2.96		2.93-2.96		2.93-2.96		2.93-2.96	
Optics[4]								
α	1.530 ± .001		1.530 ± .001		1.530 ± .001		1.530 ± .001	
β	1.680 ± .002		1.680 ± .002		1.680 ± .002		1.680 ± .002	
γ	1.685 ± .001		1.685 ± .001		1.685 ± .001		1.685 ± .001	
2V	18° ± 2°		18° ± 2°		18° ± 2°		18° ± 2°	

[1] Calculated on the basis of 4[$CaCO_3$] to the unit cell.
[2] Determined by spectrographic analysis.
[3] Determined by sink float method on material purified for analysis.
[4] All optic values determined for sodium light.

TABLE 4

Partial X-ray data on analyzed aragonites[1]

Pnma	31-CZ-59	45-CZ-59	50-CZ-59	51-CZ-59	Aragonite N.B.S.[2]
hkl	d(Å)	d(Å)	d(Å)	d(Å)	d(Å)
221	1.977	1.977	1.977	1.977	1.977
041	1.882	1.882	1.882	1.882	1.882
202	1.878	1.878	1.878	1.878	1.877
113	1.743	1.743	1.743	1.743	1.742

[1] Spacings determined by X-ray diffractometer, using CuKα radiation and aluminum as an internal standard. All determinations are accurate within the limits $\pm$ 0.0005 Å. X-ray measurements by R. C. Erd, U. S. Geological Survey.

[2] d-spacings given by the National Bureau of Standards for aragonite (Swanson, Fuyat, and Ugrinic, 1954).

The presence of aragonite as a metamorphic mineral within the glaucophane schist facies suggests that the pressure-temperature conditions characterizing this facies may indeed be unique. The experimental work on the calcite-aragonite stability relations clearly shows that aragonite can form as a stable phase only at pressures above 4000 bars at room temperatures and above. The inversion of calcite to aragonite by dry grinding in mortar and pestle is further evidence that under high pressures and low temperatures aragonite is the stable phase (Burns and Bredig, 1956; Dachille and Roy, 1960; Jamieson and Goldsmith, 1960). However, as was indicated earlier, even though aragonite can form over a wide range of temperature, the pressures required at these temperatures are so high that it has seemed unlikely that geologic environments with both low enough temperature and high enough pressure can exist.

To attain the necessary pressure by depth of burial and still remain behind the temperature barrier imposed by the calcite aragonite inversion, an abnormally low geothermal gradient is necessary (fig. 6). Evidence for such a low thermal gradient is tentatively advanced by Birch (1955) for the Canadian Shield. Here the measurable heat flow is extremely low; however, no such evidence can now be marshaled to support the concept of a low geothermal gradient during metamorphism of the Franciscan geosyncline.

If we assume that certain ionic solutions in contact with the carbonate during metamorphism induced the metastable formation of aragonite irrespective of its stability field, then we must explain the absence of aragonite in other metamorphic facies. Furthermore, metastable formation of aragonite would be difficult to explain as its fabric is compatible with the metamorphic minerals characterizing the glaucophane schist facies. Later inversion of aragonite to calcite does indicate, however, that this polymorphic transition is sensitive to changes in pressure-temperature conditions.

Returning to the problem of high pressures at low temperatures, we find that the concept of tectonic pressures can be used to explain the stable forma-

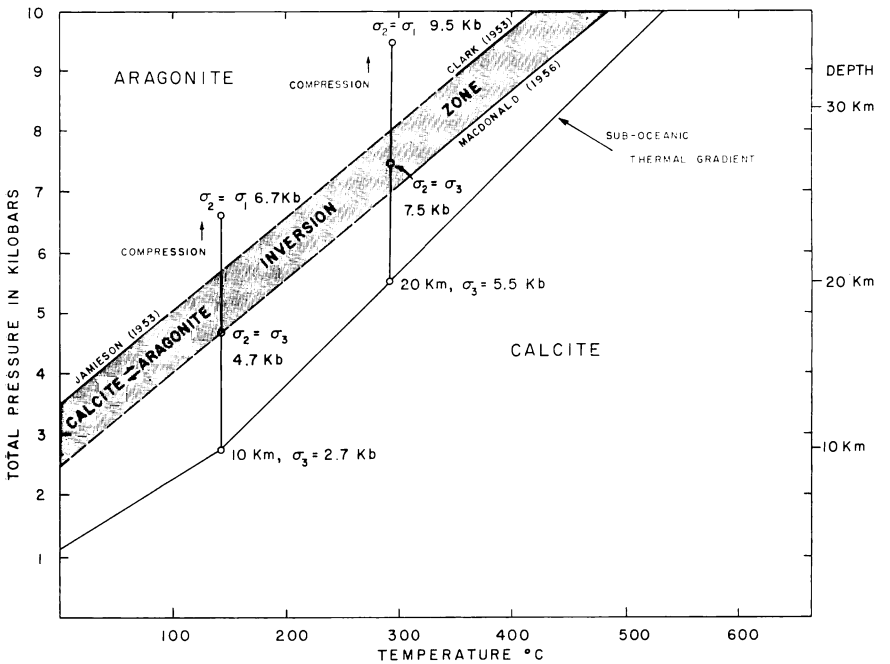

Fig. 6. Pressure-temperature diagram showing the experimentally determined equilibrium curves for the calcite-aragonite inversion. The solid line portion of these curves represents that portion that has actually been determined experimentally by Jamieson (1953), Clark, (1957), and MacDonald (1956). The calcite and aragonite stability fields are shown between the inversion zone which represents this extrapolated experimental work. The suboceanic geothermal gradient plotted is taken from Birch (1955) and it is assumed to resemble thermal conditions during Franciscan metamorphism. Erected at 10- and 20-km depths on the thermal curve are vertical lines, which represent the possible increments in total pressure over and above the lithostatic pressure due to tectonic compression. The values for $\sigma_2 = \sigma_3$ and $\sigma_2 = \sigma_1$ are taken from table 5.

tion of aragonite at moderate depths (10 to 20 km) if certain simplifying assumptions can be made. The period of metamorphism within the Franciscan geosyncline probably commenced after the maximum depth of burial was attained. For the purposes of this discussion we will assume that this depth was between 10 and 20 kilometers. Lithologic evidence suggests that the Franciscan sediments accumulated in a suboceanic trough and may have attained such depths (Bailey, 1960). The lithostatic pressures at these depths could be hydrostatic in character, and, assuming an average density (ρ) of 2.76 g/cc, the pressure can be calculated by the function ρ gh where h is depth and g the acceleration of gravity; thus the lithostatic pressure would be 2700 bars at 10 km and 5500 bars at 20 km. We can only guess at the water pressures, but the presence of lawsonite in these schists indicates that water pressure was equal to or slightly less than the lithostatic pressure (Fyfe and Valpy, 1959). Birch (1955, p. 115) has cautioned us on oversimplifying the total pressure of a geologic system into that resulting only from lithostatic load. Using Birch's reasoning, we will develop the concept of tectonic pressure.

For depths ranging from 10 to 20 km, and assuming a normal geothermal gradient, we can expect a temperature range from 150°C to 300°C (fig. 6). We further postulate that the certain rocks making up the Franciscan geosyncline will have strength enough to sustain a given amount of compression or tension before failure by shearing. Recent experimental work on rock deformation has shown that the ultimate strength of certain rocks will increase under confining pressures (hydrostatic) if the temperature remains low (<300°C) (Handin, 1960). Therefore, if we follow Birch's (1955, p. 115) suggestion, it is necessary to consider three principal stresses involved during the period of deformation and metamorphism within the Franciscan geosyncline. To do this, a graphical representation is afforded by using a two-dimensional Mohr diagram (fig. 7).

Generally this graphical approach is applied to geologic problems where types of faulting may be predicted (Hubbert and Rubey, 1959) and more generally to represent the results of experimental deformation by triaxial compression (Handin and Hager, 1957). For the present purpose we use the Mohr diagram to illustrate that the ultimate strength of a rock must be considered before the mean pressures of a metamorphic event can be evaluated.

The vertical component of stress will be designated ρ gh = σ_3 (minimum principal stress). The maximum and intermediate principal stresses σ_1 and σ_2 must then lie in the horizontal plane and represent the tectonic movements accompanying metamorphism. The metamorphic fabric and lineations of the Ward Creek schists suggest that compressional folding was contemporaneous with the formation of the schists and aragonite marbles. To assess the possible contribution of these tectonic compressional stresses on the total pressure, a certain original rock strength has to be assumed. The aragonite marbles are predominantly contained within pillow basalts; therefore, the experimentally determined strength of basalt could be applied. Griggs, Turner, and Heard (1960) have given values of shear strength for basalt under a confining pres-

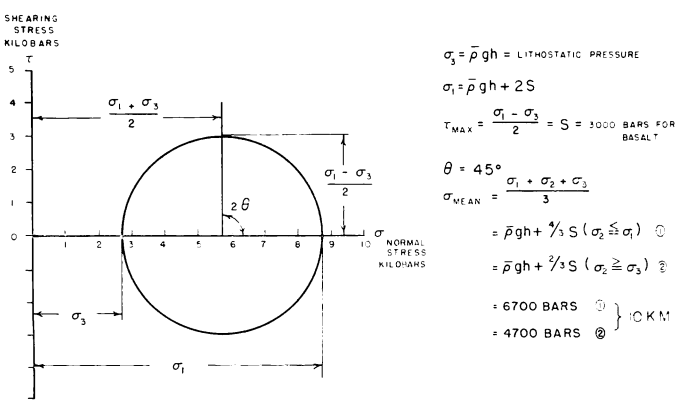

Fig. 7. Two-dimensional Mohr diagram showing relationships between normal stresses and shear stresses of tectonic origin. Lithostatic pressure is the least principal stress, and tectonic compression combined with lithostatic pressure gives the greatest principal stress. Intermediate stress normal to the plane of σ_1 and σ_3 may be somewhere between the greatest and least principal stresses, as shown above.

sure of 5 kilobars at 300°C, as 7 kilobars, and at 25°C, 8.5 kilobars. Handin (1960) suggests that these laboratory results may exceed the actual strength of rocks in the Earth's crust by a factor of five. If we use Handin's scale factor, a shear strength of 1500 bars would be expected for basalt. However, Birch (1955) describes rather steep horizontal gravity gradients across the Appalachian Mountains that indicate long-term stress differences of several thousand bars may exist. The metamorphic period within the Franciscan was of short duration, and therefore higher strengths may have obtained. We have selected 3000 bars (S) as the probable shear strength of basalt during metamorphism; this is an empirical value that seems reasonable when based on our present knowledge of rock strength. The value S will be regarded as the maximum shearing stress (τ max) the basalt can sustain during compressional tectonic stress. If we plot these values on a Mohr diagram (fig. 7), σ_1 (maximum principal stress) can be expressed as follows:

$$\sigma_1 = \sigma_3 + 2S = \rho gh + 2S \text{ for compression.}$$

The shear stress τ on the Mohr diagram will have a maximum value equal to S, the selected shear strength value of basalt, and has the following relations to the principal stresses when θ is 45°:

$$\tau \text{ max.} = S = \frac{\sigma_1 - \sigma_3}{2} = \frac{(\rho gh + 2S) - (\rho gh)}{2} = 3000 \text{ bars}$$

The third principal stress σ_2 normal to the plane of σ_1 and σ_3 must have values between the lithostatic pressure $\rho gh = \sigma_3$ (minimum principal stress) and $\rho gh + 2S = \sigma_2$ (maximum principal stress). The mean pressure σ_{mean} is the average of the three principal stresses

$$1/3\ (\sigma_1 + \sigma_2 + \sigma_3)$$

and is hydrostatic in nature. The possible limits of mean hydrostatic pressures can then be calculated for compressional tectonic movements if the depth of burial and rock strengths can be estimated:

$$1\ \sigma_{mean} = \rho gh + 2/3S \text{ when } \sigma_2 = \sigma_3$$
$$2\ \sigma_{mean} = \rho gh + 4/3S \text{ when } \sigma_2 = \sigma_1$$

The estimated pressures for these two conditions at 10 and 20 kilometers are given in table 5 and compared with the necessary pressures needed to convert calcite to aragonite. The total stress consists of this mean pressure, for which the shearing stress is zero, and a shearing stress for which the hydrostatic pressure is zero. It has been shown by Griggs, Turner, and Heard (1960, p. 98) that shearing stress does not seem to affect the transition of calcite to aragonite under their experimental conditions.

These calculations suggest that hydrostatic pressures in excess of the lithostatic load pressures could develop at these more reasonable depths and thus promote the inversion of calcite to aragonite. There is little or no evidence to support the idea that such tectonic pressures may persist and that geologic materials could sustain such stress for geologic periods of time. The effect of pore pressure on the ultimate strength of basalt has not been evaluated, but Handin (1960) has shown that in porous materials, such as sandstone and shales, high pore pressures reduce rock strength. Further experimental evidence is needed to allow a realistic appraisal of the total pressures acting on rocks undergoing metamorphism at depth.

TABLE 5

Estimated possible mean pressures (hydrostatic) acting on basalt buried 10 and 20 km and having a shearing strength (S) of 3000 bars at 5000 bars confining pressure.

Depth in kilometers	Lithostatic pressure bars σ_3	Estimated temperature[1] °C	Mean Pressure bars assuming $\sigma_2 = \sigma_3$[2] Compression	Mean Pressure bars assuming $\sigma_2 = \sigma_1$[3] Compression	Pressures necessary to form aragonite at these temperatures[4]
10	2700	140°	4700	6700	4700-5700
20	5500	290°	7500	9500	7000-8000

[1] Temperature estimates taken from suboceanic geothermal gradient of Birch (1955).
[2] Intermediate principal stress, σ_2 taken as equal to ρ gh or σ_3, total pressure = ρgh + 2/3S.
[3] Intermediate principal stress, σ_2 taken as equal to ρ gh + 2S or σ_1, total pressure = ρ gh + 4/3S.
[4] Pressure ranges taken from figure 6 where the uncertainties in the experimental stability of aragonite are shown.

Up to the present, the pressure-temperature stability fields of high pressure phase transformations, such as

albite → jadeite + quartz or sillimanite → kyanite

have been entered as evidence to demonstrate the great depths of burial necessary to allow their stable formation. The depth of burial necessary to allow these phase transformations is excessive and places the scene of metamorphism at the base of the crust or even into the mantle (Billings, 1960). For instance, if only lithostatic pressure is considered, kyanite would need a minimum lithostatic overburden of 30 kilometers at 25°C to form as a stable phase, jadeite + quartz would need 20 kilometers at 25°C, and aragonite would need 10 kilometers at 25°C. It is unlikely that at these depths the temperature could be maintained at this low 25°C value, because the assumed normal geothermal gradients would prohibit the stable formation of these high pressure phases within the Earth's crust. Geologic evidence does not support the concept of forming these minerals in the Earth's mantle, as the uplift and erosion required after burial are not demonstrable for metamorphic rocks containing these high pressure minerals. Conversely the phase transition of basalt to eclogite at the Mohorovičić discontinuity may indeed be an important mechanism in maintaining isostatic and thermal equilibrium during sedimentation and erosion, but evidence for regional metamorphism having taken place at the Mohorovičić discontinuity is completely lacking.

CONCLUSIONS

Aragonite has been established as a metamorphic mineral within the glaucophane schists of Ward Creek by a combination of field and laboratory studies. Its association with lawsonite, glaucophane, jadeitic pyroxene lends support to Turner's (in Fyfe, Turner, and Verhoogen, 1958, p. 226) observations that the glaucophane schist facies is characterized by high pressures and moderate temperatures. It is well established that the glaucophane schist facies

is restricted to Mesozoic and Cenozoic orogenic zones characterized by strong compressional folding (van der Plas, 1959; de Roever, 1956). Therefore some significance can be placed on the tectonic setting in which the glaucophane schist facies forms. To allow a high pressure-low temperature facies to develop within the Earth's crust demands the existence of unusual pressure-temperature conditions. If depth of burial is called upon to achieve these conditions, an abnormal geothermal gradient combined with rapid deposition followed by accelerated uplift is necessary to achieve a presently exposed glaucophane schist terrain. These restrictions are imposed by the slope of the calcite-aragonite inversion curve (fig. 6).

Alternatively, the aragonite temperature barrier can be overcome if it is assumed that rock strengths at moderate depths are enough to sustain lateral tectonic pressure. The increase in total mean hydrostatic pressure during the tectonic period would promote the stable formation of aragonite-lawsonite-glaucophane-jadeitic pyroxene assemblage. The erratic distribution of the glaucophane schists within the Franciscan (Bailey, 1960) lends support to the concept that tectonic pressures may have been effective in producing such an assemblage. Certainly lateral pressure gradients existed during compressional folding concomitant with metamorphism, as rock strengths would not be uniform. Thus in areas where rock strengths sustained a lateral compression, without failing by shear, high pressure-low temperature assemblages may have formed; and in zones of tension and shear failure the total pressure may have been insufficient to allow these reactions to proceed.

Further careful experimental and field work are needed to define completely the tectonic conditions characterizing the glaucophane schist facies. The evidence, up to now, however, strongly suggests that low geothermal gradients combined with strong lateral tectonic pressures provide the conditions necessary to promote such an assemblage.

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