

ARAGONITE IN THE FRANCISCAN ROCKS OF THE PACHECO PASS AREA, CALIFORNIA

BATES MCKEE, *Department of Geology, University
of Washington, Seattle 5, Washington.*

ABSTRACT

Aragonite has crystallized in veins and has partly replaced the adjacent wall rock throughout 140 square miles in the Pacheco Pass area, 80 miles southeast of San Francisco. The country rock consists predominately of clastic and volcanic rocks of the Franciscan formation (Jura-Cretaceous). Widespread glaucophane schist-facies metamorphism has produced an unusually extensive crystallization of lawsonite, jadeite-rich pyroxene, and glaucophane. Textural evidence indicates that the aragonite crystallized later than these minerals, possibly during a late stage of the episode of metamorphism. Subsequently part of the aragonite was replaced by calcite.

INTRODUCTION

Stability relations in the system CaCO_3 have been the subject of numerous experimental investigations, especially in recent years. Most of the experiments were made in a "bomb" or "squeezer" apparatus at varied controlled physical conditions (Johnston *et al.* 1916; Jamieson, 1953, 1957; MacDonald, 1956; Clark, 1957; Goldsmith, 1959). These studies have established with reasonable agreement the reaction curve for the aragonite-calcite transformation, which shows that calcite rather than aragonite is the stable polymorph of CaCO_3 under normal near-surface conditions. Burns and Bredig (1956) and Jamieson and Goldsmith (1960) transformed calcite to aragonite by grinding the mineral in a mechanical mortar, and Burns and Bredig suggested that shearing stress might be essential to this transformation.

Aragonite occurs in a variety of geologic materials, such as marine sedimentary beds (both organically and inorganically precipitated), cave and hot spring deposits, the oxidized zone of ore deposits, and in some basalts, serpentines and greenstones (Dana, 1951, p. 189-191). Johnston *et al.* (1916) suggested that the presence of impurities in the carbonate structure could explain the crystallization of aragonite rather than calcite at surface conditions. Jamieson (1953, p. 1390) concluded that both organic and inorganic precipitation of aragonite must be metastable.

Coleman (1959, 1961) has reported the occurrence of metamorphic aragonite as a minor constituent of a serpentine mass near New Idria, California, that also contains jadeite. Metamorphic aragonite has been discovered also in carbonate-rich stringers in a Franciscan glaucophane-schist belt in the Ward Creek area of northern California (Coleman and Lee, 1961). The evidence in both these areas suggests that aragonite

formed as the stable polymorph of CaCO_3 in response to metamorphic conditions of the glaucophane schist facies (as defined by Fyfe, Turner, and Verhoogen, 1958).

GENERAL GEOLOGY OF THE PACHECO PASS AREA

Aragonite is the dominant CaCO_3 mineral in the metamorphosed Franciscan rocks in the vicinity of Pacheco Pass, 80 miles southeast of San Francisco (McKee, 1961; Fig. 1, this paper). The occurrence is of special interest because of the large area (140 square miles) throughout which the mineral is developed. The Franciscan formation here consists of geosynclinal clastic rocks, especially arkoses and lithic (chert and volcanic) sandstones with minor amounts of radiolarian chert and intermediate to basic igneous rocks (McKee, 1959; in press). Glaucophane schist facies metamorphism has affected almost all rocks in the area, although the newly formed minerals in many of the rocks are apparent only under the microscope. Thoroughly reconstituted schist, gneiss, and hornfels crop

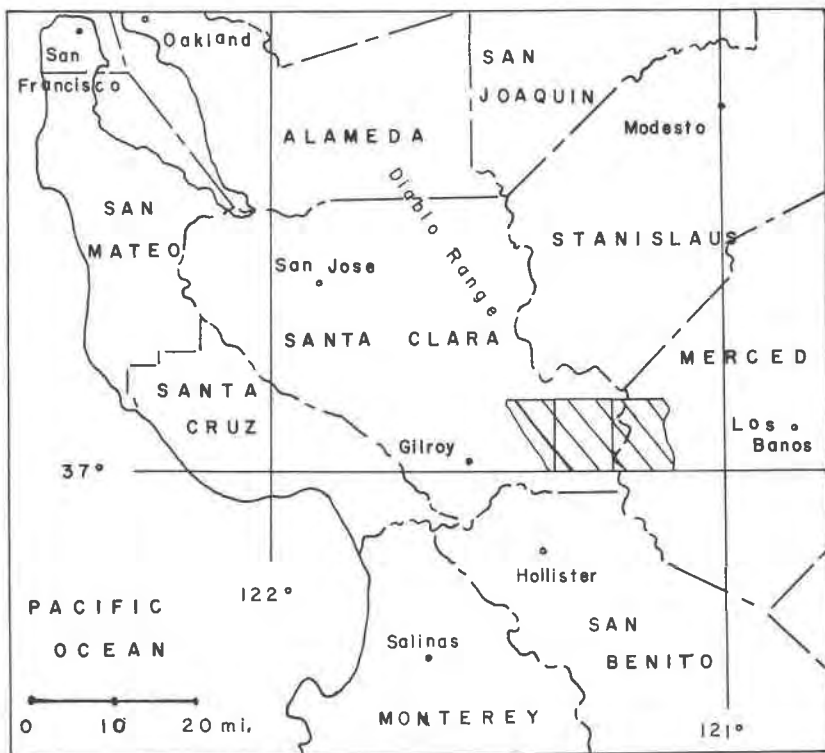


FIG. 1. Map showing location of Pacheco Pass area.

out locally. Characteristic metamorphic minerals are glaucophane, lawsonite, and a jadeitic pyroxene. The latter (plus quartz) has replaced albite (either partly or completely) in almost all rocks in the eastern half of the area. The optical properties and *x*-ray diffraction patterns of the jadeitic pyroxene from five metasandstones, when compared to data published by Coleman (1961), suggest that the mineral is a complex solid solution, containing as much as 25 per cent combined acmite, diopside, and hedenbergite (McKee, in press). Lawsonite and glaucophane have crystallized with jadeitic pyroxene in most rocks sampled in the eastern half of the area, but lawsonite is the only one of the three minerals that is common in rocks from the western half. Microscopic and *x*-ray studies of rocks from throughout the area indicate a progressive metamorphism involving the successive crystallization of lawsonite, jadeitic pyroxene, and glaucophane (McKee, 1958; 1959; 1960; in press).

The aragonite, described in detail below, has crystallized in veins in all rock types in the area. Limited replacement of the wall rock has occurred adjacent to many veins, and the matrix of a few of the less metamorphosed sandstone and conglomerate beds has been replaced largely by aragonite. Calcite is the only CaCO_3 mineral in Upper Cretaceous sandstones and shales that are in fault contact with the Franciscan formation along the east and west borders of the area.

METHODS OF MINERALOGICAL DETERMINATION

The nature of the carbonate minerals present in samples from the Pacheco Pass area was determined by various methods. Thin sections of approximately 100 samples that contain a carbonate mineral were examined with a petrographic microscope. The biaxial nature of aragonite was the property most helpful in distinguishing this mineral from calcite (present in some samples). The optic angle of the aragonite in 43 thin sections was measured with the Fedorov stage. The twinning on (110) and the relative inferiority of cleavage in aragonite also aided in distinguishing it from calcite. Carbonate grains in unsectioned samples were crushed and immersed in oil to study their optic character, and the refractive indices of several aragonite grains were determined precisely by immersion (Table 1).

Several mineral staining techniques were tried. The most satisfactory stain is obtained by using a hot saturated cobaltous nitrate solution (Holmes, 1921, p. 262-263). After immersion of the sample for fifteen minutes followed by washing, aragonite is stained a lilac-rose by the precipitation of a basic cobalt carbonate (the Meigen reaction), while calcite is not affected appreciably. Sawed rock chips are especially useful because the stained chip can be studied easily with a binocular microscope and the

TABLE 1. MINERALOGY OF THE PACHECO PASS ARAGONITE

$\alpha = 1.529 (\pm 0.002)$
$\beta = 1.676 (\pm 0.002)$
$\alpha = 1.681 (\pm 0.002)$
$2V(-) = 18^\circ (\pm 1^\circ)$ (Fedorov stage)
Dispersion = $v > r$ (weak)
Twinning on (110); Cleavage (010) distinct
Specific gravity = $2.93 \pm .03$ (Clerici solution)

results can be compared directly with the thin section made from the same slice. Etching with hydrochloric acid and scratching with a needle under the binocular microscope are methods helpful in distinguishing calcite from quartz when these minerals occur in veinlets with aragonite.

Several tests were made to insure that the biaxial carbonate was neither strontianite nor witherite. The mineral was dissolved in hydrochloric acid and the metallic sulfate was precipitated by the addition of dilute sulfuric acid. The precipitate was invariably soluble in boiling water, indicating the sulfate of calcium rather than barium or strontium. A second test was the immersion of the unknown carbonate grain in bromoform (sp. gr. 2.89). In each case the grain sank very slowly (aragonite)—it did not sink readily as would strontianite or witherite. Flame tests were also made, and these, too, indicated the presence of the calcium rather than the strontium or barium ions. All of these methods were used jointly on known grains of calcite, aragonite, strontianite, and witherite, as a safeguard against faulty techniques.

The x -ray powder diffraction patterns of six vein samples were studied. Thin sections and stained chips of these veins indicated that both calcite and aragonite were present, and this was confirmed by the x -ray analysis. The patterns of both the aragonite (Table 2) and the calcite conform closely to the standard ASTM patterns for calcite and aragonite, suggesting that both minerals are relatively pure. Four of the veins also contained quartz, which provided an excellent internal standard for the patterns. The relative intensities of the principal calcite and aragonite peaks agree with visual estimates of the proportions of these minerals in each sample.

PETROGRAPHY

The aragonite occurs primarily in veins and small replacement patches adjacent to veins. Most outcrops of greenstone contain many aragonite veins and veinlets, and where the rock is brecciated the aragonite fills the voids and is post-kinematic. Minor replacement of the host rock minerals (albite, chlorite, and in some rocks lawsonite, jadeitic pyroxene and

TABLE 2. X-RAY POWDER DIFFRACTION DATA ON PACHECO PASS ARAGONITE

hkl	A		B	
	d(Å)	I	d(Å)	I
110	4.212	2	N.O.	
111	3.396	100	3.39	100
021	3.273	52	3.27	39
002	2.871	4	2.866	7
121	2.730	9	2.727	15
012	2.700	46	2.703	90
200	2.481	33	2.485	50
031	2.409	14	2.408	12
112	2.372	38	2.373	45
130	2.341	31	} 2.338	28
022	2.328	6		
211	2.188	11	2.188	12
220	2.106	23	2.106	37
221	1.977	65	1.977	98
041	1.882	32	} 1.880	43
202	1.877	25		
132, 230	1.814	23	1.812	30
141	1.759	4	N.O.	
113	1.742	25	1.743	27
231	1.728	15	1.728	16

Patterns made with a Norelco diffractometer, $\text{CuK}\alpha$ radiation, Ni filter.

$I = I_{hkl}/I_{100}$. N.O. = not observed.

A = Aragonite prepared by National Bureau of Standards (ASTM 5-0453).

B = Aragonite sample from Pacheco Pass. Five other x-ray powder diffraction patterns proved to be essentially identical with this pattern.

glaucofane) by aragonite has occurred adjacent to some veins. Aragonite veins are common also in the clastic metasedimentary rocks, and in a few localities aragonite veins occur in brecciated chert beds. Aragonite locally has replaced the matrix of a few of the less metamorphosed sandstone and conglomerate beds. Aragonite generally is confined to veins in metasedimentary rocks of the eastern half of the area where albite has been replaced partly or completely by jadeitic pyroxene and quartz. Aragonite is relatively uncommon in the thoroughly recrystallized schists, gneisses, and hornfels, and is confined to late veins that cut across metamorphic structures, with again some replacement adjacent to the veins.

Other minerals occur with aragonite in the veins. Quartz has crystallized in most veins that contain aragonite, and calcite is present in minor amount in about half of the veins. Other minerals found occasionally

include albite and chlorite, and in one gneiss sample, pumpellyite and brown stilpnomelane. Not all of these minerals appear to have formed at the same time as the aragonite. Veins that contain chlorite or pumpellyite and stilpnomelane appear to have reopened at some later time to permit the introduction of aragonite, which has crystallized in the center of the vein and partly replaced the silicate minerals. In many rocks sampled aragonite has partly replaced quartz or albite also, but in some veins aragonite is intergrown with these minerals with smooth grain contacts suggesting contemporaneous crystallization.

The relationship of calcite to aragonite is especially significant because, if pure, these minerals represent polymorphous forms of CaCO_3 . The aragonite is generally well formed and more coarse-grained than is the calcite, which has crystallized around the margins and along internal cleavage planes and cracks in the aragonite. The grain contacts between the two minerals are extremely irregular and are clearly seen under crossed nicols because the two minerals have different extinction positions. These textural relations suggest that calcite has formed by partial replacement of aragonite.

The aragonite in all rocks sampled appears to post-date the principal metamorphism and shearing. Not only has the aragonite crystallized in unshered veins that cut across the various rock types, but the mineral typically has replaced in part the characteristic metamorphic minerals (lawsonite, jadeitic pyroxene, glaucophane) adjacent to the veins. The relationships are not always obvious. The aragonite replaced albite grains more easily than lawsonite crystals included in the albite. The result in some cases is an inclusion of relict lawsonite in aragonite. The outlines of lawsonite grains are less regular in aragonite than they are in albite, however, and some grains have quite ragged terminations and clearly have been partly replaced by aragonite. Jadeitic pyroxene has been replaced by aragonite more easily than has lawsonite, but it, too, has offered stronger resistance to replacement than has albite. Thus, where an albite grain that had been partly replaced by fibrous jadeite subsequently was partly replaced by aragonite adjacent to a vein, the jadeite fibers extend into the aragonite beyond the edge of the preserved portions of the albite grain. Aragonite and albite have crystallized simultaneously in a vein in one greenstone sample, the albite of which had been replaced previously by jadeitic pyroxene. Thus albite, unstable during glaucophane schist facies metamorphism, apparently was again stable at the time of aragonite crystallization. No evidence of crystallization of either aragonite or calcite simultaneously with lawsonite, jadeitic pyroxene, or glaucophane has been found. The apparent order of crystallization was 1) lawsonite, jadeitic pyroxene, and glaucophane; 2) aragonite; and 3) calcite.

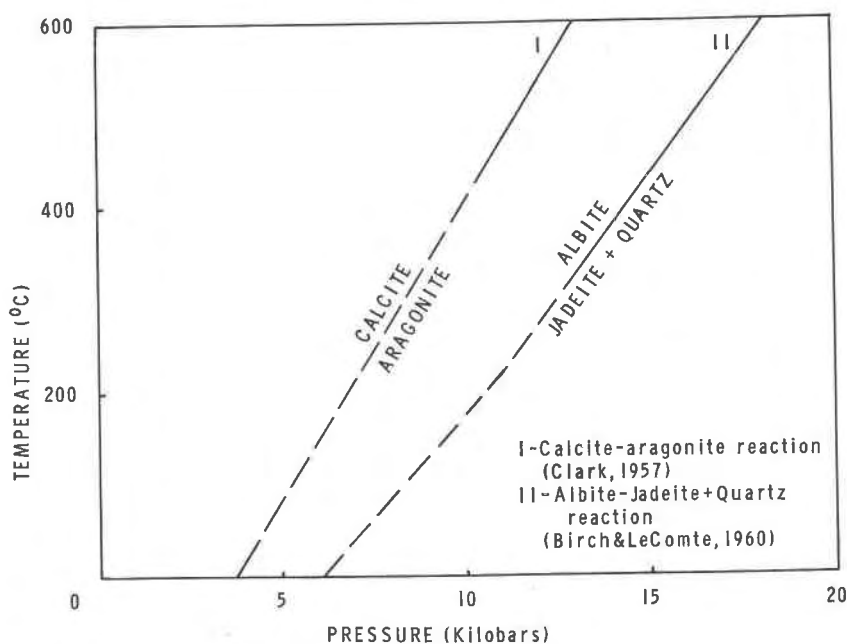


FIG. 2. Experimental reaction curves for the transformations.
I Calcite→Aragonite; II Albite→Jadeite & Quartz.

DISCUSSION

Aragonite probably crystallized from solutions with a high partial pressure of CO_2 , but the origin of these solutions is uncertain. Their apparent introduction after the principal metamorphism suggests that the solutions were not derived from the metamorphosed sedimentary or igneous rocks. However, much of the calcium now in aragonite may have been present in other minerals before and during the principal metamorphism. This calcium may have combined with CO_2 , introduced in fissures at a later time, to form the aragonite.

The question why aragonite rather than calcite crystallized first can be answered with somewhat greater assurance. Figure 2 shows the relative stability of aragonite and jadeite, as determined experimentally. The crystallization of aragonite clearly requires less extreme pressure at a given temperature than does the formation of jadeite in the presence of quartz. These reaction curves cannot be compared directly, however, because even if the aragonite at Pacheco Pass is relatively pure, the jadeite is not, and the effect of impurity would be to lower the stability pressure (Coleman, 1961, p. 242). Still the experimental work does suggest that aragonite rather than calcite should be the stable CaCO_3

polymorph during glaucophane schist facies metamorphism, a prediction confirmed by the Ward Creek study (Coleman and Lee, 1961). The Pacheco Pass occurrence does not indicate which form of CaCO_3 would have been stable during the main stage of metamorphism, but it does demonstrate that aragonite rather than calcite formed first after the crystallization of lawsonite, jadeitic pyroxene, and glaucophane. This, plus the absence of aragonite in the unmetamorphosed Upper Cretaceous rocks adjacent to the Franciscan formation in this area, suggest that the aragonite crystallized during the late stages of the episode of unusual P-T conditions that produced widespread glaucophane schist facies metamorphism. The Pacheco Pass occurrence demonstrates a regional stability of aragonite and indicates that shearing, as proposed by Burns and Bredig (1956), is not essential to the crystallization of aragonite.

ACKNOWLEDGMENTS

I would like to thank Julian Barksdale, Howard Coombs, Adolph Knopf, and Peter Misch for critically reading this manuscript and offering many helpful suggestions.

REFERENCES

- BIRCH, FRANCIS AND PAUL LECOMTE, (1960), Temperature-pressure plane for albite composition. *Am. Jour. Sci.*, **258**, 209-217.
- BURNS, J. H. AND M. A. BREDIG, (1956), Transformation of calcite to aragonite by grinding. *Jour. Chem. Phys.*, **25**, 1281.
- CLARK, S. P. (1957), A note on calcite-aragonite equilibrium. *Am. Mineral.*, **42**, 564-566.
- COLEMAN, R. G. (1959), Genesis of jadeite from San Benito County, California (abs.). *Geol. Soc. Am. Bull.*, **70**, 1583.
- (1961), Jadeite deposits of the Clear Creek area, New Idria district, San Benito County, California. *Jour. Petrol.*, **2**, 209-247.
- AND D. E. LEE, (1961), Metamorphic aragonite in the glaucophane schists of Cazadero, California (abs.). *Program Geol. Soc. Am. Cordilleran Sect. Meet., San Diego*, Mar. 27-29, 26.
- DANA, J. D. (1951), *A System of Mineralogy* (7th ed.), vol. 2; rewritten by C. Palache, H. Berman and C. Frondel: John Wiley and Sons, Inc., New York.
- FYFE, W. S., F. J. TURNER, AND JOHN VERHOOGEN, (1958), Metamorphic reactions and metamorphic facies. *Geol. Soc. Am. Mem.* **73**.
- GOLDSMITH, J. R. (1959), Some aspects of the geochemistry of carbonates; in *Researches in Geochemistry*, P. H. Abelson, ed. John Wiley and Sons, Inc., New York, 336-358.
- HOLMES, ARTHUR (1921), *Petrographic methods and calculations*. Murby, London, 262-263.
- JAMIESON, J. C. (1953), Phase equilibrium in the system calcite-aragonite. *Jour. Chem. Phys.*, **21**, 1385-1390.
- (1957), Introductory studies of high-pressure polymorphism to 24,000 bars by x-ray diffraction with some comments on calcite II. *Jour. Geol.*, **65**, 334-343.
- AND J. R. GOLDSMITH, (1960), Some reactions produced in carbonates by grinding. *Am. Mineral.*, **45**, 818-827.

- JOHNSTON, J., H. E. MERWIN, AND E. D. WILLIAMSON, (1916), The several forms of calcium carbonate. *Am. Jour. Sci.*, 4th ser., **41**, 473-512.
- MACDONALD, G. J. F. (1956), Experimental determination of calcite-aragonite equilibrium relations at elevated temperatures and pressures. *Am. Mineral.*, **41**, 744-756.
- MCKEE, BATES (1958), Jadeite alteration of igneous and sedimentary rocks (abs.). *Geol. Soc. Am. Bull.*, **69**, 1612.
- (1959), The geology of the Pacheco Pass area, California. Unpub. Ph.D. dissertation, Stanford Univ.
- (1960), Tectonic significance of the phase change. Plagioclase→Jadeite+Quartz (abs.). *Geol. Soc. Am. Bull.*, **71**, 1926-1927.
- (1961), Widespread distribution of aragonite in the Pacheco Pass area, California (abs.). *Program Geol. Soc. Am., Cordilleran Sect. Meet., San Diego*, Mar. 27-29, 53.
- (in press), Widespread occurrence of jadeite, lawsonite, and glaucophane in central California. *Am. Jour. Sci.*

Manuscript received, June 18, 1961.