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AN EXPERIMENTAL STUDY OF THE RECRYSTALLIZATION OF PORCELANITE AND ITS BEARING ON THE ORIGIN OF SOME BEDDED CHERTS

W. G. ERNST* and S. E. CALVERT**

ABSTRACT. The Monterey Formation of California consists in part of unaltered diatomite (amorphous silica), porcelanite (fine-grained cristobalite), and chert (quartz). Other prominent units include tuff and tuffaceous, phosphatic, and diatomaceous siltstones, and claystones. Although intimately interlayered locally, the siliceous rock types occur in a rough stratigraphic order: chert principally at the base, porcelanite chiefly in the middle portion, and diatomite mainly toward the top of the formation. This spatial relationship suggests that the biogenically precipitated silica has been progressively recrystallized from diatomite through porcelanite to chert.

Hydrothermal experiments on the transformation of porcelanite to quartz at 2000 bars aqueous fluid pressure and at temperatures of 300, 400, and 500°C demonstrate that the percentage of material recrystallized per unit time is constant. This process appears to be a zero-order reaction with an activation energy of 23.2 kcal/mole. Although the number of intermediate species in the reaction is thought to be zero, an aqueous fluid nevertheless is necessary for rapid recrystallization to take place. The reaction mechanism proposed involves hydrated transition interfaces between the cristobalite employed as starting material and the numerous newly-generated quartz nuclei. Growth of quartz normal to these interfaces with cristobalite is at a fixed velocity dependent on the temperature.

Extrapolation of the time required for complete conversion of porcelanite to quartz at temperatures approaching 20°C in the presence of a virtually pure H_2O pore fluid indicates a period of about 180 m.y., assuming that the high experimental pressures provide a negligible effect on reaction rates. Previous workers have shown that the conversion takes place much more rapidly in the presence of alkaline solutions, and that a solution-redeposition mechanism is involved. In the Tertiary Monterey Formation, which has been subjected to neither high pressures nor high temperatures, chertification has occurred only along bedding planes and fractures where apparently alkaline aqueous fluids have been present for long periods of time. Deeper portions of the formation probably are more thoroughly "chertified" because they have been subjected to slightly higher temperatures during burial. Complete recrystallization has obliterated all traces of these reactions in much older bedded cherts.

INTRODUCTION

Bedded cherts and siliceous shales are widely distributed rock types ranging in age from Precambrian to Tertiary. They may reach substantial thicknesses (on the order of 1000 m), and some are very pure, and many display abundant primary sedimentary structures. These features suggest a primary origin for much, if not all, of the silica in the rocks, and a persistent problem has been that of recognizing an adequate source for the large quantities of SiO_2 involved.

It seems clear that, in many cases, extensive recrystallization of silica initially precipitated in the sediments has taken place so that clues to its original nature are lacking. This is particularly true of Paleozoic cherts where rather infrequent molds or microorganic remains are the only recognizable traces of silica in a primary form.

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On the other hand, many late Mesozoic and Tertiary bedded cherts are associated with considerable thicknesses of unaltered biogenically precipitated silica—namely diatomites and radiolarites (Anderson, 1933; Bramlette, 1946; Audley-Charles, 1965; Grunau, 1965). Richly diatomaceous and radiolarian sediments are accumulating presently in certain oceanic areas (Bezrukov, 1955; Calvert, 1966), and the modern oceans appear to provide adequate amounts of silica for incorporation into sediments without recourse to excessive stream supply or volcanism (see Calvert, 1966, for a detailed discussion).

Taking the Monterey Formation as an example, let us consider under what conditions late Mesozoic and Tertiary biogenic silica persists as a recognizable deposit, and what recrystallization it undergoes. Various workers have suggested that the primary silica recrystallizes to chert so that the rocks become progressively "chertified" with age. However, mechanisms and intermediate stages of this proposed transformation are not well understood. Observations and experimental work described in this paper are designed to investigate this aspect of chert genesis.

THE MONTEREY FORMATION

General relationships.—The Monterey Formation of California, which includes highly siliceous strata of early Miocene to early Pliocene age, was described in detail by Bramlette (1946). The formation is widely distributed in the Coast Ranges, from Marin County in the north to Orange County in the south. The areal distribution of sections measured by Bramlette is shown in figure 1. Rocks of similar lithologies apparently occur in Washington State and on the Tres Marias Islands in Mexico. Throughout this vast area, the highly siliceous rocks are evidently not time equivalent (Woodring and Bramlette, 1950; Hall and Corbató, 1967). It is reasonable to conclude that smaller areas of siliceous rocks represent the deposits of individual isolated basins or gulfs in which biogenic silica accumulated at some time during early Miocene to early Pliocene.

The siliceous rocks reach thicknesses of 1700 m in central California. In general, the lower part of the formation consists of chert and porcelanite, whereas diatomaceous strata increase in volume toward the upper part of the formation (Bramlette, 1946, p. 12, 48). Other rock types are also represented, notably tuff, mudstone, shale, sandstone, and some limestone. Some of the clastic units are phosphatic (Dickert, 1966).

Diatomite.—The Monterey Formation contains the thickest diatomaceous deposits known. Where mined commercially at Lompoc, Santa Barbara County, the diatomite is 300 m thick. The beds are white to cream-colored, porous, and finely laminated. Diatoms are particularly conspicuous, but radiolarian and silicoflagellate remains are also common. Foraminiferida are rare in most samples. Pure diatomites, with silica contents ranging from 70 to 80 wt percent (Bramlette, 1946, p. 13), appear to grade into pale brown mudstones containing very few diatoms.

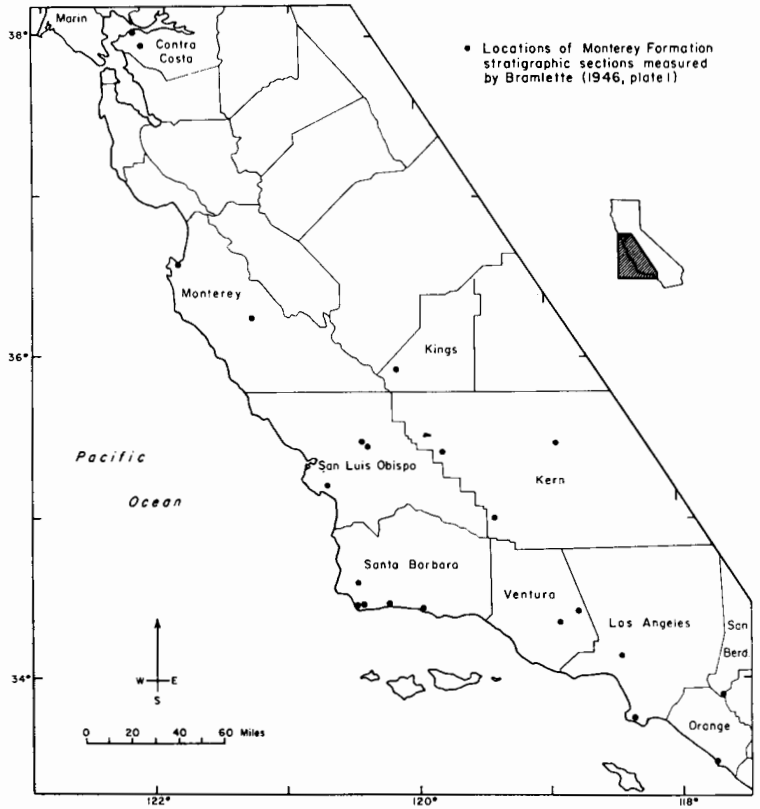


Fig. 1. Locations of stratigraphic sections of the Monterey Formation measured by Bramlette (1946, pl. 1). Selected counties indicated.

The unaltered diatomites consist of poorly ordered opaline silica. X-ray diffraction patterns (for example, see fig. 2A) show a very broad, low-intensity reflection centered at approximately 4Å (2θ Cu_{K_α}=22.0°), suggesting some short-range order, which is similar to that of silica gels and glasses (Warren and Biscoe, 1938; Cartz, 1964) and precious opals (Jones, Sanders, and Segnit, 1964). A small amount of clastic quartz is also present. Heat treatment at 1000°C and one atm total pressure for 4 hours promotes crystallization of the diatomite to α-cristobalite, as shown in figure 2B.

Porcelanite.—Rocks included under this term (Taliaferro, 1934; Bramlette, 1946) are opaline cherts which are less dense than vitreous cherts. They are typically light in color and somewhat porous; broken surfaces have a characteristic matte luster. The rocks grade into porcelanous shales and mudstones, and as with the diatomites, there seems to be continuous gradation between porcelanite and mudstone depending on the proportions of clay and opaline silica.

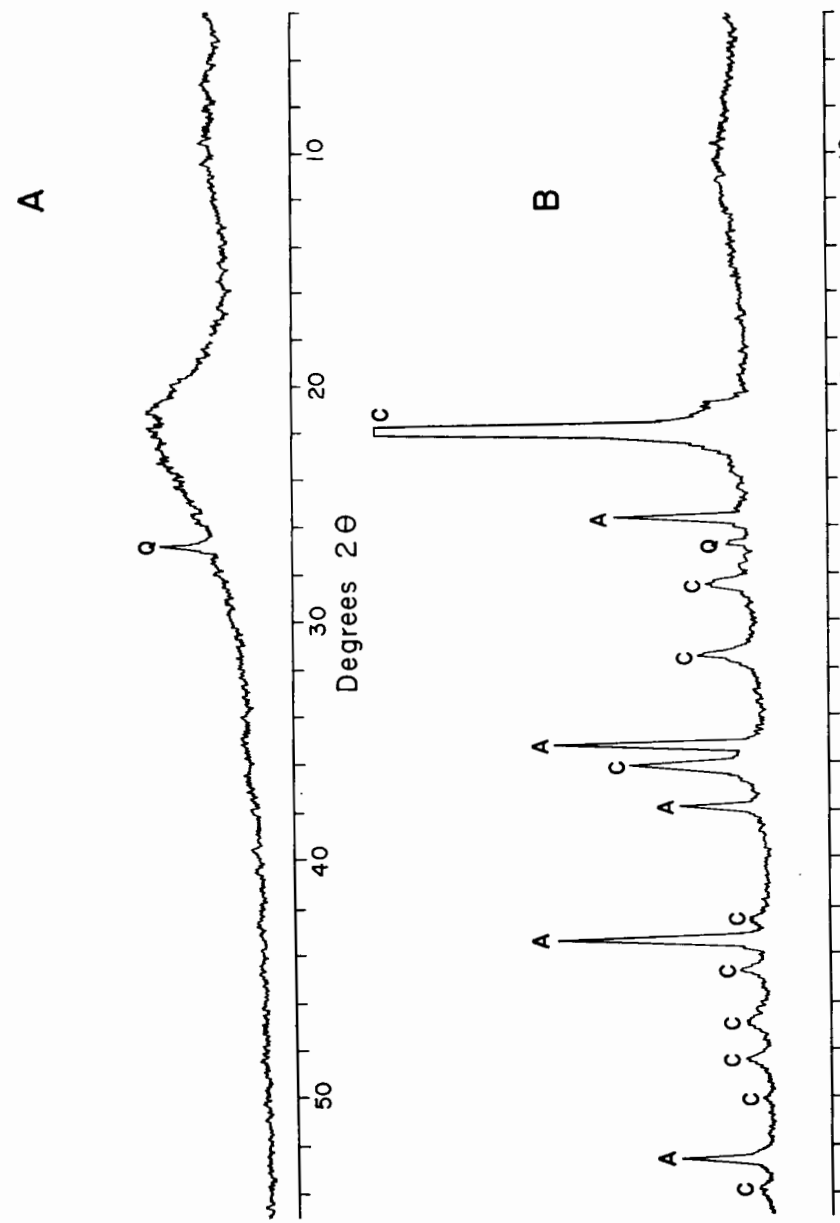
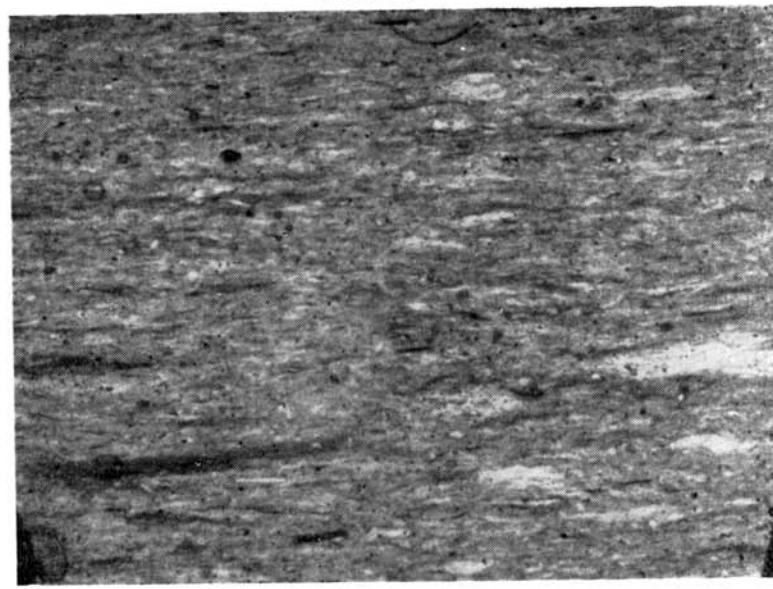
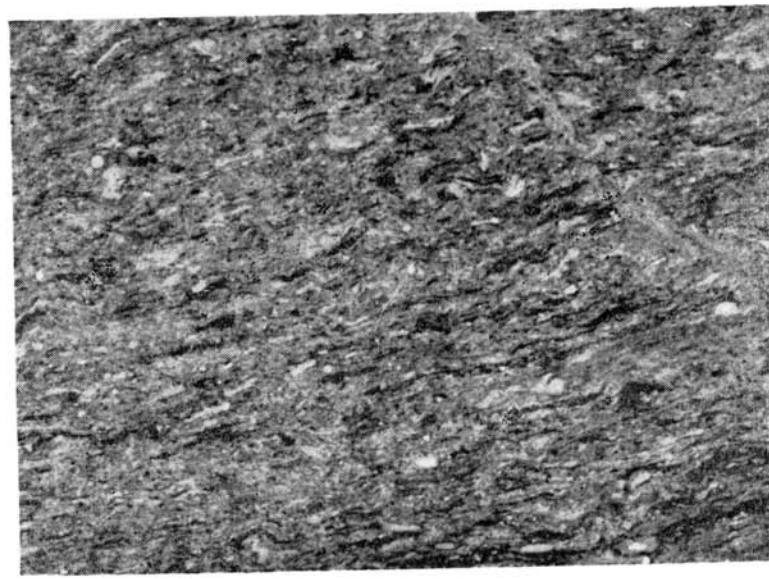


Fig. 2. A. X-ray diffraction pattern of Monterey diatomite. Cu K_α radiation, nickel filter, 35 KV, 20 MA. The quartz (Q) is present as scattered clastic grains.
B. X-ray diffraction pattern of Monterey diatomite heated at 1000°C for 4 hrs, with α-Al_2O_3 as an internal standard. Same operating conditions as in (A). C = cristobalite, A = corundum, Q = quartz.

PLATE 1



A



B

Chert generally is intimately associated with porcelanite in the field, the two rock types being interbedded on a fine scale. Chert also fills fissures and fractures within porcelanite.

In thin section, porcelanite shows fragmented diatom frustules in a fine-grained, weakly anistotropic groundmass (pl. 1-A). Scattered silt-sized clastic quartz and rare feldspar grains also are present. Little else can be seen, either in hand specimen or thin section.

X-ray diffraction patterns of porcelanite (for example, see fig. 3A) exhibit a broad reflection at about 4.1Å (2θ Cu_{K_a}=21.7°), with a weak reflection at 2.5Å (2θ Cu_{K_a}=36.0°) corresponding to the 101 and 200 reflections, respectively, of α-cristobalite; weaker reflections at 4.25Å, 3.33Å, and 1.81Å correspond to the $10\bar{1}0$, $10\bar{1}1$, and $11\bar{2}2$ reflections of α-quartz. Measurements of line width at half intensity of the 4.1Å peak give cristobalite crystallite size values of 50 to 60Å, or approximately 8 times the unit cell dimension of α-cristobalite (for example, see Klug and Alexander, 1954, p. 491). Heating porcelanite at 1000°C for 4 hours at atmospheric pressure causes an increase in grain-size; X-ray diffraction patterns (for example, see fig. 3B) of the product show a complete pattern of α-cristobalite and very minor quartz (the α-Al_2O_3 was added to the porcelanite as an internal standard).

Chert.—The Monterey cherts are dense, vitreous rocks consisting of cryptocrystalline quartz. Color ranges from cream to black. The rocks occur as thin beds, and many are conspicuously laminated. Chert beds pass laterally and vertically into porcelanite. Some chert also occurs as fracture fillings or as concretionary, nodular masses where silica evidently has been added to already siliceous rocks (Bramlette, 1946, p. 46).

In thin section, the bedded cherts are seen to be composed almost entirely of cryptocrystalline quartz occurring as granular mosaics and as chalcedony (pl. 1-B). Diatoms are entirely absent, and Foraminiferida have been replaced by fine-grained quartz. Few other features are evident.

ASSOCIATION OF SILICEOUS ROCKS

Both Bramlette (1946) and Lohman (1960) state that the Monterey chert originated by alteration of diatomite, and the stratigraphic relationships plus the wealth of microscopic and stratigraphic detail collected by Bramlette support this suggestion.

The following sequence of alterations may therefore be suggested, based on textural relationships and heating experiments described above. Diatomaceous opal in the diatomite slowly "ages", and cristobalite crystallites are formed. This is analogous to the devitrification of some

PLATE 1

A. Thin section of Monterey porcelanite, plane-polarized light. Same sample as that used for experimental work in this investigation. Scattered diatom frustules and clastic silt-sized quartz and rare feldspar grains occur in a very fine-grained, nearly isotropic groundmass. Length of bar, 1 mm.

B. Thin section of Monterey chert, plane-polarized light. The rock possesses lamination on a fine scale as in (A), although it is composed of granular and chalcedonic microquartz plus scattered clastic grains. Length of bar, 1 mm.

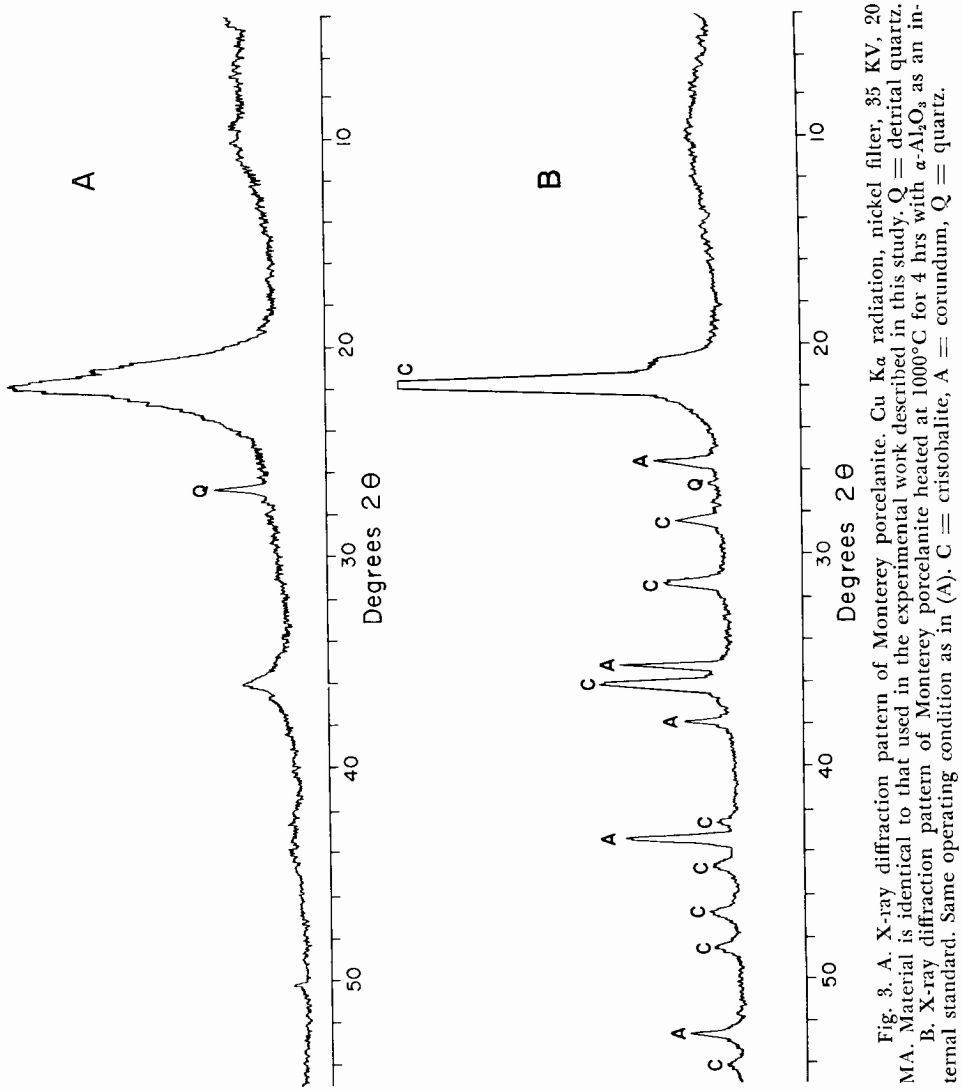


Fig. 3. A. X-ray diffraction pattern of Monterey porcelanite. Cu Kα radiation, nickel filter, 35 KV, 20 MA. Material is identical to that used in the experimental work described in this study. Q = detrital quartz.
B. X-ray diffraction pattern of Monterey porcelanite heated at 1000°C for 4 hrs with α-Al_2O_3 as an internal standard. Same operating condition as in (A). C = cristobalite, A = corundum, Q = quartz.

glasses where cristobalite is the common product (Rieck and Stevels, 1951; Sosman, 1965, p. 178). There appears to be an upper limit to the size of crystallites produced, because they cannot be resolved optically, and X-ray diffraction patterns of all porcelanites examined have a broad 4.1Å reflection.

The transformation of porcelanite to chert was investigated more thoroughly by means of rate study experiments now to be discussed.

EXPERIMENTAL PROCEDURES

Conventional hydrothermal synthesis techniques were employed throughout this investigation (Ernst and Blatt, 1964). Externally heated pressure vessels similar to those described by Tuttle (1949) were used. All experiments were conducted at approximately 2000 bars confining pressure, with H_2O as the pressure medium. Large-volume, pressure-reservoir tanks limited fluctuations to $\pm$ 10 bars P_{fluid} on individual runs. Pressure vessels were placed in resistance furnaces equipped with temperature regulators and heated to the desired value. Run temperatures were maintained to within $\pm$ 3C° as measured using chromel-alumel thermocouples calibrated against the melting point of sodium chloride (at 1 atm, 800.4°C) for a specific furance + pressure vessel assembly.

Each sample, consisting of approximately 30 mg of finely ground porcelanite and 10 mg distilled water, was placed in a silver or silver-palladium alloy seamless tube, the ends of which were sealed by welding. The sealed tube had negligible strength under experimental conditions and expanded or contracted to equalize the pressure between the internal charge of solid particles + fluid and the external pressure medium.

The starting material, Monterey porcelanite from near San Luis Obispo, California, consists of approximately 98 percent cryptocrystalline and finely crystalline α-cristobalite; individual, weakly birefringent clots and masses are roughly equant and measure up to 10 microns in diameter. The remaining 2 percent is subrounded siltsized particles, mostly quartz grains of about 10 to 25 microns in longest dimension. The relative abundances of phases in the starting material were determined by averaging the petrographic mode (= 3 percent quartz) and the mode determined from the area under the quartz $10\bar{1}1$ and cristobalite 101 X-ray diffractogram peaks (= 1.7 percent quartz).

During the course of an individual run, small grains of higher refractive index than the starting material, and roughly 1 to 5 microns in diameter were produced pervasively throughout the charge. Where the grains were large enough to measure the indices of refraction, they were identified as quartz; there is no evidence to suggest that the finer-grained material is a different phase. Even smaller grains and nuclei of quartz may have been generated in addition but could not be resolved optically. The extent of the transformation of cristobalite to quartz was obtained employing the X-ray determinative curve presented in figure 4. This determinative curve was established by mixing weighed proportions of

quartz and cristobalite and measuring the X-ray intensity ratio of the quartz $10\bar{1}1$ peak to the cristobalite 101 peak. The standardized preparation technique for X-ray powder diffraction involved combination of the sample with an amorphous binder (in our case, instant coffee) followed by impressment into a special flush-mounted specimen holder.

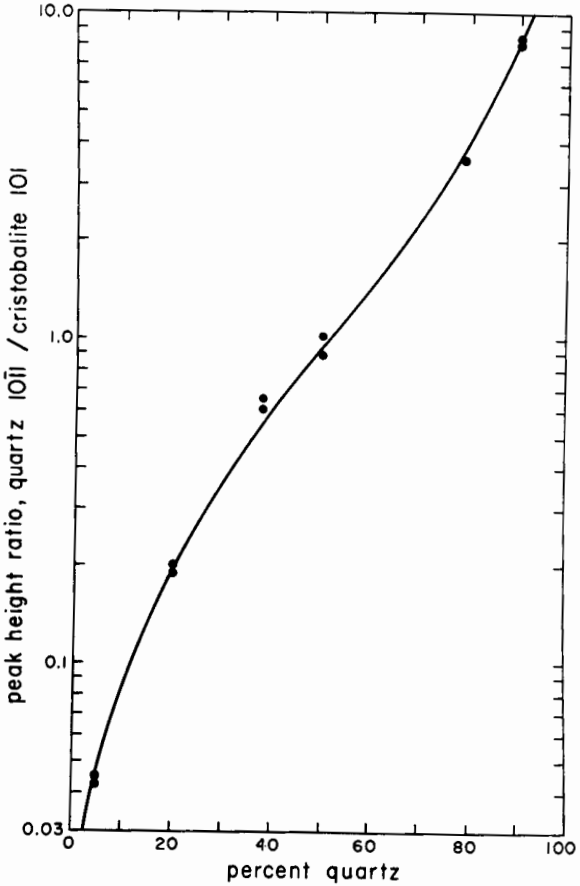


Fig. 4. The ratio of quartz $10\bar{1}1$ to cristobalite 101 X-ray peak heights as a function of percent quartz in the sample.

RUN DATA

Rate experiments were performed at 2000 bars fluid pressure and at temperatures of 300, 400, and 500°C; run data are presented in tables 1, 2, and 3 respectively. Replicate pairs of X-ray mounts and 2 to 5 scans of individual mounts of the run products yielded phase proportion determinations customarily within ± 2 percent quartz of one another and in all cases within ± 3 percent quartz.

TABLE 1

Conversion of Monterey porcelanite (cristobalite) to quartz

at 300°C, 2000 bars fluid pressure

Temperature in °C	Pressure in bars	Run duration in hours	$C_{(101)}$*	$Q_{(10\bar{1}1)}$*	$Q_{(10\bar{1}1)}/C_{(101)}$	Percent quartz
300	2010	219	47.1	3.3	0.072	8
296	2000	312	53.5	4.4	0.082	9
299	1990	551	46.2	4.0	0.087	10
299	2000	1071	54.4	6.9	0.127	14
301	1980	1583	54.2	15.2	0.281	25
302	2025	1599	62.0	18.0	0.291	26
300	2000	2460	45.0	36.7	0.816	47**
295	1990	3154	38.7	64.0	1.65	63**
304	2000	4032	44.7	42.4	0.948	51?
299	1980	5824	0.0	78.1	∞	100

*Peak amplitude in arbitrary units.

**Average of two sample mounts.

TABLE 2

Conversion of Monterey porcelanite (cristobalite) to

quartz at 400°C, 2000 bars fluid pressure

Temperature in °C	Pressure in bars	Run duration in hours	$C_{(101)}$*	$Q_{(10\bar{1}1)}$*	$Q_{(10\bar{1}1)}/C_{(101)}$	Percent quartz
402	2000	14	59.8	8.3	0.139**	15?
399	1980	15	73.3	6.9	0.094	11
396	1990	20	58.6	6.4	0.109**	12
400	1965	32	61.2	9.1	0.149	16
402	2000	40	43.8	7.6	0.173**	18
397	2000	53	69.8	10.3	0.148	16
403	2000	61	34.7	9.8	0.282**	25
399	2000	91	62.7	11.9	0.190**	20
402	2000	96	83.0	17.6	0.212	21
403	2000	108	73.0	25.3	0.346	29
396	1950	119	54.1	18.1	0.335	29
401	2010	153	48.1	34.0	0.706**	43
395	2000	158	43.4	36.5	0.841	47
403	2000	193	56.5	55.2	0.978	51
399	2000	199	35.4	63.0	1.78	65
403	2000	263	21.1	86.5	4.10	80
398	2000	289	19.8	46.7	2.36	71
398	2000	311	0.0	71.3	∞	100
402	2000	423	0.0	92.2	∞	100

*Peak amplitude in arbitrary units.

**Average of two sample mounts.

However, larger differences in the phase proportions on different runs resulted from either of two situations: (1) if the run was "dry", that is, if most of the H_2O had been driven off inadvertently during welding of the capsule, little recrystallization took place; (2) in contrast, where an imperfect seal was made during the welding, circulation of fluid unsaturated with respect to silica took place between charge and pressure vessel, resulting in a marked preferential dissolution and removal of cristobalite from the system (see experiments by Carr and Fyfe, 1958). A total of seven run products which obviously were either "dry" or leached

TABLE 3

Conversion of Monterey porcelanite (cristobalite) to quartz at 500°C, 2000 bars fluid pressure

Temperature in °C	Pressure in bars	Run duration in hours	$C_{(101)}$*	$Q_{(10\bar{1}1)}$*	$Q_{(10\bar{1}1)}/C_{(101)}$	Percent quartz
503	2010	3	76.7	6.8	0.089**	10
499	2000	6	71.1	12.3	0.173**	18
502	2000	12	69.7	28.8	0.413**	32
503	2020	16	66.9	81.3	1.216	56
504	2000	17	72.5	62.4	0.861**	49
502	2000	21	18.0	73.1	4.06**	80
497	2000	25	4.6	89.9	19.5	98
496	2010	27	1.2	74.7	62.3**	99
500	2000	30	0.0	78.1	∞	100

*Peak amplitude in arbitrary units.

**Average of two sample mounts.

were disregarded. Two aberrant experimental results are included in the tables, however, the run at 304°C, 2000 bars, 4032 hours (table 1) and the run at 402°C, 2000 bars, 14 hours (table 2). These experiments are suspect[1] but were not discarded because of the uncertainty that leaching had occurred in the latter or that fluid was absent during recrystallization of the former.

RATE OF RECRYSTALLIZATION

The run data of tables 1, 2, and 3 are illustrated in figures 5, 6, and 7 respectively. These diagrams demonstrate that, *to a first approximation,* the percentage conversion of cristobalite to quartz is a linear function of time. The general form of the rate equation for a reaction at constant T and P, r(= reactant) → p(= product) is:

$$(dC_r/dt)_{P,T} = -k\,C_r^n$$

where C_r is the concentration of the reactant, t is time, k is the rate constant, and n indicates the reaction order. In the present case, this equation is represented adequately by

$$(dC_r/dt)_{P,T} = -k$$

signifying a zero-order reaction.[2] In a plot of concentration of the product ($C_p = 1 - C_r$) versus time, the curve slope is k. Experimentally determined values for the rate constant and times necessary for the complete conversion of porcelanite to quartz are presented in table 4.

Assuming the classical Arrhenius equation applies to the reaction, the (isobaric) rate constant is related to an activation energy, E, by the equation:

$$k = Ae^{-E/RT}$$

[1] "Sputtering" of silver and of $Ag_{70}Pd_{30}$ alloy tubing during welding precluded use of the method of monitoring for weight change.

[2] The experimental data were also plotted on diagrams of log C_r versus time, assuming a first-order reaction; in this case however, straight lines fit the data very poorly.

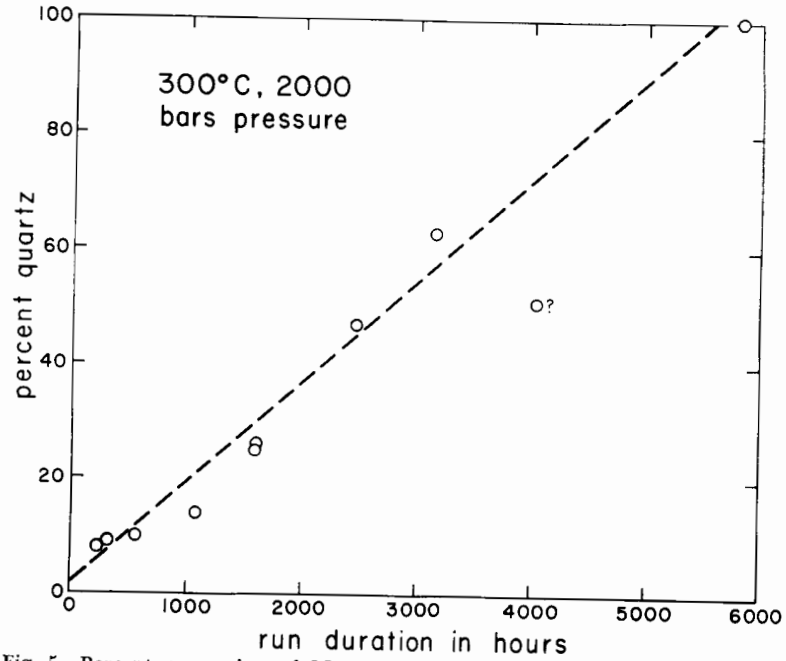


Fig. 5. Percent conversion of Monterey porcelanite (cristobalite) to quartz as a function of time at 2000 bars P_{fluid} and 300°C.

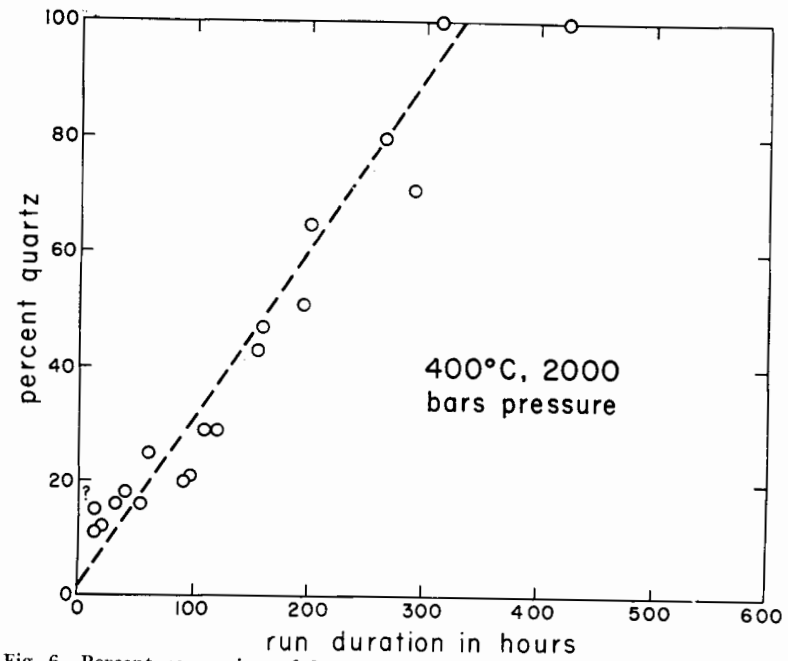


Fig. 6. Percent conversion of Monterey porcelanite (cristobalite) to quartz as a function of time at 2000 bars P_{fluid} and 400°C.

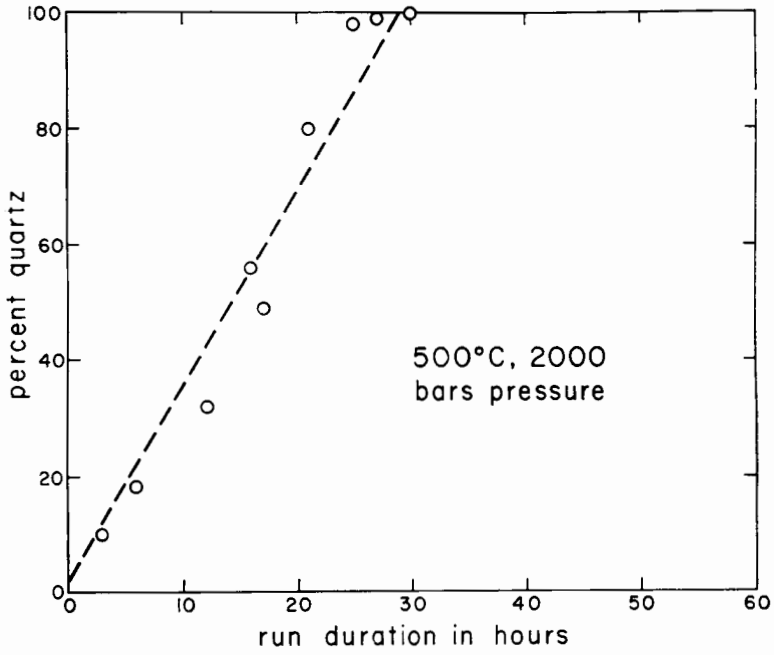


Fig. 7. Percent conversion of Monterey porcelanite (cristobalite) to quartz as a function of time at 2000 bars P_{fluid} and 500°C.

TABLE 4

Rate constants and times for the complete conversion of Monterey porcelanite to quartz

	Temperature in °C	Rate constant, k, in reciprocal hours	Time for complete conversion to quartz	
			Hours	Years
Experimentally determined	500	$3.45 \cdot 10^{-2}$	29	...
	400	$3.03 \cdot 10^{-3}$	330	...
	300	$1.79 \cdot 10^{-4}$	5,600	0.64
Calculated	200	$2.4 \cdot 10^{-6}$	410,000	47.
	100	$3.2 \cdot 10^{-9}$	...	36,000.
	50	$2.6 \cdot 10^{-11}$	...	4,300,000.
	20	$6.2 \cdot 10^{-13}$	...	180,000,000.

where A is a constant (a probability function), R is the universal gas constant, and T is the absolute temperature. Figure 8, a log k versus 1/T plot, was constructed from the experimentally determined values of k listed in table 4. The slope of the curve through the points in this diagram (essentially constant over the experimentally investigated temperature range) is $-E/2.303R$, yielding an activation energy of approximately 23 kcal/mole. Rather than employing graphical methods, however, the activation energy may be determined more precisely provided values for

the rate constant are known at any two temperatures (that is T_1 and T_2), using the expression:

$$E = \frac{2.303\ RT_1T_2\ (\log k_1 - \log k_2)}{T_1 - T_2}$$

as pointed out to us by J. M. Christie. Similar to the graphical method, this relationship assumes constant E, determined as 23.2 kcal/mole, over the range 300 to 500°C. Provided the same activation energy applies at lower temperatures, k may be evaluated using the above equation. Figures for the rate constant and times for complete conversion of porcelanite to quartz at 200, 100, 50, and 20°C were estimated and are also listed in table 4. The value of the constant term A is 1.27×10^5.

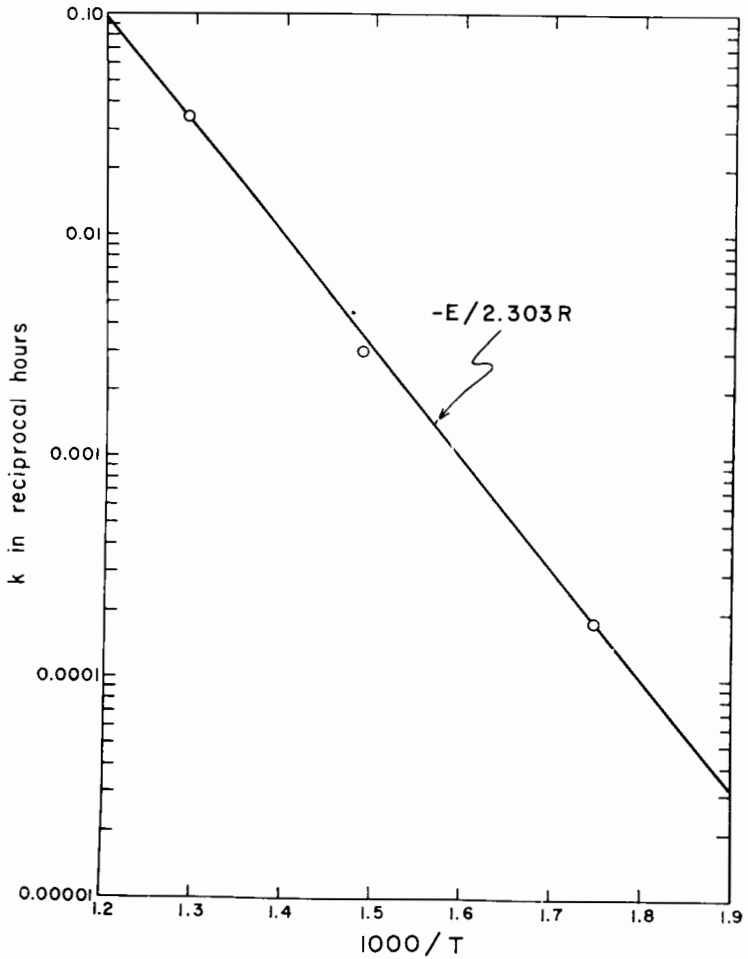


Fig. 8. Arrhenius-type plot of experimentally determined rate constant (2000 bars P_{fluid}) against the reciprocal of the absolute temperature.

REACTION MECHANISMS

The order, n, of a reaction is considered to be a measure of the number of species that interact to transform reactants to products. Inasmuch as the conversion of porcelanite to quartz in our experiments evidently is a zero-order reaction, no interaction of chemical species appears to be required; rather, the percentage of material recrystallized per unit time is virtually constant.

Thus we may conceive of transition interfaces between cristobalite and quartz which move at fixed velocities through each grain. These interfaces are initiated by the appearance of many newly generated quartz nuclei in each of the original cristobalite grains. If nucleation of quartz were the rate controlling step, it would be expected that some grains might be transformed completely prior to the generation of quartz crystallites in other particles; apparently this is not the case, because microscopic examination reveals the presence of small quartz anhedra distributed pervasively throughout partially recrystallized run products. Evidently the conversion rate of porcelanite to chert depends on the presence of an aqueous fluid, for in "dry" experiments (that is, where devolatilization occurred during welding of the capsules, as well as on 1 atm runs in which H_2O was not added) the reaction velocity was sharply decreased. Although the newly formed quartz grains are distributed at random throughout the clots of initial fine-grained cristobalite, their presence might be accounted for by migration of fluid along fractures and crystal boundaries followed by dissolution of cristobalite and deposition of quartz.

Let us therefore consider three alternative models that involve the dissolution of cristobalite and redeposition of quartz. (1) If the concentration of silica in solution were buffered by metastable equilibration with cristobalite (that is, supersaturation), the composition of the fluid phase would remain fixed at a high SiO_2 value until the nutrient (cristobalite) was completely dissolved. In this case, the nucleation and growth of quartz would provide the rate controlling step. Although the rate of nucleation of quartz from solution undoubtedly would remain constant, it would have to exceed the growth rate of quartz greatly (which, depending on the increasing surface area of quartz available, could not be of zero order) in order to explain the production of many small newly generated quartz grains rather than a few large ones. (2) If the composition of the solution were buffered by equilibration with quartz (that is, saturation), the composition of the fluid phase again would remain fixed, but at a lower silica concentration than for the model involving metastable equilibration with cristobalite. Here the dissolution of cristobalite would be the rate-controlling step (which would decline as the amount of cristobalite decreased, and again could not be of zero order). (3) If the composition of the solution were not truly buffered by metastable equilibration with cristobalite or stable equilibration with quartz, the degree of silica supersaturation would not only lie intermediate to these values

but should decrease with time as the amount of cristobalite diminished. A zero-order reaction therefore would not be expected.

Because the three dissolution and redeposition mechanisms just discussed do not conform to the apparent zero-order reaction observed experimentally, we tentatively conclude that the recrystallization reflects a solid-solid type of transition with such interfaces being produced more or less continuously in each original clot of cristobalite. However, aqueous fluid apparently is involved, and it is possible that limited amounts of H_2O are available at each transition interface to catalyze the conversion; this "structurally bound" H_2O would play a role quite distinct from its behavior in the various dissolution and redeposition models.

Thus far we have assumed the operation of a single reaction mechanism in our experiments and have attempted to distinguish the various possibilities. At this stage it is appropriate to point out that, although the rate studies illustrated in figures 5, 6, and 7 are interpreted most simply as of a zero-order reaction, the scatter of the data is not quite random. All diagrams show a tendency, more pronounced in the 400°C and 300°C isotherms, for an initial, rapid, first-order (?) conversion which tails off and is replaced in the medial and terminal stages of recrystallization by the nearly straight line zero-order curve. Perhaps both types of transformation mechanism described above were operative, with the rate of dissolution of cristobalite and redeposition of quartz initially exceeding that of the postulated solid-solid (hydrated) transition interface mechanism, but the former naturally declined with decreasing cristobalite concentration.

The influence of three other variables, pH, fluid pressure and grain size, on the recrystallization of cristobalite to quartz were not evaluated in this study. They are discussed briefly below.

Mizutani (1966) showed that at temperatures of 131, 182, and 278°C, the conversions of amorphous silica (reagent grade silicic acid) to cristobalite and of cristobalite to quartz in KOH-bearing aqueous solutions at low H_2O pressures were first-order; furthermore, reaction rates were significantly greater than determined in the present study. Mizutani's work supports the suggestion made above that two contrasting mechanisms probably were operative under the conditions of our investigations. In the study by Mizutani, increased pH favored elevated solubility of silica, hence the rapid dissolution of cristobalite and precipitation as quartz; an activation energy of 14.3 kcal/mole determined by Mizutani for this reaction also implies a fundamental difference in the dominant mechanism of recrystallization.

Although principally concerned with hydroxyl ion catalysis, experiments at 245°C and 330°C in NaOH-bearing aqueous solutions at low fluid pressures by Campbell and Fyfe (1960) and by Fyfe and McKay (1962), respectively, also demonstrated the rapid conversion of amorphous silica to cristobalite and the even more rapid recrystallization of

cristobalite to quartz. Here too, alkaline hydrothermal conditions probably account for dominance of a solution-redeposition mechanism.

Somewhat earlier, Carr and Fyfe (1958) evaluated the effect of pressure and temperature on the transformation of amorphous silica contained in open capsules to cristobalite and keatite, and of these latter phases to quartz, using a pressure medium of pure H_2O. Keatite was not found in the latter investigations of Campbell and Fyfe (1960), Fyfe and McKay (1962), or by Mizutani (1966); apparently high pH in hydrothermal solutions completely suppress the formation of this phase. The absence of keatite in the present investigation presumably reflects hydrolysis of the minor salts initially present in the Monterey porcelanite, yielding very mildly alkaline solutions. Carr and Fyfe (1958) concluded that elevated fluid pressure increases the rate of transformation to quartz more significantly than increase in temperature; they invoked a dissolution-redeposition mechanism to account for the observed conversions of amorphous silica, cristobalite, and keatite to the stable phase. Leaching of cristobalite must have been an important factor in their experiments; dissolution would be promoted by higher fluid pressure (= increased silica solubilities), judging from the data of Kennedy (1950). It is difficult to see how variation in P_{fluid} could markedly influence the solid-solid (hydrated) transformation mechanisms hypothesized to be operative in the present study, but admittedly this variable has not been evaluated.

The grain-size of the starting material should influence both the rate of hydrothermal dissolution and, to some extent, the saturation value. Hence this variable would be of considerable importance for the recrystallization of cristobalite to quartz by a dissolution mechanism. Grain-size is not expected to be a critical factor in the present study where dissolution and precipitation are inferred to play minor roles, with the postulated transformation of cristobalite to quartz apparently being dominated by a mechanism that involves many solid-solid (hydrated) interfaces moving with constant velocity through each grain.

GEOLOGIC APPLICATIONS

On the basis of our experiments, it is evident that conversion of porcelanite to chert takes place sluggishly in the presence of a virtually pure H_2O aqueous fluid and without an intermediate phase. (We do not, of course, suggest that chert in general, or the Monterey Formation in particular, was subjected either to high pressures or to high temperatures.) Inasmuch as the Monterey Formation contains siliceous rocks of three different types—amorphous silica, cristobalite and quartz—the transformations to the end product, chert, apparently are extremely slow.

The data of table 4 show that, in the presence of stagnant but essentially pure connate water, Monterey porcelanite should recrystallize to chert over a period of about 180 m.y. subsequent to the conversion of the original deposit to porcelanite, provided rock temperatures never exceeded 20°C. This assumes that departures to lower values of P_{fluid} in the natural system compared to those studied experimentally do not

seriously alter reaction rates. Increased temperatures would of course reduce drastically the time necessary for complete recrystallization; the conversion of porcelanite to chert would be accomplished in approximately 4 to 5 m.y. at 50°C. Moreover, if circulating fluids undersaturated with respect to silica had passed through the strata or if the pore solutions had been somewhat alkaline, the formation of fine-grained quartz would have been accelerated markedly.

We tentatively conclude from this study that along certain bedding plane channelways now marked by chert (see descriptive section), moderately alkaline aqueous fluids were present for a sufficient length of time to convert porcelanite and diatomite locally to cryptocrystalline quartz. Other intimately interlayered portions of the Monterey Formation apparently have remained partially or completely unrecrystallized, virtually since deposition and lithification, presumably because the interstratal solutions had low alkalinities or because fluids were locally absent due to impermeability of the units. This explanation may account for the puzzling association of thin interbeds of unaltered diatomite with porcelanite or chert, or both (see Bramlette, 1946, pts. 14 and 16). The greater abundance of chert in the lower portion of the Monterey Formation suggests that, in general, interstratal (perhaps alkaline) solutions were present here in rocks of slightly higher temperatures (on the order of 40 or 50°C) for longer durations than in the upper, cooler parts of this unit.

To some extent the Monterey Formation bears similarities to certain hot spring deposits. In many such occurrences, opal is present only in the upper 30-40 m or so of the deposit, whereas chalcedony (that is, microquartz) occurs below this depth (White, 1955). This apparently reflects a much higher rate of alteration of the original amorphous silica due to increased temperatures at depth in the springs. In some bore-holes in the Steamboat Springs area, Nevada, cristobalitic opal is present from within a meter or two of the surface to more than 30 m depth (White, Thompson, and Sandberg, 1964). Cristobalite may therefore be an intermediate alteration product of opaline sinter to chalcedony.

The alteration of biogenically precipitated silica to bedded chert is a process that effectively obliterates traces of the original siliceous material except under unusual circumstances. The Monterey Formation contains vital clues to this alteration because a starting material, diatomite, and an intermediate stage, porcelanite, are preserved together with chert. Radiolarian cherts of late Mesozoic age may also show this transformation (Audley-Charles, 1965). However, pre-Mesozoic siliceous formations contain only chert because the presence of even pure H_2O would have caused their recrystallization; clues to the original nature of the silica in these deposits unfortunately have been destroyed.

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