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OXYGEN ISOTOPE RELATIONS BETWEEN DIAGENETIC SILICA MINERALS IN MONTEREY SHALE, TEMBLOR RANGE, CALIFORNIA

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ABSTRACT. Oxygen isotope ratios in silica phases from the three diagenetic zones of Miocene Monterey Shale along Chico Martinez Creek, Temblor Range, Calif. decrease down section in the following manner.

Diagenetic zone	Characteristic silica phase	$\delta^{18}O$ per mil SMOW	Isotopic temp °C
1	Biogenic opal	37.4	15
2	Disordered cristobalite Ordered cristobalite	29.4 ± 1.5	48 ± 8
3	Microquartz	23.8 ± 0.3	79 ± 2

These and comparable data on samples from the Taft area 45 km to the southeast indicate that $\delta^{18}O$ remains fairly constant in the silica phase of each zone and changes substantially only at interzone boundaries. The phase transformation at these boundaries most likely is a solution-deposition process in which the $\delta^{18}O$ of the new phase reflects the ambient temperature and the $\delta^{18}O$ of interstitial water. In this light, the progressive structural ordering of cristobalite of virtually constant isotopic composition within zone 2 seems to be a solid-state reaction not involving interstitial water.

Temperatures of formation of disordered cristobalite (about 48°C) and of microquartz (about 80°C) were computed by assuming that these phases formed in isotopic equilibrium with diagenetic interstitial water having $\delta^{18}O$ of 0.0 per mil SMOW. Cristobalitic and quartzose cherts from the Taft area are consistently heavier by 3.7 per mil than comparable cherts from Chico Martinez Creek, suggesting that the diagenetic water in the Taft area may have been heavier by about that much.

INTRODUCTION

The thick sections of Miocene Monterey Shale in the Temblor Range of western Kern County, Calif. are especially suitable for studying diagenetic alteration of metastable biogenic opal through intermediate cristobalite into stable quartz, which occurred while the whole sedimentary pile lay at the bottom of the sea (Bramlette, 1946; Lohman, 1960). In the section along Chico Martinez Creek, the opal-cristobalite and cristobalite-quartz transformations occur rather abruptly at depths of about 700 and 2030 m, respectively (Murata and Larson, 1975). The approximate temperatures at these respective depths were calculated to be 50° and 100°C, assuming an average heat flow of 1.3 heat flow units and a depth-dependent heat conductivity of 2.0 to 2.8 mcal cm^{-1} s^{-1} $°C^{-1}$ for wet siliceous sediments. We here report further attempts to deduce diagenetic temperatures and mechanisms of polymorphic transformations by means of oxygen isotope analyses of biogenic opal, cristobalitic cherts, and quartzose cherts from progressively deeper parts of the Monterey Shale at Chico Martinez Creek and the Taft area.

The main factors that control rates of polymorphic transformations of silica in Monterey Shale appear to be temperature and pressure as determined by depth of burial and by the geothermal gradient. Pressure as

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an independent variable could more strongly affect transformation rates than temperature according to Carr and Fyfe (1958). However, fluid pressures within Monterey Shale probably were always close to hydrostatic, and primary (non-tectonic) overpressures of the kind found in Tertiary rocks of the Gulf Coast were absent (Berry, 1973). Chemical factors such as alkalinity of interstitial waters (Campbell and Fyfe, 1960) or carbonate content of the sediment (Heath and Moberly, 1971; Lancelot, 1973; Kastner, Keene, and Gieskes, 1976) apparently had little effect.

We express the isotopic ratio $^{18}O/^{16}O$ in the conventional delta notation relative to Standard Mean Ocean Water, SMOW (Craig, 1961; Hoefs, 1973). Under conditions of isotopic equilibrium, fractionation factor α of the oxygen isotopes between biogenic opal or derivative cherts and water is related to the δ-values of the coexisting phases by

$$\alpha\,\frac{SiO_2}{H_2O} = \frac{1 + 10^{-3}\,\delta^{18}O_{SiO_2}}{1 + 10^{-3}\,\delta^{18}O_{H_2O}} \tag{1}$$

Since the $\delta^{18}O$ of interstitial waters that equilibrated with the silica minerals of Monterey Shale is generally indeterminate, it must be estimated in various ways in order to derive the most probable value of α for each mineral sample.

Isotopic data on interstitial waters from five DSDP sites (Lawrence, 1973; Lawrence, Gieskes, and Broecker, 1975) show $\delta^{18}O$ decreasing downward at four sites to values of −1 to −3 per mil at subbottom depths of 300 to 400 m; at the fifth site, $\delta^{18}O$ is constant at 0.0 per mil. According to Lawrence, Gieskes, and Broecker (1975), diagenetic alteration of a volcanic material to montmorillonite or zeolite at 20°C or lower would strongly decrease $\delta^{18}O$ of interstitial water in a closed system. On the other hand, alteration of biogenic opal to cristobalite or quartz at 30°C or higher would increase $\delta^{18}O$. With the right combination of diagenetic reactions, $\delta^{18}O$ of interstitial water could remain virtually constant at 0.0 per mil.

Oilfield waters from Eocene to lower Miocene formations underlying the Monterey Shale in the region of Chico Martinez Creek have $\delta^{18}O$ mostly in the range 0 to +6 per mil (White, Barnes, and O'Neil, 1973; Kharaka, Berry, and Friedman, 1973). It seems reasonable to assume that the interstitial waters of Monterey Shale, which were involved in the transformation of the silica phases, also had $\delta^{18}O$ in this range.

The uncertainty due to the unknown isotopic composition of interstitial water could be eliminated if the isotopic composition of some other coexisting mineral that had equilibrated simultaneously with the same water were known. Thin beds of diagenetic dolomite occur sparsely throughout the Monterey Shale of the Temblor Range. The $\delta^{18}O$ of dolomite samples from Chico Martinez Creek (Murata, Friedman, and Madsen, 1969) is always *heavier* than that of associated cherts, which unfortunately indicates that the dolomites and cherts could not have equilibrated simultaneously with the same water (Clayton and Epstein, 1958; Friedman and Hall, 1963).

Fractionation factor α is a function of temperature, its numerical value decreasing as temperature increases. Many equations, both theoretical and empirical, relating α of the quartz-water system to temperature have been proposed (Becker, ms; Wenner and Taylor, 1971; Clayton, O'Neil, and Mayeda, 1972; Shiro and Sakai, 1972; and Knauth and Epstein, 1975; among others). The equation found by Clayton, O'Neil, and Mayeda (1972) to hold between 200° to 500°C is

$$1000 \ln\alpha = 3.38 \, (10^6 \, T^{-2}) - 3.40 \tag{2}$$

where T is absolute temperature, and its curve is the only one that coincides at 0° to 30°C with the diatom-water fractionation curve recently published by Labeyrie (1974). We have used eq (2), plotted in figure 1, to obtain isotopic temperatures (°C) for diatom frustules and for cristobalitic and quartzose cherts of Monterey Shale. Within the range 20° to 150°C, this curve yields temperatures 13° to 20°C higher than the curve of Knauth (ms), 11° to 20°C lower than the curve of Wenner and Taylor (1971), and 0° to 2°C higher than the curve of Becker (ms).

The low temperatures yielded by the curve of Knauth (ms) and that of Knauth and Epstein (1975) would suggest that the transformation of biogenic opal into disordered cristobalite occurs before or during shallow burial (generally $<$ 100 m) at temperatures within 5°C of those at the ocean-bottom. Shallow-lying cristobalitic Cretaceous and Paleogene rocks have been found in apparently continuous sections at a few DSDP sites characterized by extremely slow rates of deposition, for example, at site 257, leg 15, in the Perth Absyssal Plain (Davies, Luyendyk, and others, 1974). On the other hand, the higher temperatures indicated by the curve of figure 1 are more in agreement with the greater depths of transformation ($>$ 200 m) noted at many localities of the Monterey Shale (Bramlette, 1946, p. 53) and at many DSDP sites, notably those in the Bering Sea (Scholl and Creager, 1973) and in the Venezuelan Basin (Saunders and others, 1973).

SAMPLES AND ANALYTICAL TECHNIQUES

A sample of diatom frustules was separated from the diatomaceous mudstone of Chico Martinez Creek and of the Taft area by settling out detrital sand and silt and by removing the predominantly montmorillonitic clay minerals through alternate treatment with hot 1-1 HCl and 10 percent Na_2CO_3 with intermediate filtration. The purified frustules were ignited (Labeyrie, 1974) prior to analysis. The cristobalitic and quartzose diagenetic zones of the two localities are represented by the few samples of chert that were pure enough for analysis. Porcelanite is far more abundant than chert in these zones but is always heavily contaminated with tightly cemented detrital minerals. For the sake of completeness, a rare type of pisolitic and drusy quartz that replaces diagenetic dolomite in both the cristobalitic and quartzose diagenetic zones was analyzed, although its relation to the other kinds of diagenetic silica is obscure.

The δ^{18} of the various silica samples (table 1) was determined by the bromine pentafluoride method (Clayton and Mayeda, 1963); the 2-sigma precision of determination is ± 0.12 per mil (Friedman and Gleason, 1973).

GENERAL ASPECTS OF THE ISOTOPIC COMPOSITION

The isotopic compositions will first be discussed separately from considerations of isotopic temperatures. The $\delta^{18}O$ of samples from Chico Martinez Creek decreases down section from 37.4 per mil for diatom frustules through a mean of 29.4 per mil of cristobalitic cherts to a mean of 23.8 per mil for quartzose chert. The $\delta^{18}O$ of samples from the Taft area, though involving a different set of numerical values, also decreases downward, with about the same contrast in $\delta^{18}O$ among the three recog-

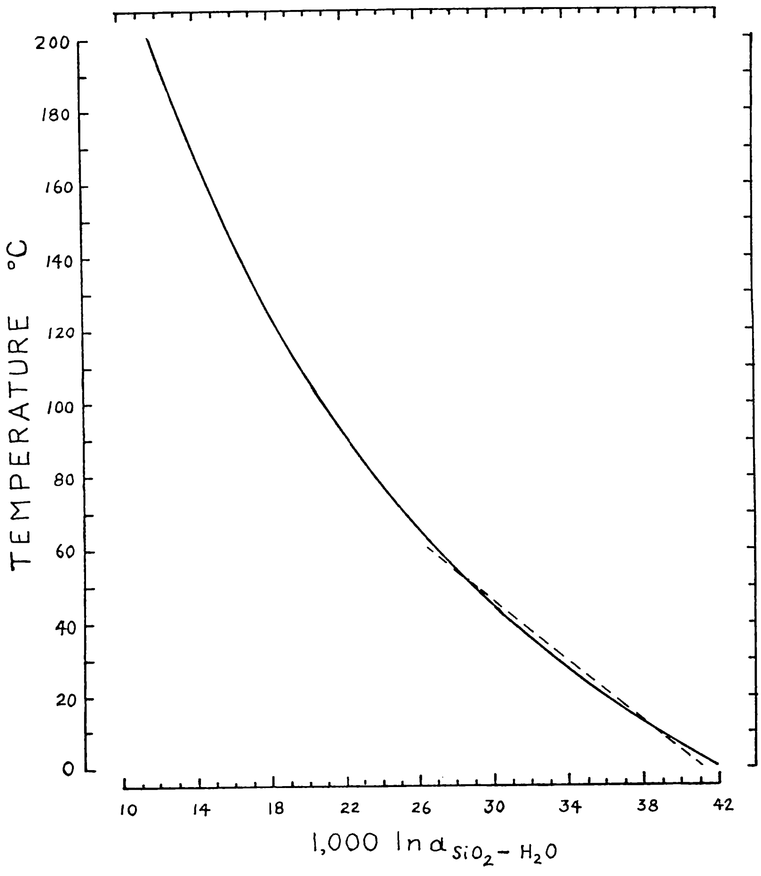

Fig. 1. Variation with temperature of ^{18}O fractionation factor α between quartz and water, shown as a solid line (Clayton, O'Neil, and Mayeda, 1972) and between diatom frustules and water, shown as a dashed line (Labeyrie, 1974. The dashed line above 30°C represents an extrapolation). The solid curve was used to obtain isotopic temperatures for diatoms and cherts of Monterey Shale.

TABLE 1

Oxygen isotopic composition ($\delta^{18}O$, per mil relative to SMOW) and isotopic temperature (°C) of diatom frustules and cherts in the Monterey Shale of Temblor Range, Calif.

	Chico Martinez Creek				Taft area			
Silica phase	Sample no. CM-	d(101) of Cristobalite A	$\delta^{18}O$	Isotopic temp*	Sample no. T-	d(101) of Cristobalite A	$\delta^{18}O$	Isotopic temp*
Diatom frustules	1	—	37.4	15	1	—	36.2	19
	5	4.117	29.8	46	4	4.114	33.8	28
Cristobalitic	9	4.098	28.3	53	6	4.107	33.6	29
chert	12	4.092	30.8	41	8	4.097	32.2	35
	15	4.092	30.4	43	—	—	—	—
	17	4.071	27.9	56	—	—	—	—
Mean	—	—	29.4	48	—	—	33.2	31
					Corrected** for water of $\delta^{18}O$ = +3.7 per mil	—	(29.5)	(47)
Quartzose	21	—	24.1	77	19	—	27.6	57
chert	27A	—	23.6	80	146	—	27.1	60
Mean	—	—	23.8	79	—	—	27.4	58
					Corrected** for water of $\delta^{18}O$ = +3.7 per mil	—	(23.7)	(80)

* Isotopic temperatures were derived from the solid curve shown in figure 1, assuming that the phases had equilibrated with water, either marine or diagenetic interstitial, having a $\delta^{18}O$ of 0.0 per mil.

** The mean temperatures of comparable cherts from the two areas become virtually the same if the diagenetic interstitial water in the Taft area were assumed to be 3.7 per mil heavier than the water at Chico Martinez Creek.

nized zones. The only other analyzed chert from the Monterey Shale known to us is a cristobalitic sample from Lompoc, Calif., with $\delta^{18}O$ of 34.0 per mil (Henderson and others, 1971), which is close to the values for similar cherts from the Taft area. The general decrease in $\delta^{18}O$ seen in table 1 most likely reflects a rise in temperature rather than a downward change in some other physicochemical parameter or an isotopic exchange with some kind of light water.

The isotopic composition changes abruptly at the transition from biogenic opal into disordered cristobalite and again at the transition from ordered cristobalite into microquartz. These stepwise changes indicate that each phase retains its original isotopic composition during progressive burial until at some limiting depth it becomes transformed into another phase (Blattner, 1975; Knauth and Epstein, 1975). The transformation is primarily a process of solution-deposition during which the newly formed phase acquires a $\delta^{18}O$ that reflects the ambient temperature and the $\delta^{18}O$ of interstitial water. A remarkable thin section that shows dissolution of diatom frustules and associated formation of chert has been figured recently by Schrader (1974, pl. 13).

Isotopic temperatures (table 1) were computed by means of eqs (1) and (2) under the assumption that the silica phases equilibrated with water having $\delta^{18}O$ of 0.0 per mil. Diatom opals equilibrated with ocean water having such an isotopic composition. Derivative cristobalitic and quartzose cherts equilibrated with diagenetic interstitial water, which also had the isotopic composition of 0.0 per mil as a result of an appropriate combination of diagenetic reactions within the closed system of the sedimentary pile.

The isotopic temperatures of samples (excluding the original diatoms) from the Taft area are consistently lower than those of comparable materials from Chico Martinez Creek but become similar if it is assumed that the diagenetic interstitial water in the Taft area had a $\delta^{18}O$ of + 3.7 rather than 0.0 per mil. The reverse assumption (that the $\delta^{18}O$ of interstitial water at Chico Martinez Creek was −3.7 per mil and that of the Taft area, 0.0 per mil) was not made because the resulting geothermal gradient at Chico Martinez Creek would be so low as to require improbable values of thermal conductivity and rates of heat flow.

TEMPERATURE INDICATED BY DIATOM FRUSTULES

Diatoms from the two studied localities differ somewhat in age within the late Miocene, those from Chico Martinez Creek being "Delmontian" corresponding to Schrader's (1973) diatom zone 11, and those from the Taft area being late Mohnian corresponding to Schrader's (1973) zone 13 (J. A. Barron, written commun., Aug. 1974). Diatom frustules from Chico Martinez Creek and the Taft area yield isotopic temperatures of 15° and 19°C respectively, which probably approximate the temperature of the seawater in which the diatoms grew (Labeyrie, 1974).

A method (Barron, 1973) of estimating paleotemperatures from ratios of cold- to warm-water diatoms in a deposit was kindly applied by Barron to sample T-1 from Taft; diatoms of sample CM-1 from Chico Martinez Creek have been subject to much post-depositional leaching and cannot be studied by this method. The late Mohnian assemblage of Taft suggests a winter minimum temperature of 10° ± 5°C compared to the isotopic temperature of around 19°C. The agreement between the two methods for determining paleotemperatures is fairly good when one considers that most of the diatom growth probably occurred when temperatures were warmer than those of the winter minimum.

ISOTOPIC TEMPERATURE OF CRISTOBALITIC CHERTS

The discussion henceforth will be based mainly on isotopic temperatures of samples from Chico Martinez Creek, plotted in figure 2. Isotopic temperatures of cristobalitic cherts fluctuate randomly between 41° and

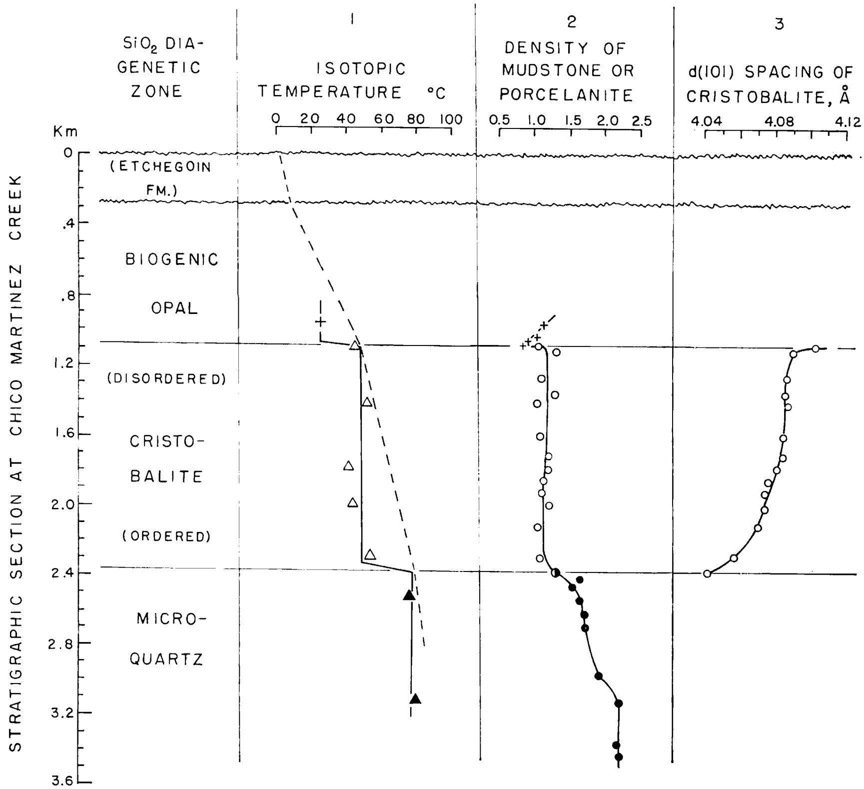

Fig. 2. Variation with depth of isotopic temperature and related properties of Monterey Shale at Chico Martinez Creek. Depths are relative to the top of the Etchegoin Formation, the youngest marine formation in the area. Cross denotes a purified sample of diatom frustules in column 1 and diatomaceous mudstone in column 2. Open and filled triangles, cristobalitic and quartzose cherts, respectively; open and filled circles, cristobalitic and quartzose porcelanites, respectively. Dashed line in column 1 represents a geothermal gradient for Monterey Shale computed from existing data on thermal conductivity of submarine siliceous sediments and a heat flow of 0.8 H.F.U.

56°C, with a mean of 48°C. These temperatures of transformation of biogenic opal into cristobalite are comparable to those (36°-51°C) found in submarine Miocene diatomaceous sediments by down hole temperature measurements at DSDP sites 184 and 185 of leg 19 (Erickson, 1973; Scholl and Creager, 1973).

The relatively constant isotopic temperature of cristobalitic cherts parallels the constant density (1.2g/cm^3) of the host cristobalitic porcelanites (fig. 2, column 2). The parallelism further supports an earlier conclusion (Murata and Larson, 1975) that the structural ordering of cristobalite, manifested in changes of the d(101) spacing (fig. 2, column 3), occurred through reactions in the solid state rather than through solution-deposition of silica.

ISOTOPIC TEMPERATURE OF QUARTZOSE CHERTS

The indicated temperature of origin of quartzose chert is about 80°C at a subbottom depth of about 2.4 km (fig. 2, column 1). The conversion process is accompanied not only by shifts of isotopic ratios to values indicative of exchange at higher temperature but also by a rapid increase in the density of the host porcelanite (fig. 2, column 2). The two samples of microquartz from Chico Martinez Creek and the two from the Taft area consistently yield an isotopic temperature of about 80°C (assuming water with $\delta^{18}O$ of +3.7 per mil in the Taft area) regardless of the depth of occurrence within the quartzose diagenetic zone. This consistency suggests that diagenetic microquartz, like diagenetic cristobalite, retains its original isotopic composition as long as it retains its mineralogic identity.

An original temperature of about 80°C for microquartz of Monterey Shale is much higher than isotopic temperatures of 8° to 21°C found for microquartz in sediments from widely scattered DSDP sites (Kolodny and Epstein, 1974; Knauth and Epstein, 1975). The lower temperatures may be characteristic of microquartz formed in a calcareous matrix, in which silica diagenesis seems to follow a different pathway (Lancelot, 1973) than in a carbonate-poor matrix like the Monterey Shale. The microquartz of Chico Martinez Creek formed at a burial depth of more than 2 km, and considerations of geothermal gradient make it very unlikely that the transition occurred at such low temperatures.

The original temperature of microquartz at Chico Martinez Creek can also be estimated by means of existing experimental data on the kinetics of the cristobalite-microquartz transformation. According to Ernst and Calvert (1969), the time required for this polymorphic transformation is strongly dependent on temperature, varying from 36,000 yrs at 100°C to 180,000,000 yrs at 20°C.

At Chico Martinez Creek, the cristobalite-microquartz conversion takes place within a transition zone 90 ± 30 m thick (Murata and Larson, 1975). The time (and hence the temperature) involved in the conversion here can be estimated by assuming that the transition zone is a migratory feature that moves upward in the sedimentary pile at about the same rate as sediments are laid down on top of the pile and that its thickness is a measure of the rate of conversion. Sediments of "Delmontian" and Mohnian age along Chico Martinez Creek have a total thickness of 1760 m (Dibblee, 1973) and were deposited over a period of about 7 m.y. according to the time scales of Ingle (1973) and Schrader (1974), which yield about 4000 yrs as an average period of deposition of a meter of sediment. According to this calibration, the 60 to 120 m thickness of the transition zone corresponds to a time lapse of 240,000 to 480,000 yrs for the conversion of cristobalite into microquartz. The experimental results of Ernst and Calvert (1969) show that these periods correspond to conversion temperatures of 73° to 80°C, in surprisingly good agreement with the isotopically indicated 79°C.

RECONCILIATION OF THE ISOTOPIC TEMPERATURES WITH THOSE COMPUTED ON THE BASIS OF HEAT FLOW

Existing data (Lee and Clark, 1966) on normal flow of heat through sedimentary strata allow certain limits to be put on temperatures that would be expected in a submarine pile of sediments; we shall compute such temperatures for comparison with the isotopic temperatures. Two different rates of heat flow are assumed (table 2, row 1), one being the average oceanic heat flow of 1.3 Heat Flow Units (Langseth and Von Herzen, 1970), forming the basis of condition 1, the other, 0.80 H.F.U., the basis of condition 2.

Selection of an average conductivity of 1.85 mcal cm^{-1} s^{-1} $°C^{-1}$ for biogenic opal zone and of 2.90 cm^{-1} s^{-1} $°C^{-1}$ for the cristobalite zone (row 2) is consistent with the best data available (Erickson, 1973) for comparable submarine rocks. The differing conductivities correlate with the differing densities (row 4) of the rocks of the two zones.

The original thickness of 0.8 km estimated for the biogenic opal zone (row 3) is uncertain because of the unconformity at the top of the Belridge Diatomite member of Monterey Shale. A remnant of the Belridge 250 m thick is exposed at Chico Martinez Creek; a possible thickness of 350 m has been reported by Ritzius (1950) in oil wells 16 km to the east. As much as 670 m of the Belridge is preserved 50 km to the south, near Taft (Dibblee, 1973). The overall evidence suggests that a thickness of 0.8 km for the complete section of Belridge Diatomite is possible.

The 1.3 km thickness of the cristobalite zone (row 3) is intact. The thermal conductivities (row 2) coupled with the heat flows of conditions 1 and 2, yield the gradients given in row 5 and the computed temperatures of interest given in row 6.

Temperatures based on the subnormal heat flow of 0.8 H.F.U. (condition 2) are 44°C for the bottom of the biogenic opal zone and 80°C for the bottom of the cristobalite zone (row 6) in general agreement with the respective isotopic temperatures of 48 ± 8° and 79 ± 2°C (row 7). Temperatures for these levels computed on the basis of the heat flow of 1.3 H.F.U. (condition 1) are higher than the isotopic temperatures by 22° and 49°C, respectively.

The geothermal gradient in the Taft area was earlier thought (Murata and Randall, 1975, fig. 2) to have been steeper than that at Chico Martinez Creek because the cristobalite zone, consisting essentially of the McLure Shale Member of the Monterey Shale, seemed to be thinner in the Taft area. The McLure Shale Member in a relatively undisturbed part of the Taft area (well no. 42 of Vedder, 1970), however, is as thick as that at Chico Martinez Creek. Consequently, the low heat flow of 0.8 H.F.U. is also indicated for the Taft area and may indeed have prevailed throughout the whole region. As the present heat flow in the region of Chico Martinez Creek is 1.29 H.F.U. (Benfield, 1947), the lower rate must have prevailed earlier when the Monterey Shale was accumulating (Von Herzen and Uyeda, 1963) at a rate of about 0.3 mm yr^{-1}.

The isotopic temperatures of phase transformations (table 1) thus seem plausible when viewed against the background of flow of heat through sedimentary rocks. Moreover, the oxygen isotope composition throws some light on mechanisms of phase transformation among the silica minerals. A phase will retain the original isotopic composition

TABLE 2

Thermal and related properties of rocks from the Etchegoin Formation and the Monterey Shale along Chico Martinez Creek, Temblor Range, with a comparison of temperatures computed from these properties and temperatures determined isotopically

	Etchegoin Formation	Monterey Shale	
	Silty sandstone	Biogenic opal zone	Cristobalite zone
1. Assumed heat flow, Heat Flow Units			
Condition 1	1.3	1.3	1.3
Condition 2	0.8	0.8	0.8
2. Thermal conductivity, mcal $cm^{-1}s^{-1}$°C^{-1}			
Conditions 1 and 2	3.1*	1.85	2.90
3. Total thickness, km			
Conditions 1 and 2	0.28**	0.8†	1.30
4. Density, g/cm^3	—	1.0 ± 0.14	1.16 ± 0.15
5. Computed gradient, °C km^{-1}			
Condition 1	41.9	70.3	44.8
Condition 2	25.8	43.2	27.6
6. Computed temp at bottom of zone, °C			
Condition 1	13.7††	69.9	128.2
Condition 2	9.2††	43.8	79.6
7. Isotopic temp at bottom of zone, °C (from table 1)	—	48 ± 8	79 ± 2

* Conductivity of silty turbidite (?) at DSDP site 183 (Erickson, 1973). An upper limit of 3.6 mcal/cm sec °C is set by the present-day average conductivity of Etchegoin rocks (Benfield, 1947).

** Thickness from Weddle (1968).

† Previously estimated as 0.40 km (Murata and Larson, 1975); the greater thickness is suggested by the new data on isotopic temperatures.

†† Includes a bottom-water temperature of 2°C.

despite changes in ambient conditions as long as it retains its structural identity or undergoes structural changes only through reactions in the solid state. On the other hand, a phase produced through a solution-deposition mechanism of transformation will acquire a new isotopic composition that reflects the ambient temperature and the isotopic composition of the water involved.

ISOTOPIC COMPOSITION OF QUARTZ THAT REPLACES DOLOMITE

Diagenetic dolomite in beds 0.1 to 1.0 m thick occur throughout the Monterey Shale as a characteristic minor constitutent. At a few places, this dolomite, in both cristobalitic and quartzose diagenetic zones, is replaced by patches of pisolitic and drusy quartz. The replacement quartz is most abundant where the dolomite bed is intensely fractured and permeable to migrating solutions. The fact that the replacement silica is always quartz, even when the dolomite bed lies within the cristobalite diagenetic zone, suggests that dolomite provides a localized alkaline environment that promotes the formation of quartz. The section at Chico Martinez Creek and the section near Taft each yielded a sample of replacement quartz from both the cristobalitic and quartzose zones, and the four samples were analyzed to characterize this unusual kind of quartz isotopically (table 3).

$\delta^{18}O$ of the dolomite-replacing quartz in the quartzose diagenetic zone is smaller than the delta value of similar quartz in the cristobalitic zone, seemingly as a function of the higher temperature of the deeper-lying quartzose zone. As discussed below, however, this kind of quartz

TABLE 3

Oxygen isotopic composition ($\delta^{18}O$ per mil relative to SMOW) of replacement quartz in dolomite and of associated rocks in the Monterey Shale of the Temblor Range

	Chico Martinez Creek			Taft area	
Silica diagenetic zone	Mineral or rock	Sample no. CM-	$\delta^{18}O$	Sample no. T-	$\delta^{18}O$
Cristobalitic	Replacement quartz in dolomite	8A	30.6	42(9A)	28.4
	Host dolomite	614B-37	34.6	42	35.2
	Nearby cherts	5 and 9	28.7 ±0.7	6 and 8	32.6 ±0.7
Quartzose	Replacement quartz in dolomite	23A	27.3	18	25.8
	Host or nearby dolomites	22, 22A, 23B	30.7 ±1.0	18	30.4
	Nearby chert	21	23.9	19	27.4

may have formed in post-orogeny time through interaction of silica-bearing groundwater and dolomite. The $\delta^{18}O$ of dolomite at Chico Martinez Creek decreases down section from 36 to 31 per mil, and this trend, which was established in pre-orogeny time, could be reflected in the quartz that replaced the dolomite.

The isotopic composition of such a late quartz would not be closely related to that of either diagenetic cristobalite or diagenetic quartz. At Chico Martinez Creek, $\delta^{18}O$ of replacement quartz is heavier than that of associated cristobalite or quartz, whereas in the Taft area it is lighter (table 3).

A late origin for the dolomite-replacing quartz is suggested by its striking resemblance in form to the pisolitic caliche of the Persian Gulf, called to our attention by P. A. Scholle (Scholle and Kinsman, 1974, fig. 6E), and to the nodular replacement chert, also a product of "calichification", in the Permian Alibates Dolomite Lentil of Texas (Bowers and Reaser, 1975). The present climate of the Temblor Range is sufficiently arid for caliche of various kinds to form and for the isotopic composition of normally light groundwater to be changed through intense evaporation. This possibility of the dolomite-replacing quartz having originated in a caliche environment needs to be investigated further.

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