An Evaluation of Temperature Scales for Silica Diagenesis in Diatomaceous Sequences Including a New Approach Based on the Miocene Monterey Formation, California

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Abstract

Geologic relations indicate that silica phases transformed in the Monterey Formation in two zones that persist over a narrow depth/temperature range and do not stratigraphically overlap. The wide and overlapping range of reported temperatures of these transformations is mainly a result of the many uncertainties inherent in the different methods used to estimate temperature and does not indicate that phases transform throughout these ranges. Our approach to a reliable temperature scale for silica diagenesis combines an empirical zonation of silica phases with temperature calibration from a sequence at maximum temperature and depth of burial.

Introduction

The Miocene Monterey Formation is a sequence of fine-grained sedimentary rocks composed primarily of marine shell material (both siliceous and calcareous) and moderate amounts of organic matter and terrigenous clay. As originally deposited, the biogenous silica (opal-A) in diatom frustules is X-ray amorphous and metastable. Burial diagenesis produces two crystalline silica phases: opal-A transforms to metastable opal-CT, which transforms to stable quartz. Also, the principal d-spacing of opal-CT decreases with increasing burial depth and temperature until quartz forms [1–5]. This sequence of silica phases has been widely recognized in the Monterey Formation (Fig. 1) [1–5] and in other diatomaceous deposits [6].

Because silica diagenesis is temperature-dependent, the two phase transformations of silica have potential as geothermometers. A temperature scale based on silica diagenesis could be applied to the determination of the maximum temperature reached during burial diagenesis in both surface and subsur-

face opal-CT-bearing sequences of the Monterey Formation in California. Such a scale would be especially valuable where post-Monterey tectonism has disturbed or erased other parameters needed for the determination of maximum diagenetic temperature.

In constructing a temperature scale, the methods of determining temperature must be evaluated with care since each method involves different assumptions and associated errors. Also important is the method of determining the relative diagenetic grade of silica. In this paper we: 1) discuss the interrelation of composition and temperature of silica diagenesis, 2) evaluate methods that have been used to determine the temperatures of the two phase transformations of silica, and 3) propose an approach to a reliable temperature scale for silica diagenesis in the Miocene Monterey Formation.

Influence of Composition on Silica Diagenesis

Although temperature is generally thought to be the principal factor in determining the rates of silica-phase transformations, many other factors have been suggested to influence rates [2–5]. One of the most important of these secondary influences is the composition of the rock or sediment. In the Monterey Formation, for example, empirical data indicate that the temperature of silica-phase transformations varies with the relative abundance of terrigenous detritus (the abundance of terrigenous detritus in the sum of terrigenous detritus and biogenous silica); opal-CT formed at slightly lower temperature and has a larger d-spacing in rocks containing relatively less detritus, and diagenetic quartz formed at slightly lower temperature in rocks containing relatively more detritus [5].
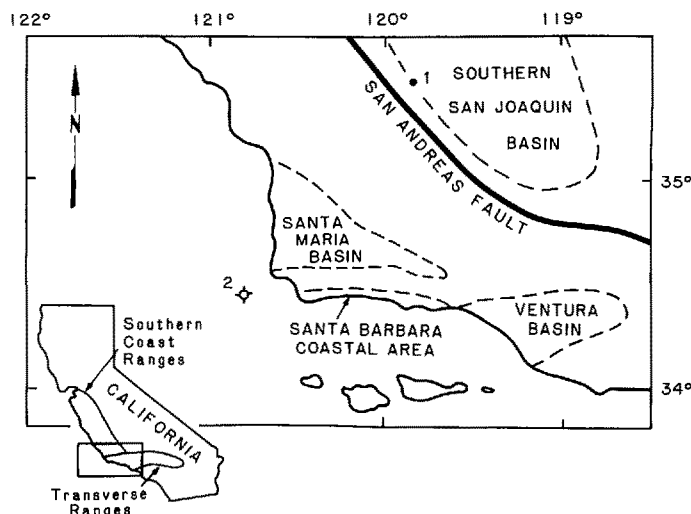
Figure 1. Location of Monterey Formation sequences in central California where silica diagenesis has been studied, including Chico Martinez Creek (=#1) in the Temblor Range of the San Joaquin basin [1–3], the onshore Santa Maria basin [4], the Point Conception COST well OCS-CAL 78-164 No. 1 (=#2) in the offshore Santa Maria basin [7], the Santa Barbara coastal area [5], and the Ventura basin [7].

This close relation between the abundance of terrigenous detritus and temperatures of silica-phase transformations may be caused by the influence of smectite on the chemistry of pore waters during diagenesis [8]. Smectite is abundant in the detrital component of the Monterey Formation.

The maximum effect of composition on the temperature of silica-phase transformations can be estimated from the thicknesses of phase-transition zones (zones in which interbedded strata have different silica phases) in Monterey sections that are the most compositionally variable. In the heterogeneous Monterey sequences of the Santa Barbara basin, these phase-transition zones are 200 m thick for opal-A to opal-CT and about 300 m thick for opal-CT to quartz [5 and references therein]. Assuming a geothermal gradient of 35° C/km (approximate average for this area), these thicknesses indicate that opal-A transforms to opal-CT over a range of 7° C, and opal-CT transforms to quartz over a range of 11° C, in compositionally heterogeneous sequences. In contrast, diatomaceous/siliceous sequences which are compositionally homogeneous, as in the Bering Sea, have silica-phase transition zones that are much narrower [9,10]. Similarly, in sequences that have been selectively sampled to represent a restricted composition, such as Chico Martinez Creek in the Temblor Range (Fig. 1), silica-phase transition zones appear to be much narrower (20 to 80 m) [2].

The Temperatures of Phase Transformations of Silica

Temperatures of the two silica-phase transformations have been estimated in several recent studies of silica diagenesis

of the Monterey Formation. These estimates of temperature are based primarily on: 1) estimated maximum overburden thickness combined with estimated geothermal gradients in uplifted sections on land [2–4], and 2) oxygen-isotope ratios [3,4]. By the second method, a measured oxygen-isotope ratio from a rock sample is combined with an estimated oxygen-isotope ratio for the equilibrating pore water, and interpreted using fractionation relations for the quartz-water system which are extrapolated from high temperature experimental results or other relations [11,12].

Temperatures estimated by these methods are problematic because of geologic unknowns and analytic uncertainties [7,9], including: 1) uncertain amounts of erosion in uplifted sections [2,4]; 2) possible changes in thermal gradients through time [13], including possible effects of uplift on geothermal gradients [2,4]; 3) unknown actual geothermal gradients where lower than actual values have been derived from uncorrected nonequilibrium bottomhole temperatures [4]; 4) undetermined compositional variations [2–4]; 5) uncertainty of
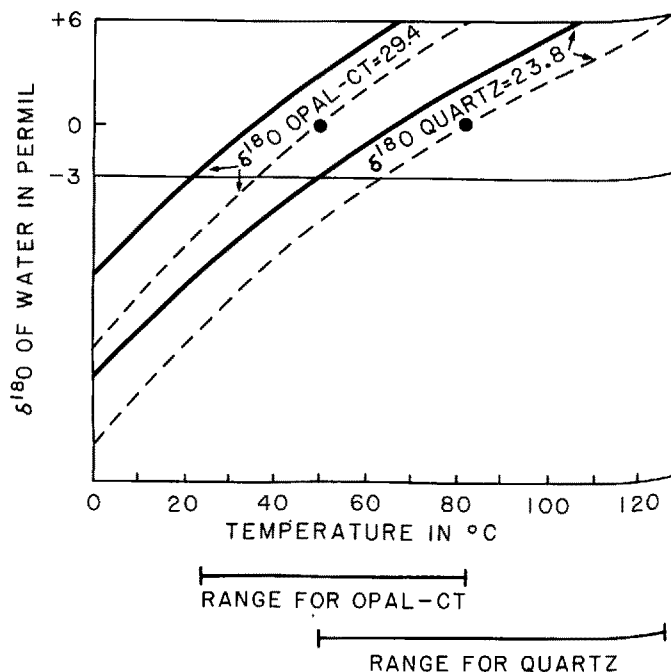
Figure 2. The range of temperatures for the formation of opal-CT and quartz inferred from: 1) a single determination of oxygen-isotope ratios for opal-CT ($\delta^{18}O = 29.4$) and quartz ($\delta^{18}O = 23.8$) from Murata and others [3]; 2) two representative fractionation relations for the quartz-water system (dashed lines are from Clayton and others [11], solid lines are from Knauth and Epstein [12]); and 3) a pore water composition of +6 to −3 $\delta^{18}O$, representing the observed range in interstitial water from several DSDP sites plus oil-field waters of Eocene to Lower Miocene formations underlying the Monterey Formation in the region of Chico Martinez Creek [3 and references therein]. On the curves from Clayton and others [11], the black dots represent a pore water of $\delta^{18}O = 0$, which yields the temperature estimates listed in Table 1 from Murata and others [3]. All oxygen-isotope values are in permil SMOW.

expressions for oxygen-isotope fractionation in the opal-CT-water and quartz-water systems [3,4]; and 6) unknown oxygen-isotope ratios of pore water at the depth and diagenetic environment where phases are transformed [3,4]. In addition, many isotopic estimates of the temperature of formation of quartz are based on quartz in clay-poor carbonate-bearing beds [4] in which volumetrically minor amounts of quartz form at anomalously low temperatures [5].

The results from these temperature studies, as summarized by Pisciotto [4], suggest that the two phase transformations of silica can occur over broad and overlapping temperature ranges—18° to 56° C for opal-A to opal-CT and 31° to 110° C for opal-CT to quartz. In fact, available oxygen-isotope data might suggest even broader ranges, taking into account the uncertainty in fractionation relations and the large range of geologically reasonable values for the equilibrating pore fluid (Fig. 2).

In contrast, stratigraphic and diagenetic relations in numerous individual Monterey sequences [2,5] indicate that silica phases in the Monterey Formation transform over a much narrower temperature range. Silica phases in the Monterey Formation, with rare exception [5], co-exist only in two non-overlapping transition zones that persist over a limited depth/temperature range. Accordingly, we conclude that the wide and overlapping range of temperatures of phase transformations of silica from previous studies [4 and references therein] is mainly a product of the many unknown parameters and uncertainties inherent in the different methods used to estimate temperature, and that silica phases did not actually transform throughout this range.

Approach to a Reliable Temperature Scale for Silica Diagenesis

The range of uncertainty in individual temperatures based either on oxygen-isotope ratios or on estimated maximum burial depth is large relative to the temperature differences that are potentially distinguished by a silica geothermometer. Thus, a reliable temperature scale needs to take advantage of the constraints on temperature imposed by superposition in individual sequences of diatomaceous/siliceous strata.

Our approach to a temperature scale for silica diagenesis (Fig. 3) combines an empirical silica-phase zonation with temperature calibration from two points of phase transformation in diatomaceous/siliceous strata presently at maximum temperature and depth of burial. The empirical silica-phase zonation (modified from Isaacs [5]) is a relative scale that represents the effects of increasing temperature on rocks having various compositions (abundances of terrigenous detritus); it is based on a synthesis of relations between silica phase, rock composition, and opal-CT d-spacing at outcrops in the Santa Barbara coastal area and the western Ventura
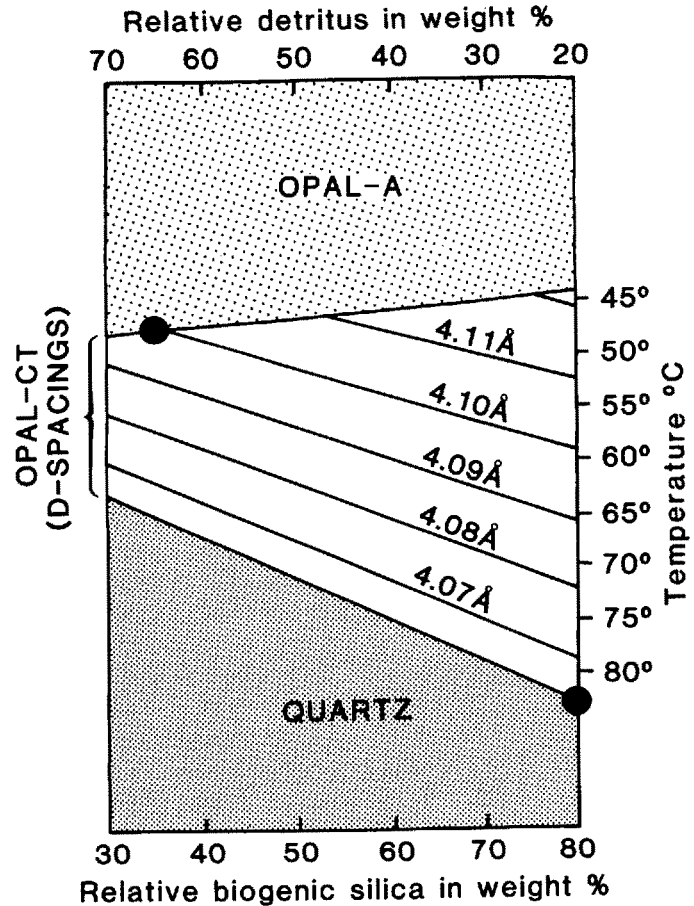

Figure 3. A preliminary temperature scale for silica diagenesis in the Monterey Formation, representing the combined effects of temperature and rock composition. The temperatures of two points of silica-phase transformation (black dots) in the Point Conception COST well were used to calibrate temperature for this empirical silica-phase zonation (modified from Isaacs [5]).

basin [5,7]. Inasmuch as empirical data from the Monterey Formation indicate that calcite affects rates of silica diagenesis only in extremely clay-poor rocks (<10% relative detri[nbtus) [5], the zonation can be used in carbonate-bearing as well as carbonate-free strata.

Our temperature calibration is based on the Point Conception COST well (OCS-CAL 78-164 No. 1) because Neogene strata in this well probably have not been uplifted or eroded and are, thus, at maximum depth of burial [14]. Moreover, several independent indicators of temperature and maturity in this well, including other diagenetic reactions and thermal metamorphism of organic matter, suggest that Neogene temperatures in the well did not exceed the present adjusted average temperature gradient [14,15]. Although temperatures were not measured at equilibrium in the well, disequilibrium values were empirically adjusted, yielding an average geothermal gradient of 48° C/km [15].

Table 1. Estimates of the Temperatures of Silica-Phase Transformations in Compositionally Comparable Rocks of the Monterey Formation

Opal-CT	Quartz	Source
52–54° C	77–85° C	Equilibrium geothermal gradients and estimated maximum overburden, onshore Santa Maria basin [4]
48 ± 8° C	79 ± 2° C	Oxygen-isotope ratios in carbonate-free sequences, Temblor Range [3]
45° C	79° C	Temperature-calibrated empirical silica-phase zonation, Santa Barbara-Ventura basin (Fig. 4)

For calibrating the empirical zonation (Fig. 3), this average gradient of 48° C/km and a bottom water temperature of 6° C [15] were used to determine the temperature of silica-phase transformations in the Point Conception COST well [7]. The determination of silica phases and composition in individual and composite cuttings throughout the COST well indicates that opal-CT formed in rocks with 65% relative abundance of detritus at a subsea-floor depth of approximately 850 m or 2850 ft (4300 ft measured well depth) corresponding to 48° C, and that quartz formed in rocks with 20% relative detritus at a subsea-floor depth of approximately 1650 m or 5450 ft (6900 ft measured well depth) corresponding to 85° C [7]. These two points of temperature and composition, shown in Figure 3, were used to calibrate the empirical silica-phase zonation.

Temperature calibration of the empirical silica-phase zonation provides a preliminary temperature scale for the entire zone of opal-CT-bearing rocks (Fig. 3). These results suggest that opal-A transforms to opal-CT at 45° C and opal-CT transforms to quartz at 79° C in rocks with 30% relative abundance of detritus. These values compare favorably with the most reliable temperature estimates presently available for these transformations in rocks of comparable composition—estimates by Pisciotto [4] based on geothermal gradients determined from equilibrium temperatures in uplifted sections and estimates by Murata and others [3] based on oxygen-isotope ratios in carbonate-free strata (Table 1).

Discussion

Further analysis will undoubtedly result in modifications of our preliminary temperature scale. For example, our temperature scale does not take into account variations in heating rate (the effects of time). Moreover, our silica-phase zonation assumes a linear relation between values of opal-CT *d*-spacings and the relative abundance of detritus at individual localities, and the zonation also combines partial diagenetic sequences from a number of localities. In addition, even though the COST well data are among the best available for determining the temperatures of the two phase transformations of

silica, our temperatures may be slightly incorrect for the following reasons: 1) temperature estimates are based on empirically adjusted, nonequilibrium temperature data; and 2) a linear geothermal gradient is assumed.

Ideally, a temperature scale would be based on silica phases of compositionally variable strata determined in a single well section (at maximum temperature) in which equilibrium temperature data were available throughout the well. The Monterey Formation is generally too thin to encompass the entire silica-phase zonation in a single well, but further study of selected sequences may more nearly approach the ideal.

Conclusions

Reported estimates of the temperatures of the two silica-phase transformations in diatomaceous sequences cover a broad and overlapping range (18°–56° C for opal-A to opal-CT and 31°–110° C for opal-CT to quartz) [e.g., 4]. This broad and overlapping range of temperatures is mainly a result of the many unknown parameters and uncertainties inherent in the different methods used to estimate temperature and does not indicate that phases transform throughout this range. Geologic relations in the Monterey Formation do not support either this broad temperature range or the overlap of the silica-phase transformations. Instead, silica phases in the Monterey Formation, with rare exception, co-exist only in two nonoverlapping transition zones that persist over a narrow depth/temperature range, indicating that silica-phase transformations have potential as geothermometers.

Acknowledgments

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