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Kinetics of Silica-Phase Transitions

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KINETICS OF SILICA-PHASE TRANSITIONS

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ABSTRACT

In addition to the stable silica polymorph quartz, several metastable silica phases are present in Yucca Mountain. The conversion of these phases to quartz is accompanied by volume reduction and a decrease in the aqueous silica activity, which may destabilize clinoptilolite and mordenite. The primary reaction sequence for the silica phases is from opal or glass to disordered opal-CT, followed by ordering of the opal-CT and finally by the crystallization of quartz. The ordering of opal-CT takes place in the solid state, whereas the conversion of opal-CT takes place through dissolution-reprecipitation involving the aqueous phase. It is proposed that the rate of conversion of opal-CT to quartz is controlled by diffusion of defects out of a disordered surface layer formed on the crystallizing quartz. The reaction rates are observed to be dependent on temperature, pressure, degree of supersaturation, and pH. Rate equations selected from the literature appear to be consistent with observations at Yucca Mountain.

I. INTRODUCTION

Although quartz is the stable form of solid SiO_2 at low temperature, several forms of opal are common in low-temperature environments. These forms may be amorphous, may show tridymite or cristobalite-like structures, or may show aspects of each. These forms commonly are derived from siliceous micro-fossils that accumulated to form biogenic oozes during diagenesis or from vitric material of volcanic rocks, as is the case in Yucca Mountain. Transitions from less stable silica polymorphs to quartz are important in two respects. First, these transitions represent a significant volume decrease. There is a 12% reduction in volume with the transition from cristobalite to quartz. Second, field observations suggest that there is a strong correlation between the presence of cristobalite or more soluble silica phases and the stability of clinoptilolite. The reason for this correlation is probably that dissolution of the less stable silica phases produces an aqueous

silica activity greater than that in equilibrium with quartz. Because silica is evolved in the reaction of clinoptilolite to analcime and/or feldspars, increased aqueous silica activity tends to stabilize the clinoptilolite.

The need for a kinetic model for silica-phase transitions is therefore twofold. (1) The model must provide a means of predicting the extent of silica-phase transitions that would take place over the repository's lifetime as a function of position in Yucca Mountain. (2) The model must provide a sufficient description of the mechanism of the reactions so that the aqueous silica activity coexisting with a mixture of silica phases can be predicted.

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II. THE SILICA PHASES

Although opal-A, opal-CT, and opal-C may not represent discrete, well-defined phases, they provide useful descriptive terms for understanding the evolution of solid silica. Along with quartz and chalcedony, these represent the important forms of solid silica present in diagenetic environments. The additional phases keatite and silica-X have been observed in low-temperature experimental studies summarized by Bettermann and Liebau (1975), but they have not been observed to occur naturally. They are not found in the natural environment because they require either high temperature (200 to 300°C) or a combination of low temperature and high pressure (>1.5 kb). At low pressure, the amorphous silica will have crystallized to opal-CT before the temperatures reach the level necessary for formation of keatite or silica-X. High pressures are uncommon at low temperature because of the depth of burial necessary. Even if the necessary high pressures were achieved at low temperature, it is unlikely that amorphous silica would survive for the time required.

For these reasons, we will consider only the phases opal-A, opal-CT, opal-C, chalcedony, and quartz. The classification of Jones and Segnit (1971) has been followed for the opals. Jones and Segnit "include those naturally occurring varieties of hydrous silica which are characterized by an X-ray diffraction pattern consisting of a prominent very diffuse band centered at about 4.1 Å" in the category opal-A. This material is nearly amorphous, although a small amount of ordering may be present. Opal-CT is a fine-grained hydrous silica phase that is primarily made up of α -cristobalite with variable amounts of stacking disorder that give rise to tridymite-like layers. Opals described as β -cristobalite

also generally fall in this group. In particular, the β -cristobalite thermodynamic data given in Walther and Helgeson (1977) appear to be for a disordered opal-CT (Murata and Larson, 1975). Opal-C, according to Jones and Segnit, is "natural hydrous silica which yields an X-ray diffraction pattern of alpha-cristobalite with only a small amount of line broadening and minor evidence of tridymite." All samples in this category studied by Jones and Segnit (1971) were associated with lava flows. Reheating by subsequent flows was considered likely.

Application of the term opal-A is reasonably straightforward. This is an amorphous phase; in the literature where the term opal-A has not been used specifically, its amorphous character has generally been noted. The break between opal-A and opal-CT is well defined by the appearance of distinct but somewhat broadened x-ray diffraction peaks for opal-CT. In the literature, opal-CT is often referred to as cristobalite, although the presence of some tridymite-like character is often noted. There is a decrease both in the interplaner spacings of the crystal lattice of opal-CT and in the width of the x-ray diffraction peaks, that marks the decrease in disorder and tridymitic character. With increased ordering, the opal-CT examined by Murata and Larson (1975) approaches closely the opal-C of Jones and Segnit (1971). Whether or not there is a distinct break between opal-CT and opal-C is unclear. Although opal-C shows minor line broadening and a small amount of tridymitic character, it is very similar to true cristobalite.

Chalcedony shows the x-ray diffraction pattern of quartz but has lower indices of refraction and undulatory extinction. It is made up of quartz crystallites with abundant submicrometer water-filled holes and has misorientation and dislocations between fibers. (Folk and Weaver, 1952; Pelto, 1956; White and Corwin, 1961). The solubility of chalcedony is higher than quartz (Walther and Helgeson, 1977), probably because of the greater surface area and abundant dislocations. Chalcedony probably grades into microcrystalline quartz. Quartz is the stable form of solid SiO_2 under most crustal conditions and certainly under all conditions to be expected in Yucca Mountain. It has a well-defined crystal structure and is generally anhydrous, except for part-per-million levels of hydrogen-bearing impurities.

III. SILICA-PHASE TRANSITIONS

Several phases of silica have been identified in Yucca Mountain (Bish and Vaniman, 1985; Bish and Chipera, 1986). Tridymite is common in the upper part of the mountain

(in the middle and upper parts of the Topopah Spring Member of the Paintbrush Tuff and above). Cristobalite is common above the water table and, in places, it persists to depths >500 m above sea level (Bish and Vanniman, 1985). In Bish and Vanniman (1985), cristobalite refers to all cristobalitic phases. Until recently (Bish and Chipera, 1986), no distinction has been made between opal-CT and cristobalite in the mineralogic studies at Yucca Mountain. Bish and Chipera found opal-CT and cristobalite that showed only a minor tridymitic character and very slight broadening in its x-ray diffraction peaks. Whether or not this cristobalite might appropriately be called opal-C is uncertain at this time. In any case, the distinction is of only minor importance because we would expect the difference in thermodynamic properties of opal-C and cristobalite to be minor, indicating only a very slightly higher solubility for opal-C. Opal-CT is found, almost exclusively, coexisting with clinoptilolite. Quartz is common in the mountain below the zone where tridymite disappears. Neither cristobalite nor opal-CT persists below the depth where clinoptilolite disappears. Of these phases, only quartz is stable under the conditions prevailing in Yucca Mountain, but the reaction trends among these phases are difficult to assess. Adjacent units may have experienced very different thermal histories during deposition and cooling, and hydrothermal alteration of some units by the nearby caldron complex is probable (Bish and Semarge, 1982).

Similar mineralogy, however, is observed during the diagenesis of biogenic opal-A (Heath and Moberly, 1971; von Rad and Rosch, 1972; Greenwood, 1973; Weaver and Wise, 1972; Murata and Larson, 1975; Mitsui and Taguchi, 1977; Kano, 1983). In these cases, the thermal history has been relatively simple, and temperature is controlled primarily by the depth of burial. The temperatures to which these rocks have been exposed are in the 0 to 100°C range, which is very typical of Yucca Mountain. The major difference in Yucca Mountain is the absence of biogenic opal-A; there, the role of opal-A appears to be taken by glass. The above studies show a general trend in mineral evolution from opal-A to opal-CT and from opal-CT to quartz. Tridymite is not generally observed. Heath and Moberly (1971) report tridymite, but the identification is based on an x-ray diffraction peak at 4.3 Å that is most likely due to opal-CT. Within the opal-CT zone, opal-CT becomes progressively more ordered with depth, as is indicated by a progressive decrease in the d(101) spacing from 4.11 to 4.04 Å (Murata and Larson, 1975; Mitsui and Taguchi, 1977; Kano, 1983). These studies also indicate that the transition from opal-A to quartz takes place in a stepwise manner. Opal-A transforms to disordered opal-CT with a d(101) spacing of about 4.11 Å. After completion of this step, opal-CT orders with a

corresponding decrease in the $d(101)$ spacing to about $4.04 \text{ \AA}$. Only when ordering of the opal-CT has been essentially completed does the transformation to quartz proceed.

Figure 1, adapted from Murata et al. (1977), illustrates the observed mineral distribution in the Monterey Shale at Chico Martinez Creek. Also shown are derived oxygen isotopic temperatures as a function of depth. The isotopic temperature changes abruptly at the reaction boundaries between opal-A and opal-CT and between opal-CT and quartz, but it appears constant through the zone of ordering of opal-CT. This strongly suggests that the opal-A to disordered opal-CT and ordered opal-CT to quartz reactions take place through dissolution into the aqueous phase and precipitation from it. The crystalline form of opal-CT supports this conclusion for the opal-A to opal-CT reaction (Weaver and Wise, 1972). However, Ernst and Calvert (1969) concluded from analysis of their experimental data that the opal-CT to quartz conversion takes place in the solid state. Supporting textural evidence for a solid state reaction is given by Heath and Moberly (1971), but they state that an intervening fluid interface is possible and that other textural evidence supports a solution-mediated reaction. Ernst and Calvert also noted that no reaction of opal-CT to quartz was observed in their experiments if their capsules had leaked and no water was present. In addition, Stein and Kirkpatrick (1976) reexamined the products of Ernst and Calvert's experiments and concluded, based on the textures observed, that a dissolution-reprecipitation mechanism involving the aqueous phase was indicated. They also presented a kinetic model based on a dissolution-reprecipitation mechanism that adequately fits the data of Ernst and Calvert.

The work of Mizutani (1966, 1967, 1970) done in $0.077N$ KOH solution suggests that the opal-A, opal-CT, and quartz zones overlap, although quartz precipitation does not appear to start until the amount of cristobalite in the system is near its maximum. However, Mizutani's conclusions are based on a kinetic model that we believe to be incorrect. Details of this model will be discussed later. The pertinent point here is that Mizutani only determined the amount of quartz present in his run products. Cristobalite, probably opal-CT, was observed but not quantified. No experimental evidence of the coexistence of amorphous silica and quartz is presented. Positive identification of amorphous silica is made only in the starting material. Clear evidence, however, is presented for the appearance of cristobalite before quartz crystallization commences. Kano and Taguchi (1982) studied the crystallization of amorphous silica in $\text{pH} = 12.6$ solutions at 200, 270, and 310°C and 10 MPa pressure. The $d(101)$ spacing of the opal-CT in their experiments was determined, and it is clear that some quartz crystallization has occurred before significant

Fig. 1. 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, which is the youngest marine formation in the area. The cross denotes a purified sample of diatom frustules in column 1 and diatomaceous mudstone in column 2. Open and filled triangles indicated cristobalitic and quartzose cherts, respectively; open and filled circles represent cristobalitic and quartzose porcelanities, respectively. The dashed line in column 1 represents a geothermal gradient for Monterey Shale computed from existing data on the thermal conductivity of submarine sediments and a heat flow of 0.8 H.F.U. (From Murata et al., 1977.)

ordering of the opal-CT. Early crystallization of quartz is most pronounced in the highest temperature experiments. It is unclear whether the sequence noted for the field observations and that seen in these experiments are different because of the higher temperature or the pH of the experiments or both. Observations in carbonate environments (Greenwood, 1973; Murata et al., 1977) suggest the possible direct conversion of opal-A to quartz; however, the absence of opal-CT may be due to increased reaction rates that result from more alkaline environments caused by the carbonates. The effect of pH on reaction rate will be discussed later.

Other experimental results summarized by Bettermann and Liebau (1975) tend to confirm the stepwise nature of the reaction of amorphous silica/opal-A to quartz; however, as noted above, additional or different intervening phases have been observed as the experimental conditions are varied. The probable sequence of reactions in Yucca Mountain begins with the conversion of glass to opal-CT plus additional phases such as zeolites, feldspars, and clays. This reaction most likely takes place by dissolution of glass, followed by precipitation of opal-CT and additional minerals from solution. This reaction is followed by ordering of the opal-CT, which apparently takes place in the solid state. Only when opal-CT has reached a highly ordered state does the crystallization of quartz begin. However, it is possible that at temperatures above 100°C or at a high pH, quartz precipitation may proceed before complete ordering of the opal-CT.

IV. TRANSITION RATES

Lasaga (1984) has suggested that mineral precipitation rates can be obtained from dissolution studies because dissolution and precipitation rates must be equal but opposite at equilibrium. This approach makes the assumption that the processes of attachment and detachment at the crystal surface are the same in the highly undersaturated conditions of typical dissolution experiments and the supersaturated conditions of interest for mineral precipitation. Rimstidt and Barnes (1980) took this approach to derive precipitation and dissolution rate constants for quartz and other silica polymorphs from experimental dissolution rates for quartz. We have used these data to calculate the conversion time of cristobalite to quartz (Wolfsberg and Vaniman, 1984). The calculated conversion times at 35°C are less than 10^5 yr, whereas observed lifetimes for cristobalite under similar conditions are greater than 10^7 yr. The experimental study of Ernst and Calvert (1969) also indicates conversion times of tens of millions of years at 35°C.

The model of Rimstidt and Barnes (1980) also suggests that quartz should precipitate most rapidly from solutions that are the most highly supersaturated. This obstruction is contrary to the apparent stepwise nature of the conversion of opal-A/glass to quartz. The solubility of the various silica phases (Walther and Helgeson, 1977) indicates that the aqueous silica activity decreases as the conversion sequence from opal-A to quartz proceeds. Yet quartz crystallizes only from the aqueous phase that coexists with ordered opal-CT and not from the higher aqueous silica activity solutions one expects to coexist with amorphous silica/opal-A.

The model of Rimstidt and Barnes does not appear to be adequate to describe the kinetics of the dissolution-precipitation steps of the opal-A/glass to quartz reaction sequence. A better understanding of the mechanism for the various reaction steps is clearly needed. Although there is no direct information on the mechanisms of these reactions (except as noted above that the ordering of opal-CT appears to take place in the solid state whereas the other reactions involve dissolution and reprecipitation), numerous studies provide information about the effect of various parameters on the rate of reaction.

Laudise (1959) studied the crystallization of quartz from 0.05-molal NaOH solutions at temperatures between 300 and 400°C. Supersaturation was achieved by heating the nutrient zone of the pressure vessel 10 to 80°C above the temperature of the growth region. Other variables considered were the relative surface areas of the quartz in the nutrient and growth zones and the fraction of the reaction vessel that was filled with liquid at the beginning of the experiment—a factor that controls the pressure of the experiment. Laudise concluded that the rate-controlling step in this system probably occurred at or near the interface between the supersaturated solution and the growing crystal. The growth rate depended on the crystal face where it occurred. This rate increased with increasing supersaturation, temperature, and the degree of fill, which correlates with increasing pressure. The temperature dependence of the rate followed an Arrhenius relationship. The activation energy for growth on the basal plan (the plane on which growth was fastest) was 22 kcal/mol.

Mizutani (1966, 1967, 1970) studied the conversion of amorphous silica gel to quartz in 0.077*N* potassium hydroxide solutions at temperatures between 86 and 280°C and about 10 MPa pressure. At temperatures above 117°C, conversion to 50% (or greater) quartz was observed in less than 3000 hr. Rate constants were derived for the reactions of amorphous silica to cristobalite and cristobalite to quartz, but the ordering of the cristobalite, which

corresponds well to opal-CT, was not considered. The rate equations used by Mizutani are

$$\frac{dA}{dt} = -k_1 A,$$

$$\frac{dC}{dt} = k_1 A - k_2 C,$$

and

$$\frac{dQ}{dt} = k_2 C,$$

where A, C, and Q are the amount of amorphous silica, cristobalite, and quartz in weight percent, respectively; k_1 is the rate constant for the reaction of amorphous silica to cristobalite; k_2 is the rate constant for the reaction of cristobalite to quartz; and t is time. The rate constants were found to follow an Arrhenius equation,

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

where A is the frequency factor; E is the activation energy; R is the gas constant; and T is the temperature in kelvin. However, the frequency factors and activation energies that were derived (Table I) are suspect because the form of the rate equation may not be applicable. Because these are dissolution-reprecipitation reactions, the reaction rate is more probably proportional to the surface area than to the amount of a phase present. Even if the surface area maintains roughly a constant proportionality to the amount present throughout the experiment, these equations seem inappropriate because they assume that it is the amount of the dissolving phase that is rate-controlling. This assumption is contrary to the conclusions of Laudise (1959) and to the observation that the model of Rimstidt and Barnes (1980), which is based on dissolution rate measurements, gives unreasonably rapid reaction rates.

Ernst and Calvert (1969) studied the conversion of porcelanite/opal-CT to quartz under hydrothermal conditions. Experiments were carried out in distilled water at 300, 400, and 500°C at 200 MPa pressure. Although the starting opal-CT in these experiments

appears to have been somewhat disordered, Ernst and Calvert treat the reaction only as the conversion of cristobalite to quartz. They found that the data could be fit with a zero-order rate equation of the form

$$\frac{dC_r}{dt} = -k,$$

where C_r is the concentration of the reactant—in this case cristobalite. The use of the term “concentration” in this context by Ernst and Calvert is certainly incorrect because cristobalite and quartz are present as pure phases, and they have actually correlated C_r with the amount of cristobalite present. The rate constant was observed to follow an Arrhenius equation. Frequency factor and activation energy are given in Table I. Using the applicability of the zero-order rate law, Ernst and Calvert concluded that the reaction takes place in the solid state. Stein and Kirkpatrick (1976) reanalyzed Ernst and Calvert's data using a nucleation and growth model applicable to dissolution and reprecipitation; this model expresses the fraction of cristobalite/opal-CT transformed, f , as

$$f = 1 - e^{(-kIY^n t^{(n+1)})},$$

where k is a geometric constant, I is the nucleation rate, Y is the growth rate, and t is time. The constant, n , takes on values of 1 for one-dimensional growth (needles), 2 for two-dimensional growth (platelets), and 3 for three-dimensional growth (spheres, cubes, etc.). The data were best fit with $n \cong 1$, which correlates well with the observation that the dominant quartz morphology in the experimental products is needle-like. However, Stein and Kirkpatrick observed that the model does not fit well for short run times, especially at 400°C. We propose that this discrepancy may be due to ordering of opal-CT at the beginning of the experiments, which results in little or no growth of quartz until the opal-CT has completed ordering.

The experiments of Ernst and Calvert also show a much slower reaction rate at a given temperature than do the experiments of Mizutani. Their results are in agreement with those of Campbell and Fyfe (1960), who observed that the rate of formation of quartz from amorphous silica increased with increasing hydroxyl ion concentration, and Corwin et al. (1953), who observed the formation of quartz from silica glass in alkaline solutions but the formation of only cristobalite in neutral to acid solutions. Carr and Fyfe (1958) observed

TABLE I

<u>A</u> <u>(yr⁻¹)</u>	<u>E</u> <u>(kcal/mol)</u>	<u>Reaction</u>	<u>Reference</u>
6.30 x 10 ⁹	17.0	Opal-A/Opal-CT	Mizutani (1966)
4.09 x 10 ⁹	14.3	Opal-CT/Quartz	Mizutani (1966)
2.62 x 10 ⁷	20.0	Ordering of Opal-CT	Kano (1983)
1.11 x 10 ⁹	23.2	Opal-CT/Quartz	Ernst and Calvert (1969)

that the rate of crystallization of amorphous silica through cristobalite and silica-K to quartz was strongly dependent on pressure.

Mizutani (1977) examined the $d(101)$ spacing of opal-CT in 0.077*N* KOH solution as a function of time at temperatures between 117 and 278°C and 10 MPa pressure. Kano and Taguchi (1982) conducted similar experiments in 0.1*N* KOH solution at 200, 270, and 300°C and 10 MPa pressure. They found that the rate of ordering could be expressed as

$$\frac{dS}{dt} = -kS,$$

where

$$S = d(101) - 4.040 \text{ \AA},$$

in which t is the reaction time and k is the rate constant. They also found that the temperature dependence of the rate constant followed an Arrhenius equation. Kano (1983) used this rate constant and derived a frequency factor that closely describes the variation of $d(101)$ for opal-CT in MITI Hamayuchi, a borehole in the Tempoku district, western Hokkaido, Japan. The resulting frequency factor and activation energy are given in Table I. Like the rate for the reaction of opal-CT to quartz, the rate ordering of opal-CT proceeds much more rapidly in a high-pH environment than in a more nearly neutral natural environment.

Kastner et al. (1977) studied the transformation of opal-A to opal-CT in distilled water and in seawater at 25 and 150°C. They found that the reaction rate of opal-A to opal-CT increased with increased temperature and at higher alkalinity. They concluded

that the presence of nucleation sites was an important control on the formation of opal-CT and that, in their experiments, magnesium hydroxide nuclei provided sites for opal-CT nucleation.

V. PROPOSED THEORY

It seems likely that the conversion of opal-A or glass to quartz at low temperature is a stepwise process; however, increased temperature or pH may modify the sequence. The rate of reaction is affected by temperature, pressure, and pH. Although at low supersaturation and moderately high temperature, as in the experiments of Laudise (1959), the rate is proportional to the degree of supersaturation, the rate of quartz crystallization in general is a complex function of supersaturation. This finding is not compatible with the kinetic model put forth by Rimstidt and Barnes (1980). The model of Rimstidt and Barnes also does not yield reasonable conversion times for cristobalite/ordered opal-CT to quartz.

Although there has been some success in developing empirical rate equations for the ordering of opal-CT and the conversion of ordered opal-CT to quartz, an improved understanding of the mechanism of the reaction would have several benefits.

- (1) Although the solubilities of the individual silica phases are reasonably known (Walther and Helgeson, 1977), the aqueous silica activity coexisting with a mixture of silica phases cannot be predicted without a knowledge of the mechanism of reaction.
- (2) An understanding of the reaction mechanism would improve understanding of the functional form of the dependence of rate on temperature, pressure, pH, and supersaturation. Because the rates of ordering of opal-CT and the rates for conversion of opal-CT to quartz in Yucca Mountain are very slow, correct functional forms are extremely important if we are to accurately extrapolate rates from conditions where they are rapid enough to be measured.
- (3) An understanding of the reaction mechanism could indicate other factors that might affect the rates.

A viable mechanism for quartz precipitation must be consistent with the rate's observed dependence on pressure, temperature, and pH. It should also provide an explanation for the stepwise nature of the crystallization of amorphous silica to quartz at low pressure as well as the reason that the precipitation rate is much slower than the dissolution rate.

Baumann (1971) placed quartz in pH 8.5 solutions (at 25°C) that initially were saturated with respect to amorphous silica. The decrease in aqueous silica activity was observed with time. The results of his experiments are shown in Fig. 2. With fresh quartz crystals, the solution composition came to quartz saturation within 40 days. However, when the same crystals were repeatedly placed in the amorphous silica saturated solution, the final value of the aqueous silica activity increased with each experiment. Iler (1979) suggested that the increase in solubility results when successively less-well-ordered surface layers are deposited. We propose that if quartz crystals are maintained in a supersaturated solution, layers with successively higher defect concentrations are formed on the quartz. Additional layers are no longer formed when the surface of the disturbed layer comes into equilibrium with the solution. Further growth of the quartz occurs only as defects diffuse out of the surface layer. Not only Al^{3+} and associated alkali cation defects but also the hydrogen (both hydroxyl and water-like) defects are well known for quartz (Aines and Rossman, 1984). Martin and Armington (1983) studied the effect of growth rate on quartz defects. Two types of defects were identified: (1) aluminum ions and their associated alkali ions substituting for silicon, and (2) OH molecules on unidentified sites. Both types of defects increased with increasing rate of crystallization. Both water and hydroxyl have been identified in chalcedony and opal-C (Fron del, 1982; Florke et al., 1982; Graetsch et al., 1985).

Hydroxyl groups are probably the dominant type of defect in the surface layer because the initial attachment of silica probably takes place as $\text{Si}(\text{OH})_4$ groups. The rate of diffusion of H or OH defects out of the disturbed surface layer probably controls the precipitation rate of quartz. Diffusion constants—with few exceptions—show an Arrhenius-type dependence on temperature (Zener, 1952) that is consistent with the rate dependence of quartz precipitation. However, the diffusion equation (Fick's law) is normally written in terms of the concentration gradient with material diffusing from those of high concentration to areas of low concentration. This equation would predict diffusion of defects into the quartz crystal rather than out of it. The actual driving force for diffusion is the gradient in chemical potential (Bardeen and Herring, 1952). The chemical potential of the defect μ_d can be written as

$$\mu_d = \delta W / \delta N_d + kT \ln(N_d/N),$$

Fig. 2. Concentration of aqueous silica coexisting with quartz as a function of time. Successive curves, numbered 0 through 7, are for quartz taken from the previous experiment. An arrow indicates the point in each experiment at which quartz was removed for the next experiment. (From Baumann, 1971.)

where N_d is the number of defects, N is the total number of defect sites available, W is the free energy (excluding contributions from configurational entropy), k is Boltzmann's constant, and T is temperature in kelvin. The second term on the right side of the equation is the contribution from the entropy of mixing. The first term contains all other contributions to the chemical potential. Only when this first term is constant throughout the diffusing medium can the diffusion equation be written in terms of the concentration gradient.

In experiments with a disturbed layer on a quartz surface, the first term will probably be larger for the less disturbed region near the quartz than for the more disturbed region near the liquid/solid interface because the energy required to create a defect in a well-ordered region should be greater than that required in a zone where large numbers of defects are already present. It is therefore possible that the chemical potential gradient may run counter to the defect concentration gradient, and defects may diffuse out of the surface layer. Because the defect concentration gradient may vary as a function of solution supersaturation, it is also possible that diffusion may be inward under some conditions and outward under others; there may also be an intermediate condition in which the chemical potential of defects is constant throughout the disturbed zone and no diffusion occurs.

Such a situation would provide an explanation for the observation that quartz does not crystallize until opal-CT has become highly ordered. We propose that when the aqueous silica activities are higher than those in equilibrium with ordered opal-CT, defects diffuse inward until an equilibrium defect gradient is established, inhibiting growth of the quartz crystals, and that at lower levels of aqueous silica activity, diffusion of defects is outward and quartz precipitation proceeds. The rate is pH dependent, probably because the majority of defects are either hydrogen or hydroxide ions. It seems reasonable then that variation in pH would affect the defect gradient and/or the disturbed zone thickness. The pressure dependence likely arises from the volume increase that almost certainly accompanies the incorporation of defects, which in turn will cause their chemical potential to increase relative to that of defect-free regions with increasing pressure. The condition observed by Laudise (1959), in which the rate of quartz crystallization is proportional to the degree of supersaturation at low supersaturation, probably corresponds to a condition in which the defect layer is insignificant. The data of Baumann (1971) indicate that the defect layer is only a few monolayers thick even at moderate supersaturation at 25°C. We would expect that at low supersaturation and high temperature, where considerable thermal energy is available for bond rearrangement (Jones and Segnit, 1972), a defect layer may not be present.

The proposed diffusion mechanism controlling quartz crystallization implies that the surface area of the quartz should also be an important parameter controlling the rate of growth. Some of the variation in reaction rate may therefore result from a variation in grain size. This factor could complicate application of the data discussed here to Yucca Mountain. However, the very fine grained nature of opal-CT (and the chalcedony and microcrystalline quartz derived from it) suggests that the variation in surface area may be limited.

The ordering of opal-CT appears to take place in the solid state through the rearrangement of Si-O bonds. Such a mechanism is consistent with the observed temperature-dependence of the rate, but the apparent dependence of the rate on the pH of the solution does not at first seem consistent. However, ordering may also involve the migration of hydrogen defects. Their concentration and distribution may be dependent on the pH of the solution from which the initial disordered opal-CT crystallized, thus accounting for the observed pH-dependence of the rate of ordering.

VI. CONCLUSIONS

The reaction of opal-A to opal-CT is poorly defined, and the rate of crystallization of opal-CT from rhyolitic glass is virtually unstudied. The rate of ordering of opal-CT and of the conversion of opal-CT to quartz has been studied. Although reaction time is too great to study the kinetics at near-neutral pH and temperatures $<200^{\circ}\text{C}$, conditions of most interest for Yucca Mountain, reasonable rate laws are available to examine these conditions.

The work of Ernst and Calvert (1969) was done in distilled water and probably represents near-neutral conditions. Although the rate equation may not be strictly correct, it appears to provide a good description of the temperature-dependence of the rate. From the sedimentation rate and the observed thickness of the opal-CT-to-quartz transition zone, Murata et al. (1977) estimated that the conversion took 240 000 to 480 000 yr at Chico Martinez Creek. If we use the rate equation of Ernst and Calvert, these times correspond to conversion temperatures of 73 to 80°C , which is in excellent agreement with the isotopic temperature of 79°C determined by Murata et al. Although the activation energy for the ordering of opal-CT (Kano, 1983) has been determined experimentally, it was consistent with borehole data from a mudstone, shale, and sandstone terrain with temperatures in the 5 to 45°C range. The frequency factor is based on data from the borehole. Kano

reports that the model fits the observed $d(101)$ spacings within $0.007 \text{ \AA}$, which is slightly smaller than the measurement error.

Table II shows the times necessary for ordering opal-CT from $d(101) = 4.122$ to $4.05 \text{ \AA}$. Using the data presented by Kano (1983), we estimate that $d(101) = 4.05 \text{ \AA}$ represents the state of order necessary for quartz crystallization. Opal-CT disappears in drill hole USW G-1 at Yucca Mountain and is replaced by cristobalite/opal-C at a depth of 700 to 800 m (Bish and Chipera, 1986). The temperature at this depth is 36 to 38°C . If we assume that the temperature has been constant for the lifetime of the mountain, the time calculated for the ordering of opal-CT is 9 to $11 \times 10^6 \text{ yr}$, which is in good agreement with the $12 \times 10^6 \text{ yr}$ age of the rocks. The additional time may have been required for initial crystallization of the disordered opal-CT.

TABLE II
TIMES FOR ORDERING OPAL-CT FROM $d(101) = 4.122$ to $4.05 \text{ \AA}$

Temperature <u>($^\circ\text{C}$)</u>	Time <u>(yr)</u>
30	2.1×10^7
40	7.0×10^6
50	4.1×10^4
100	4.1×10^4
150	1.7×10^3
200	1.4×10^2

Table III presents the conversion times necessary for the conversion of opal-CT to quartz as calculated by the equation of Ernst and Calvert (1969). This equation may not be strictly applicable to Yucca Mountain because the pressure used for the experiments was considerably greater than that in the mountain; however, this factor may be partially offset by ordering of opal-CT at the beginning of the experiments. Cristobalite/opal-C disappears from USW G-1 at a depth of 850 to 1100 m (Bish and Chipera, 1986), corresponding to a temperature of 40 to 46°C . At 40°C , ordering of the opal-CT would take $7 \times 10^6 \text{ yr}$ and the conversion of opal-CT to quartz $14 \times 10^6 \text{ yr}$, for a total of $9 \times 10^6 \text{ yr}$ longer than the lifetime of the rocks. However, at 46°C the reaction

TABLE III
REACTION TIME FOR CONVERSION OF OPAL-CT TO QUARTZ

Temperature (°C)	Time (yr)
30	4.8×10^7
40	1.4×10^7
50	4.0×10^6
100	3.6×10^4
150	8.7×10^2
200	4.7×10

times are 4 and 7×10^6 , respectively, for a total of 11×10^6 yr, which compares favorably with the age of the rocks.

The rate equations are consistent with the observations in USW G-1 and suggest that the temperatures may have been nearly constant over the lifetime of the rocks, although there may have been minor temperature elevation in the 800- to 1100-m-depth interval. This is consistent with the observations of Bish and Semarge (1982) that suggest alteration temperatures of $<40^\circ\text{C}$ at depths <1100 m but indicate increased alteration temperatures below that depth.

Table III indicates that in the Topopah Spring Member, where conversion to cristobalite/opal-C is complete, conversion of cristobalite to quartz will probably be minor where the temperature does not rise to $>100^\circ\text{C}$ for more than a few thousand years. However, if temperatures $>150^\circ\text{C}$ are reached, conversion of cristobalite to quartz is likely to be complete if fluid pressures are high enough to maintain liquid water.

The diffusion-controlled model put forth here for the conversion of opal-CT to quartz indicates that aqueous silica activities coexisting with cristobalite and quartz will remain at cristobalite saturation until cristobalite has disappeared. In upper zeolite beds in Yucca Mountain, where significant heating is possible, clinoptilolite and mordenite generally coexist with opal-CT. Although the state of order of the opal-CT is not known, some ordering is probably necessary before conversion of cristobalite to quartz can begin. The time for both the complete conversion to quartz and the possible destabilization of clinoptilolite and mordenite in rocks that reach $<100^\circ\text{C}$ is probably tens of thousands of years.

The conclusions are certainly tentative. They also depend on the pH conditions remaining near neutral. Although we cannot yet quantify the effects of increased pH on the reaction rates, it is obvious that increased pH will accelerate the conversion of opal-CT to quartz.

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