The nucleation and growth of polycrystalline quartz: Pressure effect from 0.05 to 3 GPa

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Abstract: Polycrystalline quartz was formed from amorphous silica in seawater and distilled water at temperatures and pressures ranging from 50 to 450°C and 50 MPa to 3 GPa, respectively. The data at 100 and 200 MPa pressures can be reasonably modeled using Avrami's nucleation and growth equation. Experimental results reveal a dramatic pressure effect on transformation rate, which increases approximately by five orders of magnitude as pressure increases from 50 MPa to 3 GPa at 400°C. The effect is more prominent in a low-pressure regime than in a high-pressure regime; the transition pressure between the high- and low-pressure regimes is temperature-dependent. The pressure can significantly enhance both nucleation and growth rates although the effect is stronger on nucleation than on growth. This finding leads to the successful synthesis of polycrystalline quartz at a temperature as low as 50°C at 3 GPa in a few days, and helps predict its formation at ambient temperature and higher pressures. SEM measurements show that grain sizes decrease significantly with increasing pressure, giving rise to a new method for synthesizing nano-size (< 100 nm) polycrystalline quartz in neutral solutions.

Key-words: polycrystalline quartz, nucleation and growth, silica transformation, cristobalite, coesite.

Introduction

Polycrystalline quartz may occur in a variety of geological settings. It has long been recognized in the form of semiprecious gems as onyx, jasper, chalcedony, and agate precipitated from silica-rich solutions (White & Gorwin, 1961), and as cryptocrystalline quartz or its polymorphic precursors in petrified wood (Stein, 1982). Bedded chert and siliceous shales have been frequently found in sedimentary basins, in particular, those rimming the Pacific Ocean. These basins consist of thick biogenic silica-bearing sediments such as those in the Monterey formation, southern California, (e.g. Mizutani, 1970 and 1977; Murata & Nakata, 1974; Murata & Randall, 1975; Murata et al., 1977; Mitsui & Taguchi, 1977; Pisciotto, 1981; Isaacs, 1982; Bohrmann et al., 1994). The Deep Sea Drilling Project (DSDP) and the Ocean Drilling Project (ODP) have revealed silica-rich sediments presently accumulating in certain deep seas (Scholl & Creager, 1973; Hein et al., 1978; Riech & von Rad, 1979; Kastner, 1982; Tada & Iuima, 1983; Thein & von Rad, 1987; Behl & Smith, 1990; Compton & Locker, 1992). In these siliceous sediments, polycrystalline quartz was formed via a series of transformations from opal-A to opal-CT to polycrystalline quartz (Mizutani, 1970). Polycrystalline quartz also occurs as quartz veins in metamorphic and igneous rocks, which result from the secondary fillings of fissures by hydrothermal fluids. Polycrystalline quartz has been found as inclusions in ultra-high pressure minerals such as garnet and zircon. Some of these quartz inclusions are believed to be derived from the high-pressure SiO$_2$ polymorph, coesite, during exhumation (Wang & Liou, 1991; Mosenfelder & Bohlen, 1997; Zhang & Liou, 1996). Fine-grained polycrystalline quartz is commonly believed to form at a high nucleation rate with relatively slow growth rate (Crerar et al., 1981; Williams et al., 1985). A high nucleation rate may be due to significant silica over-saturation of a solution with respect to quartz. Solutions saturated with amorphous silica or cristobalite in the siliceous sediments favor the high nucleation rate for the formation of polycrystalline cristobalite or quartz because their solubilities are higher than that of quartz (Marshall, 1980; Williams et al., 1985; Azaroual et al., 1997). Since the degree of oversaturation of such solutions with respect to quartz varies with temperature and pressure (Fournier & Potter, 1982; Millero, 1982; Manning, 1994), the nucleation and growth rates of polycrystalline quartz in such solutions are anticipated to vary as a function of temperature and pressure.

Most previous studies on the formation of polycrystalline quartz focused on the bulk transformation rate between silica polymorphs (Carr & Fyfe, 1958; Cambell &...
Fyfe, 1960; Fyfe et al., 1962; Ernst & Blatt, 1964; Mizutani, 1966; Oehler, 1976; Hinman, 1998) while the investigations of nucleation and growth rates of the neofomed silica are scarce (Mackenzie & Gees, 1971; Mosenfelder & Bohlen, 1997). Fyfe & McKay (1962) studied the catalytic effect of the hydroxyl ion on the crystallization rate of quartz from amorphous silica. Ernst & Calvert (1969) experimentally studied the kinetics for the polycrystallite to quartz formation using distilled water at 200 MPa pressure. Their data were later fitted into Avrami’s nucleation and growth model by Stein & Kirkpatrick (1976). Most of these studies, however, focus on the effect of temperature (Ernst & Calvert, 1969) and solution chemistry (Cambell & Fyfe, 1960; Fyfe & McKay, 1962; Hinman, 1998). The effect of temperature and the degree of over-saturation on the nucleation and growth of single quartz crystals have been studied for industrial synthesis of quartz crystals (e.g., Lias et al., 1973; Laudise & Kolb, 1982). The effect of pressure has also been widely recognized; studies of the synthesis of single quartz crystals have shown that the percentage of increase in the filling of autoclave (i.e., increase of pressures) can significantly increase the crystal growth rate (e.g., Laudise, 1959 and 1987; Hosaka & Taki, 1989a and b). However, there have only a few studies of the effect of pressure on the formation kinetics of polycrystalline quartz (Mitsuyuk, 1974; Mosenfelder & Bohlen, 1997). The present study provides new data for estimating the effect of pressure on the transformation from amorphous silica to quartz over a wide range of pressure from 50 MPa to 3.0 GPa, and for quantifying the pressure effect on nucleation and growth rates of polycrystalline quartz in the pressure range of 100 to 200 MPa.

### Experimental procedures

The starting material used in the experiments is a natural diatomite (opal-A) from the Monterey formation, California. The sample was purified using dilute HCl solution to remove trace amounts of carbonates. The amorphous nature of the sample was confirmed by X-ray
diffraction (XRD). The experimental solution used was mainly seawater with some exceptions where distilled water and KCl solutions were used (Table 1).

Experiments at pressures of 200 MPa and below were performed in standard size (1” O.D. and 0.25” I. D.) cold-sealed pressure vessels (Tuttle, 1949). The starting sample powder (10 to 20 mg, < 40 µm grain size) with seawater at fluid/solid mass ratio of 1:1 was electric arc-sealed in a gold capsule (20 mm length, 3 mm diameter, and 0.25 mm wall thickness). The capsule was then loaded into the cold-sealed pressure vessel and pressurized using argon gas. A ceramic filler rod was introduced to reduce the temperature gradient within the capsules. The temperature gradient was less than 2°C/cm. Temperature measurements were accurate to ± 5°C. The sample was heated to the desired temperature using a heating rate at ~ 10°C/min while the pressure was maintained at a constant level. The heating time (30-40 min.) required to reach experimental temperatures is relatively short compared to the run time (in days) and is therefore neglected when calculating the rate of silica transformation. Experiments were conducted isothermally at 400°C, and 450°C and at a constant pressure of 50, 100, 150, and 200 MPa up to 304 days (Table 1).

High pressure experiments were performed using a piston-cylinder apparatus, similar to that described by Boyd & England (1960), using a half-inch diameter pressure vessel. The starting sample powder (4 to 6 mg, < 40 µm grain size) with seawater at fluid/solid mass ratio of 1:1 was electric arc-sealed in a gold capsule (4 mm length, 2 mm O.D., and 0.127 mm wall thickness). The apparatus was calibrated for pressure and temperature as described by Huang (1979). Temperatures measured with chromel-alumel thermocouples were precise to ± 3°C and are considered accurate to ± 10°C. The furnace assemblies were constructed from graphite, talc and pyrophyllite. All runs were brought to a final pressure with the "piston-out".

Pressures (listed in Table 1) are nominal, and are considered accurate to ± 5 percent.

Quantification of the reaction progress was made by X-ray diffraction (XRD). Our experimental results show that the amorphous silica transforms to quartz via an intermediate phase, cristobalite, at 200 MPa. The extent of amorphous silica to quartz transformation (ζ), which is represented by the volume fraction of quartz, was approximately determined by measuring the weight fraction of quartz relative to cristobalite in the run products. The approximation is reasonable because our results and other previous experimental data (e.g. Kano & Taguchi, 1982) show that the rate of amorphous silica to cristobalite transformation is much faster than that of the cristobalite to quartz transformation. The weight fraction of quartz was measured using the relative peak height of quartz (d_{101}) and cristobalite (d_{101}) against a calibration curve. The calibration curve was prepared by mixing quartz and cristobalite powders synthesized at conditions similar to those for the transformation experiments in the present study. Five mixtures with different cristobalite/quartz ratios ranging from 9, 3, 1, 0.33, and 0.11 were prepared for the calibration curve. The uncertainty was estimated from three repeated X-ray scans for two sample mounts. The weight fraction of quartz is considered accurate to ± 5 wt.%. Our calibration curve is in good agreement with that reported by Ernst & Calvert (1969). The experimental results at 300 MPa and above show that amorphous silica transformed directly to quartz without the intermediate cristobalite phase. The weight fraction of quartz in the run products at pressures higher than 300 MPa was approximately determined by measuring quartz fraction relative to an external standard using XRD method. A calibration curve was prepared from five opal + quartz + calcite mixtures. Each mixture contains 50 wt.% calcite and 50 wt.% opal + quartz; the opal/quartz ratio in the five mixtures varies from 8.5, 3, 1, 0.33, and 0.13. The calibration curve was obtained from these five mixtures by linear regression of the weight fractions of quartz relative to XRD peak-intensity ratios of quartz (d_{101}) and calcite (d_{104}). Each run product was mixed with 50 wt.% calcite and scanned under the same condition as that for preparing the calibration curve. The quartz fraction relative to the amorphous silica in the run product was determined using the calibration curve and is considered accurate to ± 10 percent.

Results and discussion

Characteristics of neoformed polycrystalline quartz

The neoformed cristobalite appears as lepispheres similar to that observed in natural opal-CT samples under SEM (Oehler, 1975; Radan et al., 1992). Each individual grain appears as a sub-rounded to rounded crystal with an average grain size of around 0.2 µm. In contrast, the morphology of quartz crystals varies with temperature, pressure and time. In general, quartz crystals grew as doubly terminated, euhedral to subhedral prisms with an aspect ratio ranging from 1.3 to 3.3 as seen in most run products. The morphology of quartz crystals grown in our experiments at 200 MPa is significantly different from that reported by Stein & Kirkpatrick (1976) who re-examined the run products of Ernst & Calvert (1969) using SEM. They found that most quartz crystals grew with needle-like shape and that significant amounts of doubly terminated hexagonal quartz prisms appeared only in run products containing nearly 100 % of quartz. In contrast, our experiments did not yield the needle-like quartz crystals except in the run product at 400°C and 3 GPa with a run duration of 48 hours. Different experimental conditions, including the nature of the starting material, water/rock ratio and solution chemistry, may account for the difference in the morphology of quartz. Polycrystalline quartz synthesized at high pressures (> 500 MPa) shows a variety of morphologies: those grown at low temperatures (< 250°C) are mostly anhedral, whereas those grown at higher temperatures appear as short subhedral to euhedral, doubly terminated hexagonal prisms. The crystals become more euhedral with increasing run time. The average particle size of quartz in the run products varies significantly with temperature and pressure. In general, quartz grown at higher temperature and for longer time shows larger crys-
tals and better crystal shapes. The effect of pressure is more complicated. The average grain size of quartz when the transformation from amorphous silica to quartz is nearly complete is significantly smaller for pressure above 300 MPa (ranging from 0.08 to 0.5 µm grain diameter) than for lower pressure (ranging from 0.5 to 1.2 µm).

Transformation rate

The experiments were first conducted in distilled water at 400°C and 200 MPa to reproduce the experimental conditions similar to those reported by Ernst & Calvert (1969). Our subsequent experiments under the same conditions using seawater instead of distilled water show no significant difference in transformation rates within the experimental uncertainty. The experiments also confirm that the amorphous silica transforms to quartz via an intermediate phase, cristobalite, at pressures of 200 MPa or below. The formation rate of cristobalite from amorphous silica is much faster than that of cristobalite to quartz transformation. At a pressure of 300 MPa or higher, amorphous silica transforms directly into quartz without the intermediate phase (Mitsuk, 1974; Oehler, 1976). The disappearance of the intermediate cristobalite may imply that the solubility of quartz is higher than that of cristobalite at high pressures. Therefore, quartz instead of cristobalite may nucleate from a solution saturated with amorphous silica (Williams et al., 1985).

The extent of transformation (z) as a function of time (t) at 400°C and 450°C for four isobaric experiments at 50, 100, 150 and 200 MPa was plotted in Fig. 1 and 2. At 400°C and 200 MPa, the data are reasonably consistent with those determined under the same P-T condition as that used by Ernst & Calvert (1969) in spite of different starting silicas, solutions and fluid/rock ratios used. In contrast to Ernst & Calvert (1969), this study uses amorphous silica and seawater instead of cristobalite and distilled water. The crystallization of cristobalite from opal-A, which occurs in a relatively shorter time under the experimental conditions (Kano & Taguchi, 1982), has little effect on the overall transformation rate obtained. Thus, the reaction rate measured in this study may approximately represent the transformation rate of cristobalite to quartz. The present study reveals two major observations that have not been reported in the work of Ernst & Calvert (1969), the effect of pressure and the non-linear relationship of the transformation curve. Our results show a dramatic decrease in transformation rates with decreasing pressures; it is about two orders of magnitude lower at 50 MPa than at 200 MPa. The present study also reveals a significant sigmoidal transformation curvature on the z-t diagram (Fig. 1 and 2), indicating a progressive increase in transformation rate with time and a subsequent decrease in rate near complete transformation. Ernst & Calvert (1969) modeled the kinetics of the transformation assuming a zero-order transformation relationship, whereas Stein & Kirkpatrick (1976) re-fitted the same data using a sigmoidal curve, which was interpreted as indicative of nucleation/growth kinetics with mutual impinging among quartz crystals during growth. Our results confirm the sigmoidal curvature of the transformation rate at 200 MPa, but show that the
initial curvature is more prominent at lower pressures. The significant decrease in the rate near the completion of transformation observed in Stein & Kirkpatrick (1976) indicates impinging growth of quartz crystals. The impinging effect is less pronounced in the present study than in the experiments of Ernst & Calvert (1969). The higher fluid/rock ratio (1:1) used in this study than that (0.3:1) used in Ernst & Calvert (1969) may account for the different degrees of impinging; the higher the water/rock ratio, the higher the porosity and the greater the space for crystal growth will be.

**Nucleation and growth rates**

The growth rate of quartz crystals was calculated from the runs at 400°C and 200 MPa with different run time by measuring the length of the longest crystals and assuming that they nucleated first (Mosenfelder & Bohlen, 1997). The maximum crystal length was represented by the average of the 10% longest grains measured by SEM. The results show a linear relationship between maximum grain length and run time during the transformation (Fig. 3). The slope of the line represents a constant growth rate of $2.3 \times 10^{-12}$ m/sec. The growth rate decreases significantly when the transformation of cristobalite to quartz is complete. A continuous but slight increase in grain size may be attributed to the Ostwald ripening process (Crerar et al., 1981; Williams et al., 1985). Additional data show that the growth rates measured at 300°C/200 MPa and 450°C/200 MPa are $6.5 \times 10^{-14}$ and $4.5 \times 10^{-12}$ m/sec, respectively. The growth rates of polycrystalline quartz measured from this study have been compared with those previously reported (Fig. 4). Mosenfelder & Bohlen (1997) reported the growth rates of polycrystalline quartz converted from coesite under dry conditions by measuring the maximum length of quartz crystals from run products at temperatures and pressures ranging from 700 to 1000°C and from 2.48 to 2.81 GPa. The extrapolation of the growth rates to lower temperatures at 200 MPa using the Turnbull equation for interface-controlled growth (Turnbull, 1956) and the activation energy determined by Mosenfelder & Bohlen (1997) show that the rates are significantly slower than those measured in this study and their difference decreases with increasing temperatures. The dramatic enhancement of the growth rate of polycrystalline quartz by about six orders of magnitude at 300°C and 200 MPa (Fig. 4) is mainly attributed either to the catalysis of water or to the difference in the type of reactions, coesite to quartz vs. cristobalite (or amorphous silica) to quartz. The type of reactions may be significant if the dissolution or decomposition rate of the reactant (original silica) is the rate-limiting step. The growth rates of quartz determined under hydrothermal conditions in this study, however, are about three orders of magnitude lower than those for growing single crystals in NaCl and KCl solutions under controlled temperature gradients (25°C) in the temperatures ranging from 380 to 480°C and pressures ranging from 100 to 200 MPa (Hosaka & Taki, 1989a and b). It appears that the maintenance of the temperature gradient or silica concentration in solutions drastically suppresses nucleation but enhances growth rates. The dramatic variation of growth rates of quartz found in the present and previous studies suggests that quartz may also grow at a variety of rates in different geological settings.

**Effect of pressure**

The experiments for studying the effect of pressure on the transformation rate have been extended up to 3 GPa at selected temperatures ranging from 50 to 450°C. The experimental data show that the effect of pressure on the future.
transformation is extremely prominent (Fig. 5). For instance, at 3 GPa and 100°C, it takes only 1 day to transform about 35% of amorphous silica to quartz while it may take, according to a simple extrapolation, as long as 300 years at 50 MPa. The effect of pressure is also obvious in Fig. 6, which shows the logarithm of time for 50% transformation (half-life, \( t_{1/2} \)) as a function of pressure and temperature. The estimates of the half-life from the experimental data at 300 MPa and above are only approximations owing to insufficient data obtained at high pressures. As seen in the data at 400 and 450°C, the pressure effect is much more prominent below 0.3 GPa (300 MPa) than at higher pressures. For instance, at 400°C, the half-life \( t_{1/2} \) is more than two orders of magnitude shorter when the pressure increases from 0.05 to 0.3 GPa, but it is less than one order of magnitude shorter when it rises from 1.0 to 2.5 GPa. The transition pressure between the high- and low-pressure regimes depends on temperature; it is around 300 MPa at 400°C. The cause of this transition is not clear and can probably be attributed to the types of reactions: cristobalite to quartz in the low-pressure regime and amorphous silica directly to quartz in the high-pressure regime.

Experiments show that coesite has not been detected by XRD in the run products even in its stability field in the temperature range of this study. The quartz was metastably formed in the coesite stability field at temperatures below 400°C. Motivated by the observed pressure enhancement of transformation rate, we attempted to synthesize polycrystalline quartz (5%) at temperatures as low as 50°C at 3 GPa in a few days. According to the prediction, significant amounts of metastable quartz or coesite may be synthesized from amorphous silica at ambient temperature within days by applying pressures close to 5 GPa. Coesite instead of metastable quartz may appear in the run products if the pressure oversteps relative to the quartz-coesite equilibrium curve exceed a certain value. Extrapolation of the data suggests that the complete conversion of amorphous silica to metastable quartz or coesite at ambient temperature may be achieved within days at pressure about 80 GPa or above.

Kinetic analysis

The sigmoidal shape of the \( \zeta \) vs. \( t \) curves for cristobalite to quartz transformation is similar to those for previously determined polymorphic transformations, including the transformation of Ni<sub>2</sub>SiO<sub>4</sub> olivine to spinel (Rubie et al., 1990), calcite to aragonite (Liu & Yund, 1993), and coesite to quartz (Mosenfelder & Bohlen, 1997). The shape of the sigmoidal curves has been interpreted by the combined effects of the relative rates of nucleation and growth, and traditionally modeled using the Avrami equation (Cahn, 1956; Christian, 1975; Stein & Kirkpatrick, 1976; Rubie & Thompson, 1985; Rubie et al., 1990):

\[
\zeta = 1 - \exp (-kt^n)
\]  

or

\[
\ln [\ln (1/(1-\zeta))] = n \ln t + \ln k
\]

where \( \zeta \) is the volume fraction of quartz transformed from cristobalite, \( t \) is time, \( \ln \) is the natural logarithm, and \( k \) and \( n \) are the rate parameters. Different mechanisms of nucleation and growth lead to different specifications for \( \zeta \) as a function of time. The rate parameter \( k \) pertains to the relative rates of nucleation and growth (Rubie & Thompson, 1985). The \( n \)-value, in principle, indicates the dominant nucleation sites (Cahn, 1965; Rubie & Thompson, 1985) or the growth dimensions of neoformed crystals (Avrami, 1939; Rubie & Thompson, 1985). The former interpretation is more applicable if nucleation occurs mainly on grain boundary (Cahn, 1956; Rubie et al., 1990). The \( n \)-value, which varies with the nucleation and growth rates of the transformation, is theoretically predicted to range between 1 and 4. When the nucleation rate is slow, which commonly occurs during the early stage of transformation, the trans-
formation rate can be assumed constant and the extent of transformation ($\zeta$) can be described as:

$$\zeta = 1 - \exp\left(-\frac{N \cdot x t^4}{3}ight)$$  \hspace{1cm} (2)

where $N$ is the nucleation rate on grain boundary, $x$ is the growth rate of product phase and $t$ is the reaction time. In this case, $n$ equals 4 and the extent of transformation depends on both growth and nucleation rates. In contrast, when nucleation occurs very rapidly, it can be assumed to occur instantaneously and eqn (2) can be simplified as:

$$\zeta = 1 - \exp\left(-2Sx t\right)$$  \hspace{1cm} (3)

where $S$ is the grain boundary area per unit volume. In this case, the $n$-value is 1 and $\zeta$ is dependent on the growth rate but independent of the nucleation rate. The $n$-values can be between the two limits of 1 and 4.

The alternative interpretation of $n$ values originally proposed by Avrami (1939) predicts that the nucleation and three-dimensional growth of the crystal are the major transformation process if $n = 4$, whereas three-dimensional (sphere), two-dimensional (plate) and one-dimensional (needle) growths are expected if $n = 3, 2,$ and 1, respectively. Stein & Kirkpatrick (1976) reported a consistent correlation between the $n$-values and the observed morphology for quartz grown from portlandite. In practice, such interpretation is quite unreliable because in most cases the values of $k$ and $n$ may vary during the transformation (Rubie & Thompson, 1985; Carlson, 1983; Rubie et al., 1990).

As a first approximation, we assume constant values of $k$ and $n$ at constant temperature and pressure when modeling our experimental data. The $n$-values determined from the data at 400°C appear to decrease from 3 at 150 and 200 MPa to 1.8 at 100 MPa, and 1 at 50 MPa (Fig. 7). The $n$-values (3.0–3.4) close to 4 suggest slow and constant nucleation rates at 150 and 200 MPa, whereas the lower $n$-values close to 1 indicate rapid and instantaneous nucleation rates at 100 and 50 MPa (Rubie et al., 1990). Alternatively, the calculated $n$-values predict the three-dimensional growth of crystal at 150 and 200 MPa, and two- and one-dimensional growth of quartz crystals at lower pressures. This morphological prediction is partially consistent with our observations by SEM. Our data also show that the values of $n$ and $k$ are slightly deviated from being constant during the transformation at constant temperature and pressure (Fig. 7). The variation in $n$-values as a function of reaction conditions and time during polymeric transformation has been reported (Rubie et al., 1990; Carlson, 1983). This study confirms the previous observations. The application of the model for the interpretation of experimentally determined $n$-values, therefore, should be made with caution (Kunzler & Goodell, 1970; Madon & Gillet, 1984). The pitfalls of using the $n$-values to unveil the reaction mechanism have been discussed in Rubie & Thompson (1985, p. 46).
In addition, we used the procedure commonly used in the studies of the polymorphic transformations of polycrystalline aggregates to estimate the average nucleation and growth rates. The experimentally determined $\zeta$-$t$ data have been fitted to a nucleation and growth kinetic model originally developed by Avrami and later modified by Cahn (1956). The model has been successfully applied to experimentally measured kinetic data for several polycrystalline, polymorphic transformations, such as the $\text{Ni}_2\text{SiO}_4$-olivine to spinel (Rubie et al., 1990), the aragonite to calcite (Liu & Yund, 1993), and coesite to quartz transformation (Mosenfelder & Bohlen, 1997). We have followed this procedure and used the computer program provided by Rubie & Mosenfelder to extract the nucleation and growth rates from the bulk transformation ratio. This technique used the grain diameter of the starting phase, constant nucleation rate ($\bar{N}$) and growth rate ($\dot{x}$) as fitting parameters to minimize a chi-square function using a weighted non-linear least squares procedure. The optimized nucleation and growth rates ($\bar{N}$ and $\dot{x}$) were considered as the most likely nucleation and growth rates of the transformation at the experimental conditions. The detailed description of the model was presented by Cahn (1956) whereas the details of the non-linear regression procedure were described by Rubie et al. (1990).

The calculated $\dot{x}$ values, however, are significantly different from the experimental measured growth rate (Table 2). The discrepancy may be partially attributed to the large uncertainty in the data and insufficient data points for modeling. The sensitivity study of this model reveals that the technique can accurately predict both nucleation and growth rates only if the number of experimental data points is high. In order to minimize the uncertainty, the experimentally determined growth rates were taken into account during the modeling. Instead of treating both $\bar{N}$ and $\dot{x}$ as variables, $\dot{x}$ was kept constant at each measured value while $\bar{N}$ was fitted for this growth rate to minimize a chi-square function; the chi-square functions thus obtained are

Table 2. Data showing measured growth rates and modeled nucleation rates.

* Nucleation rates (in $1/m^2\cdot$sec) for the corresponding growth rate (in m/sec) were calculated using Cahn’s equation.
** Minimum Chi-square if both growth and nucleation rates are simultaneously fitted during modeling.

![Diagram](image1.png)

Fig. 8. Modeling experimental data using Cahn’s equation. Symbols are the data points at 400°C: squares = 200 MPa; open diamonds = 150 MPa, and solid diamonds = 100 MPa. The solid curves are the modeling results using Cahn’s equation (see text for details).

![Diagram](image2.png)

Fig. 9. Plot of the effect of pressure on the growth and nucleation rates of polycrystalline quartz (Data shown in Table 2).
very close to the minimum values fitted by both variables (Fig. 8 and Table 2).

Figure 8 shows a reasonable agreement between the modeling ($\xi$-t) curve and the experimental data. The model enables us to estimate the nucleation rate for each corresponding measured growth rate. The results indicate that pressure can significantly enhance both the nucleation and growth rates although the effect is stronger on nucleation than on growth (Fig. 9 and Table 2). This has been confirmed by the SEM observations, which show that the grain size decreases significantly with increasing pressures (Fig. 10). The slower transformation rates at lower pressures require much higher temperatures or longer time for complete transformation and, therefore, the grains continue to grow to a larger size and have a euhedral shape. In contrast, the faster transformation rates at higher pressures lead to the synthesis of smaller quartz grains with poor crystal shapes because of the shorter time needed for the complete transformation. At high pressures, this leads to the synthesis of nano-sized polycrystalline quartz (< 80 nm) (Fig. 10; Huang, 2002).

**Conclusions**

This study represents one of the first systematic studies on the effect of pressure on the transformation rate of amorphous silica to polycrystalline quartz under hydrothermal conditions. The observed dramatic enhancement of the nucleation and growth rates, thus the transformation rate, with pressure has important geological implications. Ignoring this pressure effect, as has been done in previous studies, may lead to large uncertainties in estimating the depths and temperatures (or timing) at which the silica transformation occurs in siliceous sediments or other geological settings. The recognition of the pressure effect, on the other hand, enables us to transform amorphous silica to polycrystalline quartz at conditions close to ambient temperatures by solely increasing pressure in the laboratory. The results show that pressure can significantly enhance both the nucleation and growth rates and its effect is stronger on nucleation than on growth. This has led to a new method for synthesizing nano-sized (< 80 nm) polycrystalline quartz in neutral solutions.
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