Pressure–induced crystallization of biogenic hydrous amorphous silica

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Samples of the diatom Nitzschia cf. frustulum, collected from Lake Yogo, Siga Prefecture, Japan, were cultured in the laboratory. Organic components of the diatom cell were removed by washing with acetone and sodium hypochlorite. The remaining frustules were studied by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDX), Fourier-transform infrared (FTIR) spectroscopy, and synchrotron X-ray diffraction. The results showed that the spindle-shaped diatom frustule was composed of hydrous amorphous silica. Pressure-induced phase transformation of the diatom frustule was investigated by in situ Raman spectroscopic analysis. With exposure to 0.3 GPa at 100 °C, the Raman band corresponding to quartz occurred at $\nu = 465$ cm$^{-1}$. In addition, a characteristic Raman band for moganite was observed at 501 cm$^{-1}$. From the integral ratio of Raman bands, the moganite content in the probed area was estimated to be approximately 50 wt%. With increased pressure and temperature, the initial morphology of diatom frustules was totally changed to a characteristic spherical particle with a diameter of about 2 µm. Increasing pressure to 5.7 GPa at 100 °C resulted in the appearance of a Raman band assignable to coesite at 538 cm$^{-1}$. That is, with compression and heating, hydrous amorphous silica can be readily crystallized into quartz, moganite, and coesite. First-principles calculations revealed that a disiloxane molecule with a trans configuration is twisted 60° with a close approach of a water molecule, which leads to a trans to cis configuration change. It is therefore reasonable to assume that during crystallization of hydrous amorphous silica, an Si–O–Si bridging unit with the cis configuration would survive as a structural defect, and could subsequently crystallize into moganite by maintaining that geometry. This hypothesis is adaptable to the phase transformation from hydrous amorphous silica to coesite as well, because coesite has four-membered rings and is easily formed from hydrous amorphous silica under high pressure and temperature conditions.

Keywords: Diatom, Biogenic silica, Hydrous amorphous silica, Moganite, Raman spectroscopy

INTRODUCTION

The physical and chemical properties of amorphous silica hold great importance for geological research (Eggimann, et al., 1980; Konhauser and Ferris, 1996; Jones et al., 1997; Icenhower and Dove, 2000; Milliken et al., 2008; Kirkpatrick et al., 2013) and technological and industrial applications (Liz-Marzan et al., 1996; Lu et al., 2002; Zou et al., 2008; Wang, 2009). Table 1 shows the classification of amorphous silica, which can be generally classified by its thermodynamic property into glass and polymer. Amorphous silica that exhibits a glass transition is regarded as a silica glass. Silica glass has become a material of great interest in geophysics (McMillan et al., 1994; Blundy and Cashman, 2001; Wolff-Boenisch et al., 2004; Galan et al., 2013), and its high-pressure behavior has been also intensely studied from the viewpoint of condensed-matter physics. Today, it is recognized that silica glass never crystallizes with compression below at least 100 GPa, although the coordination of Si increases from four-fold to six-fold (Meade et al., 1992; Sato and Funamori, 2008; Benmore et al., 2010; Sato and Funamori, 2010; Salmon and Zeidler, 2015). Naturally occurring amorphous biogenic silica, called diatomite, is primarily composed of fossilized diatom skeletons identified.
as hydrous amorphous silica (Asada et al., 2005; Khraisheh et al., 2005). In contrast to silica glass, diatomite gradually crystalizes to quartz through opal–CT (disordered stacking sequence of cristobalite and tridymite) during diagenesis (Isaacs, 1982; Williams and Crerar, 1985; Williams et al., 1985). From the systematic study of the pressure effect on phase transformations (Huang, 2003), it became apparent that pressure significantly enhances transformation rate; at 0.2 GPa and 400 °C it takes one week to transform 40 wt% of diatomite to quartz, whereas at 3 GPa and 100 °C, it takes only one day to transform 42 wt% of diatomite to quartz. Raw diatomites contain a large amount of organic matter and inorganic impurities. In order to investigate the phase transformation of biogenic hydrous amorphous silica, purified diatom frustules must be employed.

In this study, we isolated and cultured a single diatom species, *Nitzschia cf. frustulum*, in the laboratory. Pure diatom frustules were studied by scanning electron microscopy coupled with energy dispersive X–ray spectroscopy (SEM–EDX), Fourier–transform infrared (FTIR) spectroscopy, and synchrotron X–ray diffraction. Diatom frustules under compression were investigated using in situ Raman spectroscopy. Moganite, a distinctive polymorph of silica, is known to be widely distributed over microcrystalline quartz varieties such as chalcedonies, agates, cherts, and flints (Heaney and Post, 1992). However, the conventional X–ray powder diffraction method is limited in the ability to discern characteristic moganite diffraction peaks because they overlap the intense quartz peaks (Rodgers and Cressey, 2001). In addition, there is very little experimental data concerning the formation of moganite. An important advantage of Raman analysis, compared with the X–ray diffraction method, is the considerably smaller amount of sample that can be detected. This technical advantage is especially suitable for investigating content and spatial distribution of moganite. The first–principles and thermodynamic equilibrium calculations were furthermore performed to aid the interpretation of moganite formation and its phase transformation from hydrous amorphous silica.

Here, we report the recrystallization of diatom frustules into quartz, moganite, and coesite, through pressure and temperature treatment. In addition, we propose a possible mechanism which can explain the formation of moganite and coesite from hydrous amorphous silica.

### EXPERIMENTAL METHODS

#### Collection and cultivation processes of diatoms

Diatom samples were collected from biofilms growing on rocks in the littoral zone of Lake Yogo, Siga Prefecture, Japan. Samples were cultured using 0.5% agar plates with d medium (Andersen, 2005) at room temperature under red and green LED lights, without shaking or aeration. After multiplying moderately, each diatom colony was carefully transferred into separate Petri dishes and multiplied under the same conditions. One of the most successfully cultured strains was identified as *Nitzschia cf. frustulum* by light microscopy and molecular work. Large–scale culture of this strain was done using a tissue culture flask (Orange Scientific, Braine–l’Alleud, Belgium) with 400 ml d medium and silica gel (Gelculture, Fuji Silysia Chemical Ltd.) using the same conditions of isolation.

#### Sample treatment

The diatom multiplied in the Petri dish was filtered through a membrane filter. Because the d medium included chlorides, salts were carefully removed by centrifugal separation. Furthermore, organic matter films covering the diatom frustule were removed by washing with acetone and sodium hypochlorite. After the cleaning treatment, diatom frustules were dried at 50 °C in a drying oven (ANS–111S, Isuzu Seisakusho Co., Ltd.) for three days, with temperature control within ±1 °C. After drying, the specimen was mounted on a brass specimen holder and

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**Table 1. Classification of amorphous silica by thermodynamic characteristic and its origin**

| Sample preparation method                                      | Reference |
|---------------------------------------------------------------|-----------|
| Glass                                                         | (1)       |
| Silica glass (fused quartz)                                   |           |
| High pressure and high temperature synthesis with piston-cylinder apparatus | (2)       |
| Hydrous silica glass                                          |           |
| Fumed silica (pyrogenic silica)                               | (3), (4)  |
| Hydrous amorphous silica                                      |           |
| Polymer                                                       |           |
| Polymer                                                       |           |
| Cultivation                                                   | This study|
| Colloidal silica                                              |           |
| Hydrolysis and condensation reaction of tetraethoxysilane     |           |

* (1) Beall (1994), (2) Newton and Manning (2008), (3) Pratsinis (1998), (4) Uchino et al. (2004), (5) Stöber et al. (1968).
given a surficial coating of Pt–Pd. Morphologic and chemical analysis were investigated by scanning electron microscope (SEM) techniques. Morphologic observation was performed using SEM (JSM–6330F, JEOL Ltd.), operated in high vacuum mode with an accelerating voltage of 5.0 kV. The SEM observation revealed that the characteristic spindle-shaped body of the diatom frustule was almost maintained during the cleaning treatment (Fig. 1). Chemical analysis was carried out by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX; JSM–6010LA, JEOL Ltd.) with an accelerating voltage of 20.0 kV. The result showed that diatom frustules used in this study were composed of >98.0 wt% SiO2 with trace elements of 0.4 wt% Na2O, 0.4 wt% SO3, and 0.3 wt% P2O5, which were included in the d medium.

**FTIR spectroscopic measurements**

Fourier-transform infrared (FTIR) spectra were acquired by an FTIR spectrometer (FT/IR–300, Jasco Co., Ltd.) equipped with a TGS detector in the 400–4000 cm–1 wavenumber range. The instrument was employed for transmission measurements using KBr pellets. The hygroscopic nature of KBr was minimized by drying in an electric oven (DRM320DA, ADVANTEC Co., Ltd.) at 100 °C. Powdered diatom frustule was diluted in KBr with approximate ratios of 3:100 and pressed into a KBr pellet. As a comparison with biogenic hydrous amorphous silica, colloidal silica (Wako Pure Chemical Industries Ltd., purity ≥99%) was also analyzed. A total of 300 scans were averaged with a resolution of 4 cm–1. Spectra were smoothed with the Jasco software but not baseline-corrected.

**Synchrotron X-ray diffraction measurements**

Synchrotron X-ray diffraction analysis was performed at BL–8B, Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Japan. An incident X-ray beam was monochromatized using a Si (111) double-crystal monochromator to a wavelength of 0.62037(1) Å, which was calibrated with a CeO2 powder diffraction pattern. The monochromatic beam was doubly focused using a cylindrical Rh-coated bent-focusing mirror. Focal spot size was approximately 0.5 mm horizontal by 0.3 mm vertical. Finally, the X-ray beam was collimated by two pin-holes of diameter 0.1 mm. Data were recorded on a large Debye–Scherrer camera with radius of 191.3 mm equipped with a curved imaging plate (IP) detector at angles of up to 2θ = 145° (R–AXIS RAPID, Rigaku Corp.). Powdered diatom frustule was introduced into a 0.5 mm Lindemann glass capillary and placed on the diffractometer axis. Colloidal silica (Wako Pure Chemical Industries Ltd., purity ≥99%) was also measured to compare the biogenic silica with synthetic hydrous amorphous silica. X-ray diffraction measurements were performed under room temperature and atmospheric pressure. The X-ray exposure time for each sample was 60 min. The glass capillary was rotated continuously about the φ-axis through 10° during exposure. Two-dimensional diffraction images were integrated as a function of 2θ using a Rigaku software (DISPLAY, Rigaku Corp.). Least-squares fitting was performed with the diffraction maxima around 2θ = 9°, using the asymmetric double Gaussian function after baseline subtraction.

**High pressure and high temperature Raman spectroscopy and SEM observation**

The schematic flow chart of this experiment is shown in Figure 2. The high pressure and high temperature experiments were conducted using a diamond anvil cell (DAC). First, the diatom frustule powder was loaded into a steel gasket hole (sample reaction chamber) of 100 μm diameter with a 16:3:1 fluid mixture of methanol–ethanol–water. The cullet size of the diamond anvil was 300 μm in diameter. A few grains of small ruby chips were also loaded into the sample reaction chamber.

Next, the DAC was set in the electric drying oven mentioned above (DRM320DA, ADVANTEC Co., Ltd.). The temperature can be controlled at 100 ± 1 °C. We applied the same temperature used in a previous study (Arasuna et al., 2014). After seven days, the DAC was removed from the drying oven and then heated with an external nichrome wire heater controlled at 100 ± 2 °C. A thermocouple was also adhered to the edge of the dia-
mond anvil.

Subsequently, in situ high pressure and high temperature Raman spectroscopic study was carried out with the micro-Raman spectrometer (Mars Stabulite 2017, Photon Design Corp.). The $\lambda = 514.5$ nm line of an Ar$^+$ laser was used to excite Raman scattering. The laser beam was focused on the sample on a 10 $\mu$m spot through a microscope objective (20×). Back-scattered Raman signal was collected by the detector with confocal setting. Spectral calibration of each measured spectrum was performed using a Si plate. Raman spectra were accumulated for 300 s. Pressure was determined by the ruby fluorescence method (Dewaele et al., 2008). The least-squares Peakfitting software PeakFit (AISN Software Inc., Chicago) was used to analyze the Raman bands at $\nu = 465$ and 501 cm$^{-1}$. The baseline was fitted to an exponential function and subtracted from the sample spectra before spectral deconvolution. Integral strengths were determined by fitting the peaks with a Lorentzian-shape function.

After the in situ high pressure and high temperature Raman spectroscopic measurements, the specimens were removed from the DAC. Morphological changes of diatom frustule were then studied by SEM (JSM–6330F, JEOL Ltd.) using the same method as described in the sample treatment section above.

Thermodynamic equilibrium calculation

Thermodynamic equilibrium and solubility calculations were conducted using the program Geochemist’s Workbench (GWB) 9.0 (Bethke and Yeakel, 2009) to assess the dissolution and precipitation reactions that occur between solid silica and dissolved silica. A program, ACT2, one of the software components of GWB, was used for constructing solubility diagrams. We calculated the saturation states of silica polymorphs including quartz, chalcedony, and amorphous silica, in a solution at different temperature and pressure. As far as we know, there are no published thermodynamic data for moganite. However, those of chalcedony are available (Helgeson et al., 1978) because chalcedony is a microcrystalline silica composed of very fine intergrowths of quartz and moganite (Heaney and Post, 1992). The values calculated in the study represent the average of the two polymorphs in chalcedony. Although the averages do not accurately reflect the thermodynamic solubility of moganite, it might be possible to estimate the effect of moganite on SiO$_2$ solubility. Consequently, data for chalcedony was applied in the thermodynamic calculations.

First-principles calculations

Molecular geometry optimizations were performed using the quantum chemical calculation software package Gaussian-09 (Frisch et al., 2009), with the second-order Møller–Plesset (MP2) perturbation theory with 6–311G+(d,p) basis set. A disiloxane molecule ($\text{Si}_2\text{O}_7\text{H}_6$, dimer structure) has been extensively applied in theoretical investigations of crystalline and amorphous silicates (e.g., Xiao and Lasaga, 1994; Al Derzi et al., 2008; Morrow et al., 2009; Noritake and Kawamura, 2015; Mitani and Kyono, 2017). We assumed the disiloxane molecule to be the simplest interior structural unit of the amorphous silica in this study.

RESULTS

Figure 3 displays FTIR spectra collected from the frustule of diatom, *Nitzschia cf. frustulum* and colloidal silica. Several intense bands at 468, 803, and 1095 cm$^{-1}$ can be observed in the spectrum of the diatom frustule. A small band at 1629 cm$^{-1}$ and one broad band around 3400 cm$^{-1}$ are also observed. No impurities such as salts or organic matters are discerned in the spectrum. The FTIR spectrum of diatom frustule is essentially identical to that of colloidal silica, although the corresponding
band observed at 953 cm$^{-1}$ in the diatom frustule is obscured in colloidal silica.

Synchrotron X-ray diffraction profiles of the diatom frustule and colloidal silica, both of which exhibit a characteristic X-ray amorphous pattern, are shown in Figure 4. Least-squares fitting conducted for the diffraction maxima around $2\theta = 9^\circ$ provides accurate estimates of peak position and full width at half maximum (FWHM). The peak positions of the diatom frustule and colloidal silica are $2\theta = 9.28^\circ$ and $2\theta = 9.12^\circ$, respectively, with corresponding FWHM values of 4.62$^\circ$ and 4.06$^\circ$, respectively.

Raman spectra of the diatom frustules at ambient and high pressure–high temperature conditions are presented in Figure 5. At ambient conditions, Raman spectrum of the diatom frustule showed one broad, poorly structured band centered around 440 cm$^{-1}$ (Fig. 5a). With compression of 0.3 GPa at 100 °C, a characteristic Raman band occurred immediately at 465 cm$^{-1}$ (Fig. 5b). It is noteworthy that another sample exposed under the same conditions, two Raman bands can be observed at 465 and 501 cm$^{-1}$ as well (Fig. 5c). With compression of much higher pressure of 5.7 GPa, one strong Raman band, which is apparently different from quartz, occurred at 538 cm$^{-1}$ (Fig. 5d). Typical morphology after the pressure and temperature treatment is shown in Figure 6. With compression and heating, the characteristic spindle-shaped body was completely lost. As a result, the initial morphology was totally changed into the spherical particles with a diameter of about 2 µm (Fig. 6).

**DISCUSSION**

**FTIR and X-ray diffraction studies of diatom frustule**

Table 2 summarizes vibrational modes and wavenumbers detected in the diatom frustule and colloidal silica. Based on previous FTIR studies, the intense bands at 468, 803, and 1095 cm$^{-1}$ can be ascribed to O–Si–O bending vibration, Si–O–Si symmetric stretching vibration, and Si–O–Si
asymmetric stretching vibration, respectively (Moenke, 1974). The band at 953 cm$^{-1}$ can be attributed to the Si–O stretching vibration in a silanol group (Hino and Sato, 1971). The Si–O stretching vibration is known to be highly sensitive to hydrogen bonding (Hino and Sato, 1971). Although the corresponding band in colloidal silica is ambiguous (Fig. 3), the band can be clearly observed in several different types of diatoms (Gélabert et al., 2004; Asada et al., 2005; Khraisheh et al., 2005). Moenke (1974) explained that absorption in this region is a common feature of spectra of diatomite and opaline silicas. Furthermore, very vigorous grinding of quartz can also induce absorption here, due to surface Si–OH groups (Takamura et al., 1964). Since the band at 953 cm$^{-1}$ can be considered to closely reflect surface structure, it is attributed to hydrogen bond formation of Si–OH with adsorbed water on the diatom frustule, whose surface has a much more complex structure than colloidal silica. The small band at 1629 cm$^{-1}$ can be ascribed to be the bending vibration of the H–O–H bond in a water molecule (Kronenberg, 1994). The broad band around $\nu = 3400$ cm$^{-1}$ is caused by the O–H stretching vibration of hydroxyl and a water molecule. A weak band at about $\nu = 3650$ cm$^{-1}$ observed in the diatom frustule (not shown in Fig. 3) is derived from silanol species in the sample.

The synchrotron X-ray diffraction profile of the diatom frustule exhibited a characteristic X-ray amorphous peak, which was essentially identical to that of colloidal silica (Fig. 4). X-ray diffraction patterns of naturally occurring opals classified into opal–A also show only one broad peak (Sodo et al., 2016). Taking into consideration the results of FTIR and X-ray diffraction analyses, the diatom frustule used in the study is classified as hydrous amorphous silica. In the XRD profile of diatom frustule, however, a slight shoulder on the broad asymmetric diffraction maximum can be recognized around $2\theta = 12^\circ$ (Fig. 4), which leads to the larger FWHM value of diffraction maxima in diatom frustule than that in colloidal silica. Although the XRD data are limited and lacking the statistical comparison among the various diatom frustules, the shoulder might be a characteristic feature of biogenic hydrous amorphous silica.

Structural and morphological changes of biogenic hydrous amorphous silica

A Raman spectrum of a diatom frustule exhibiting one

![Figure 6. SEM images of the diatom frustule exposed to 0.3 GPa at 100 °C. (a) Low magnification of 1600× and (b) high magnification of 22000×.](image)

| Mode                                      | Wavenumber (cm$^{-1}$) | Reference$^*$ |
|-------------------------------------------|------------------------|---------------|
| O-Si-O bending vibration                  | 468                    | (1)           |
| Si-O-Si symmetric stretching vibration    | 803                    | (1)           |
| Si-O stretching vibration of silanol group| 953                    | (2)           |
| Si-O-Si asymmetric stretching vibration   | 1095                   | (1)           |
| H-O-H bending vibration                   | 1629                   | (3)           |
| O-H, H-O-H stretching vibration          | 3403                   | (3)           |

* (1) Moenke (1974), (2) Hino and Sato (1971), (3) Kronenberg (1994).
broad, poorly structured band around 440 cm$^{-1}$ (Fig. 5a) is almost identical to that of opal–A (Sodo et al., 2016). The broad band can be attributed to the Si–O–Si symmetric stretching mode (Sharma et al., 1981). In this study, a Raman spectrum, clearly distinguishable from opal–A, appeared at 465 cm$^{-1}$ with the pressure and temperature treatment of 0.3 GPa and 100 °C (Fig. 5b). The most intense band of quartz lies at 464 cm$^{-1}$ at ambient conditions (Sharma et al., 1981; Kingma and Hemley, 1994). According to the study of vibrational properties of quartz as a function of pressure and temperature (Schmidt and Ziemann, 2000), the frequency of the 464 cm$^{-1}$ band is estimated to increase 2 ± 1.0 cm$^{-1}$ at 0.3 GPa at 100 °C. Therefore, the Raman band observed at 465 cm$^{-1}$ exactly corresponds to that of quartz. Consequently, the diatom frustule was crystallized into quartz with pressure and temperature treatment, similar to the transition of diatomite to quartz with diagenesis (Isaacs, 1982; Williams and Crerar, 1985; Williams et al., 1985). In addition, we observed two Raman bands at 465 and 501 cm$^{-1}$ as well (Fig. 5c). The Raman band at 465 cm$^{-1}$ is a distinguishing characteristic of six–membered rings of corner–sharing SiO$_4$ tetrahedra (Sharma et al., 1981; Matson et al., 1986). In contrast, the band at 501 cm$^{-1}$ corresponds to four–membered rings of corner–sharing SiO$_4$ tetrahedra (Kingma and Hemley, 1994). Figure 7 shows the comparison of crystal structure between quartz and moganite. Quartz has four–fold helical spirals of SiO$_4$ tetrahedra around three– and six–fold screw axes, whereas moganite is composed of alternating fragments of both left– and right–handed three–fold spirals and four–membered rings (Miehe and Graetsch, 1992). No closed four–membered rings are present in quartz. The two peaks are therefore known as a characteristic Raman pattern of a mixture of quartz and moganite (Kingma and Hemley, 1994). In the present study, a mixture including quartz and moganite was formed in the probed sample area. This domain is approximately similar to microcrystalline silica (Kingma and Hemley, 1994). The quantitative ratio of quartz and moganite was calculated using the Raman bands observed at v = 465 and 501 cm$^{-1}$, using a method proposed by Götze et al. (1998). The resultant Raman band integral ratio I(501 cm$^{-1}$)/I(465 cm$^{-1}$) is 20.3%, which suggests that the moganite content approaches about 50 wt% (Fig. 8). Chalcedony is a microcrystalline fibrous form of silica composed of a very fine intergrowth of quartz and moganite (Graetsch, 1994; Heaney, 1994). Wahl et al. (2002) found that quartzine and chalcedony from agates of different origin contain lamellar admixtures of moganite. Heaney and Post (1992) examined 150 samples of microcrystalline quartz–rich silica deposits, such as chalcedony, chert, and flint, from all over the world, and reported that moganite was found in most specimens. As can be seen in Figure 6, the granular morphology is partially like naturally occurring opals (Guillou et al., 2008), but shows a different surface morphology relative to the common habit of opal–CT, which itself exhibits a spherical aggregate with interpenetrating blades or plates called ‘lepisphere’ (Kastner et al., 1977; Graetsch, 1994).

With increased pressure and temperature to 5.7 GPa and 100 °C, respectively, one strong Raman band appeared at 538 cm$^{-1}$ (Fig. 5d). A structure with four–membered SiO$_4$ rings such as found in moganite, coesite, and feldspars, should possess symmetric Si–O–Si stretching and bending modes above 500 cm$^{-1}$ (Kingma and Hemley, 1994). At ambient conditions, the characteristic Raman band of coesite can be observed at around 520 cm$^{-1}$ (Kingma and Hemley, 1994; Cernok et al., 2014). The Raman peak at 520 cm$^{-1}$ increases approximately linearly with compression up to 10 GPa (Cernok et al., 2014). The pressure dependence of the Raman band can be therefore fitted by a linear function \( v(P) = 3.580P + 518.4 \) (\( R^2 = 0.9855 \)). The regression line obtained from previous work (Cernok et al., 2014) coincides with our observation. It is already known that colloidal silica, often called silica gel, is readily transformed to coesite at 5...
GPa and 100 °C for 1 h (Arasuna et al., 2014). The authors concluded that this is because colloidal silica has a similar structure unit to coesite. The present experimental result is therefore approximately consistent with the previous report.

**Effect of water molecule on the structure geometry of hydrous amorphous silica**

With only compression, silica glass (fused quartz) never crystallizes below at least 100 GPa (Sato and Funamori, 2010). In contrast, hydrous amorphous silica is readily crystallized with compression and heating. This result strongly suggests that the pressure response of hydrous amorphous silica is entirely different from that of silica glass. In addition, this study experimentally confirms that morganite can be formed from hydrous amorphous silica.

To clarify the effect of a water molecule on the geometry of amorphous silica structure, first-principles calculations were performed. Consequently, a disiloxane molecule, which can be defined as the smallest unit of a silica network, forms a stable complex with a trans configuration in the absence of water molecule (Fig. 9a). With a close approach of water to the disiloxane molecule, however, it is twisted 60° and changed into the cis configuration (Fig. 9b). The H•••O hydrogen bonding distances between the apical oxygen atoms and the water molecule are found to be 2.035 and 2.196 Å, implying that weak hydrogen bonds are formed between disiloxane and water molecules. That is, the Si-O-Si bridging unit in amorphous silica is rotated by the hydrogen bonding interactions from the neighboring water molecule.

![Figure 9](image-url)
Solubility of amorphous silica in water at high temperatures and high pressure

Figure 10 shows the log activities of dissolved silica in equilibrium with amorphous silica, chalcedony, and quartz. (a) 25 °C, 1 atm, activity of H2O = 1.0, (b) 100 °C, 1 atm, activity of H2O = 1.0, (c) 25 °C, 0.3 GPa, activity of H2O = 0.01, (d) 100 °C, 0.3 GPa, activity of H2O = 0.01.

Proposed mechanism of crystallization of moganite from hydrous amorphous silica

Although the conditions of the formation of moganite are not fully resolved, many authors have proposed reasonable mechanisms of moganite development. Heaney (1993) documented that when chalcedony precipitates directly from a mother fluid, varying defect concentrations lead to a transformation from a weakly polymerized silica solution to a non-polymerized fluid. This is responsible for the textural transformation from chalcedony to quartz. Göltze et al. (1998) presented evidence of single bands in agates that suggest alternating formation of fine-grained, highly defective chalcedony intergrown with moganite, and coarse-grained low-defect quartz. On the other hand, impurities may promote Brazil twinning since cations can occupy the sites of bridging tetrahedra (McLaren and Pitkethly, 1982). As a result, the bridging tetrahedron is forced into changing the configuration with opposite chirality. It may change the periodic alternate lamellae of right-handed and left-handed quartz into a superstructure of moganite. Heaney (1995) reported that non-evaporitic silica typically contains between 5 and 15 wt% moganite, whereas evaporitic silica may contain between 20 and 75 wt% moganite. No chert from non-evaporitic settings has been found to contain more than 25 wt% moganite. Consequently, Heaney (1995) proposed that moganite crystallization is favored by alkaline fluid chemistry combined with high activities of ferric iron. Furthermore, Gislason et al. (1997) mentioned that the high abundance of moganite in recent arid environments is related to the lack of water available to dissolve moganite and to precipitate simultaneously α-quartz.

In our study, a mixture of quartz and moganite, formed in the extreme dilute aqueous solution under high pressure and high temperature conditions, contained a relatively high content of moganite. It is very unlikely that all products were precipitated directly from the dissolved amorphous silica in solution. In general, hydrous
amorphous silica is composed of SiO$_4$ tetrahedra forming a discontinuous three-dimensional framework with open cavities, where hydroxyl and water molecules are accommodated. Amorphous silica is known to contain the four-membered rings in the structure (Pasquarello and Car, 1998; Uchino et al., 2000; Umari et al., 2003). Our first-principles calculation reveals that a water molecule has a great influence on the Si–O–Si bridging unit in amorphous silica (Fig. 9). The resulting structural geometry shows the cis configuration, which is regarded as a structural defect causing a twin boundary. As mentioned before, moganite also has the four-membered rings in its structure (Miehe and Graetsch, 1992). It possesses both cis and trans configurations at the four-membered rings (Fig. 11). In contrast, a cis configuration is not present in quartz. Based on the result obtained in this study, it is a reasonable assumption that there is the Si–O–Si bridging unit in the amorphous silica. During crystallization of hydrous amorphous silica, this bridging unit would survive as a structural defect and then crystalize into moganite, maintaining the geometry. This hypothesis is adaptable to the phase transformation from hydrous amorphous silica to coesite because coesite has also the four-membered rings with a slightly tilted cis configuration (Fig. 11). Arasuna et al. (2014) have experimentally observed the phase transformation from hydrous amorphous silica (colloidal silica) to coesite under 5 GPa and 100 °C for 1 h.

Heaney (1995) considered that the transformation of metastable moganite to quartz often requires tens of millions of years. However, the theoretical investigation of Hantsch et al. (2005) showed that moganite maintains its structure at least up to 10 GPa. In the case of temperature-only treatment, moganite is transformed to β-moganite at 297 °C (Heaney and Post, 2001). Therefore, moganite is never transformed to quartz if subjected to pressure effects at constant temperature, or temperature effects at constant pressure. Thus, once formed, moganite will persist as a metastable phase. Moganite will be never changed into quartz unless it is dissolved under alkaline conditions.

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SUPPLEMENTARY MATERIAL

Color version of Figure 7 is available online from http://doi.org/10.2465/jmps.170330a.

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