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Effect of Temperature and Pressure on the Structural Change of Diatom's Frustule

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This study aims to elucidate the diagenic conditions of diatom's frustules from opal-AG to α-quartz. Diatoms collected from Lake Yogo, Siga prefecture were cultured in laboratory. The initial structure of diatom's frustule was investigated by the synchrotron X-ray diffraction. The X-ray diffraction analysis showed a typical broad diffraction pattern of opal-AG. The structural change of diatom's frustules under high pressure and high temperature was observed by *in situ* Raman spectroscopic analysis. The Raman spectra showed that the structure of diatom's frustule was transformed from opal-AG to opal-CT just after compression at 100°C. Even when it was compressed further up to 6.9 GPa, the morphology almost remained unchanged. With keeping the compression of 5.7 GPa at 100°C for 7days, however, it was changed into coesite with its morphological change. After 7 days under high pressure and high temperature conditions of 0.3 GPa and 100°C, the opal-CT was changed to a mixture of α-moganite and α-quartz, and its morphology was totally changed to spherical particles with a diameter of about 2 μm. This is approximately consistent with the silica diagenesis observed in sedimentary rocks. Raman spectroscopy and SEM observation reveal that the diatom's frustule consisting of opal-AG is changed to both α-moganite and α-quartz with dissolution and re-precipitation.

1 Introduction

The diatoms in ocean, lakes, and rivers are responsible for almost a quarter of the photosynthesis of the whole earth [1]. They have a great influence on the element movement of the Earth's surface by absorbing different metal ions selectively [2]. The diatoms with complicated surface structure have a property to adsorb various substances to their frustules, but the adsorption characteristic depends on the structures of the frustule surface. It is well known that with diagenesis the diatom's frustules composed of opal-AG are transformed to α-quartz through opal-CT [3]. Although diatoms well preserved in sediment are applied as a fossil record, the shape-preserving transformation (fossilization) mechanism has not been well understood yet. In addition, the structure of diatom's frustules is transformed with the diagenesis, but details of the diagenic process have not been also clearly understood. Arasuna *et al.* [4] performed a high pressure experiment of a silica gel consisting of SiO_4 network structure with four-membered ring, which is included in the structure of diatom's frustules. Consequently, the structure of silica gel was transformed from opal-AG to coesite at 5 GPa and 100°C.

In order to clarify the diagenic conditions of diatom's frustule from opal-AG to α-quartz, living diatoms collected from a lake and cultivated separately in the laboratory were exposed under high pressure and high temperature conditions in the study. The changes of diatom's frustule were investigated by synchrotron X-ray diffraction, scanning electron microscope, and Raman spectroscopic analysis. Here, we reports the structural and morphological changes of diatom's frustule under high pressure and high temperature conditions.

2 Experiment

Collection and cultivation processes of diatoms

Diatoms were collected from Lake Yogo, Siga prefecture, Japan. They were cultured in nutrient f/2 medium and harvested under red and green LED lights at 25°C. The f/2 medium has been widely used as a general enriched seawater medium designed for growing coastal marine algae, especially diatoms. After multiplying moderately, each species of diatom was carefully transferred into separate Petri dishes and multiplied under the same condition. As a result, three species of diatom were isolated and finally only one species, *Nitchia* cf. *Fruatrum*, was successfully obtained in enough quantity for the following experiments.

Sample treatments

The diatom multiplied was filtered through a membrane filter. Because the f/2 medium included seawater, salts were carefully removed by centrifugal separation. Furthermore, organic matter films covering up the diatom's frustule were removed by washing with acetone and sodium hypochlorite. After the cleaning treatment, the diatom's frustules were dried at 50°C in an oven for three days. SEM observation revealed that the morphology of *Nitzschia* cf. *Frustrum* was maintained completely during the cleaning treatment (Fig. 1).

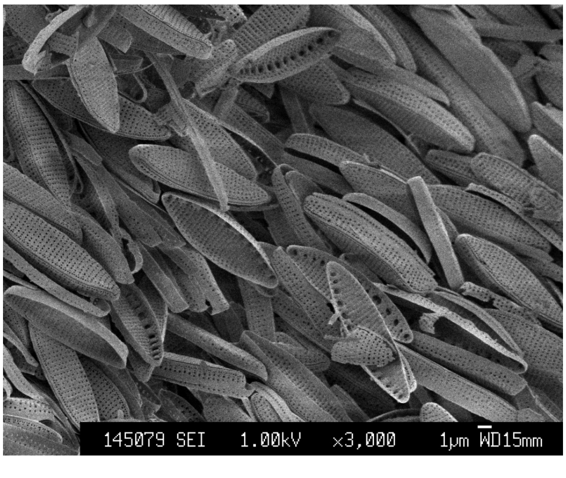

Figure 1. Diatom's frustule of *Nitchia* cf. *Frustrum.*

The observation and measurement

The synchrotron X-ray diffraction analysis was performed at BL8B, Photon Factory (PF), KEK, Japan. High pressure and high temperature experiment was conducted using Diamond Anvil Cell. Nichrome wire was applied as a heater. A methanol-ethanol-water liquid mixture 16:3:1 was used as the pressure medium. In this study, high-pressure experiment was started from 0.3 GPa, although it was too high to consider the processes of sedimentation. Raman spectra were recorded with Photondesign Mars stabulite2017 micro-Raman spectrometers. The 514.5 nm line of an Ar^+ laser was used to excite Raman scattering. The Raman light was collected in the backscattering geometry. Spectral calibration of each measured spectrum was performed using a Si film. Pressure was determined by the ruby fluorescence method. Spectra were accumulated for 300s in the ranges of 300 to 600 cm^{-1}. After Raman spectroscopic measurement at the high pressure and high temperature conditions, morphology of diatoms was observed by scanning electron microscopy using JEOL JSM6330F. All specimens were mounted on brass specimen holders and coated with Pt film on their surface. SEM observations were operated with accelerating voltage of 5.0kV.

3 Results

Synchrotron X-ray diffraction profile of the *Nitzschia* cf. *Frustrum* exhibited a typical amorphous characteristic of broadened diffraction maxima in the XRD pattern, which is a basically similar to that of amorphous silica, opal-AG (Fig. 2).

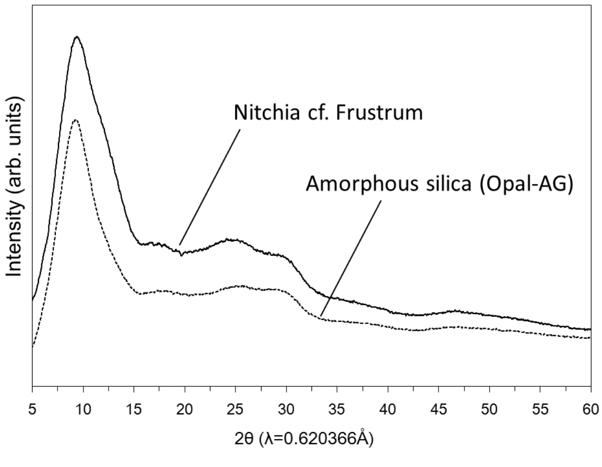

Figure 2. XRD patterns of *Nitchia* cf. *Frustrum* and amorphous silica (opal-AG).

Raman spectra of the diatom's frustule under high pressure and high temperature are given in Figures 3. At ambient condition, the Raman spectrum of the sample showed a weak band centered at 440 cm^{-1} (Fig 3a), which is attributed to a symmetrical Si-O-Si stretching mode [5]. At 6.9 GPa and 100°C, the band centered at 440 cm^{-1} became much less intense and a broad band around 350 cm^{-1} which is a characteristic of opal-CT [5] were slightly observed (Fig 3b). Since the band at 2950 cm^{-1} entirely disappeared, a hydroxyl group was removed from the structure. After 7 days at 0.3 GPa and 100°C, a weak band at 473 cm^{-1} corresponding to α-quartz was observed (Fig 3c). It is noteworthy that from the sample under the same condition two bands at 473 and 510 cm^{-1} can be observed (Fig 3d). They are known as characteristic Raman bands of α-moganite [6]. That is, α-quartz is coexisted with α- moganite in the sample. The position of the 510 cm^{-1} in the α-moganite corresponds to four-membered rings of corner-sharing SiO_4 tetrahedra [6]. On the other hand, that of 473 cm^{-1} is a distinguishing characteristic of six-membered rings of corner-sharing SiO_4 tetrahedra [7]. After 7 days at 5.7 GPa and 100°C, only one peak appeared at 540 cm^{-1} (Fig 3e), which is a characteristic band of coesite [6]. Arasuna *et al.* [4] also demonstrated that coesite is readily changed from silica gel at 5 GPa and 100°C. They therefore thought that silica gel is easily transformed to coesite because it includes a similar structure unit to coesite [4].

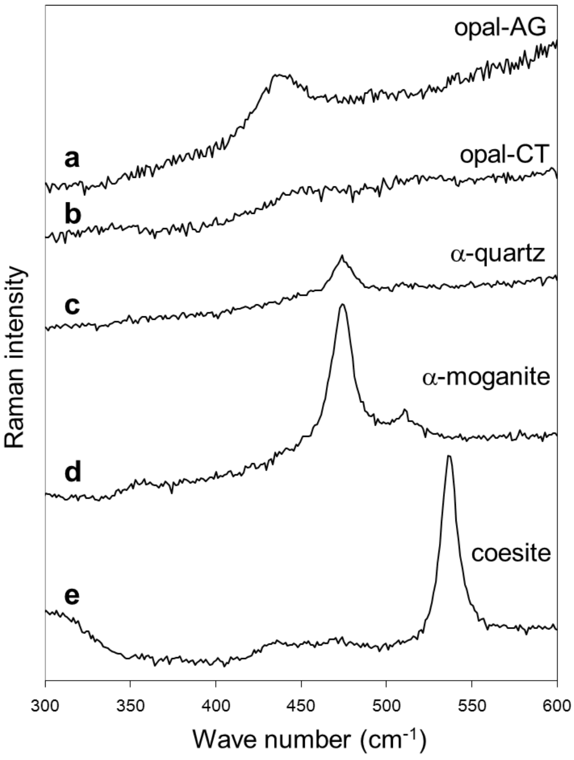

Figure 3. Raman spectra of (a) diatom's frustule and that exposed under (b) 6.9 GPa and 100°C, (c,d) 0.3 GPa and 100°C for 7 days, and of (e) 5.7 GPa and 100°C for 7 days.

Typical morphologies after high pressure and high temperature treatment are shown in Figure 4. At 6.9 GPa and 100°C, although the surface of diatom's frustules seems to be slightly dissolved, the morphology was almost maintained (Fig 4a). After 7 days under 0.3 GPa and 100°C, however, the initial form of diatom's frustule was completely lost. As a result, the spherical particles with a diameter of about 2μm was formed (Fig 4b), which are composed of α-moganite and α-quartz. After 7 days under 5.7 GPa and 100°C, the external morphology was completely lost and flat shape composed of coesite was formed (Fig. 4c).

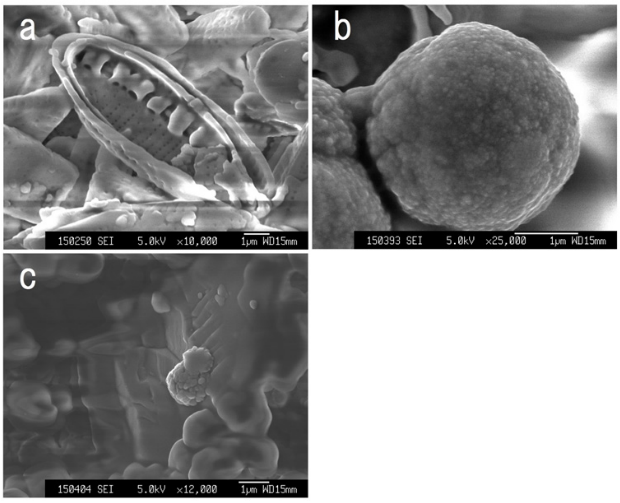

Figure 4. SEM images of diatom's frustules after high-pressure and high-temperature treatments at (a) 6.9 GPa and 100°C, (b) 0.3 GPa and 100°C for 7 days, and (c) 5.7 GPa and 100°C for 7 day.

In this study, phase transitions from opal-CT to α-moganite and from opal-CT to α-quartz occurred. However, we considered that phase changes from opal-CT to α-moganite, α-quartz, and coesite were ascribed to dissolution and re-precipitation because the external morphology was entirely changed. Therefore, phase transition from opal-CT to α-moganite and α-quartz was accompanied by the dissolution and re-precipitation.

4 Discussion

The results of high pressure and high temperature Raman spectroscopic measurement indicate that the diatom's frustule compressed under 0.3 GPa and 100°C for 7 days is partly transformed to α-moganite. In addition, α-quartz is formed simultaneously. The result suggests that a phase transition to both α-moganite and α-quartz occurs under the same condition. According to theoretical investigation [8], α-moganite is significantly more compressible than α-quartz, so it can survive at least to 10 GPa. Therefore, there is little possibility that α-moganite is directly transformed to α-quartz with compression. On the other hand, with temperature, α-moganite changes to β-moganite at 297°C [9]. That is, the phase transition from α-moganite to α-quartz would need other factor such as a complete dissolution of the network structure of SiO_4 tetrahedra. The structural stability between α-quartz and α-moganite may be explained as follows. The structure of α-moganite is composed of SiO_4 tetrahedral framework arraying right-handled and left-handled quartz alternatively, which forms four-membered rings of SiO_4 tetrahedra in the structure. This four-membered ring in α-moganite includes CIS and TRANS configurations. On the other hand, the α-quartz has only TRANS configuration. When the SiO_4 tetrahedral framework with four-membered ring is compressed, the Si-Si distance in the four-membered is shortened. As a result, repulsive force between O atoms at the CIS configuration is generated. Consequently, after the opal-CT is dissolved under high pressure high temperature conditions, SiO_4 tetrahedra with TRANS configuration should become predominant in the solution. Under high pressure, therefore, α-quartz is likely to be more stably crystalized than α-moganite.

Although the surface of diatom's frustule is slightly dissolved, most of diatom's frustule can remain its morphology at least up to about 7 GPa (Fig. 4a). It is suggested that diatom's frustules might survive an extremely high pressure condition in a short time. When the diatom's frustule is exposed under high pressure and high temperature for long time, its morphology is totally changed. The result is approximately consistent with the silica diagenesis observed in diatom sediment of the Te Kopia, Newzealand [10]. The high temperature and high pressure ranges in the study are not matched with the sedimentation condition [10], but the similar morphology of silica was observed in this experiment.

5 Conclusions

When the diatom's frustule consisting of opal-AG is compressed at a temperature of 100°C, a phase transition from opal-AG to opal-CT readily occurs. With compression at least up to 6.9 GPa, most of the external morphology of diatom's frustules is maintained. This result suggests that even when it is exposed under a high-pressure condition, its external morphology would be maintained to some extent. When it is kept under 5.7 GPa and 100°C for 7days, the external morphology of diatom is totally changed to flat shape and its structure is transformed to coesite. When it is kept under 0.3 GPa and 100°C for 7days, the diatom's morphology changes to spherical particles including both α-moganite and α-quartz. This study reveal that during the diagenesis the diatom's frustule consisting of opal-AG is changed to both α-moganite and α-quartz with dissolution and re-precipitation processes.

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