SiO₄ network structure changes and crystallization of diatom shells in diatomaceous earth by heat treatment

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Diatomaceous earth (DE) samples from the Nevada, United States of America and the Noto region, Ishikawa Prefecture, Japan were subjected to heat treatment of up to 1200 °C, and their SiO₄ network structure changes and crystallization were characterized in detail by thermogravimetric and X-ray diffraction analyses, and infrared and Raman spectroscopies. Raman spectra for the Nevada-DE revealed that the SiO₄ network structure of the unheated diatom shells in Nevada-DE may be mainly composed of 6-membered rings of SiO₄ tetrahedra. In addition, with heat treatment above 600 °C, this rings structure increased and 4- and 3-membered rings of SiO₄ tetrahedra appeared, whereby the SiO₄ network structure became similar to that of silica glass. The first diffraction peak (FSDP) position of X-ray diffraction patterns showed the size of the medium-range structure of diatom shells in Nevada-DE and Noto-DE may be smaller than that of silica glass but larger than that of silica gel. Since the FSDP position of Nevada-DE and Noto-DE is the same, the medium-range structure of Noto-DE may also compose of the 6-membered rings of SiO₄ tetrahedra. Furthermore, the crystallization temperature (1100 °C) from biogenic amorphous silica such as diatom shells in Nevada-DE and Noto-DE to cristobalite was lower than that (1200 °C) of inorganic amorphous silica such as silica gel. Raman spectra show that the SiO₄ network structure in diatom shells for unheated Nevada-DE is mainly composed the 6-membered rings of SiO₄ tetrahedra such as cristobalite, and the 6-membered rings in SiO₄ network structure is increased at a lower temperature than silica gel. It suggested that the diatom shells in Nevada-DE easily crystallize to cristobalite at a lower temperature than silica gel.

Keywords: Diatomaceous earth, Amorphous silica, Heat treatment, Cristobalite, Ring structure

INTRODUCTION

Diatomaceous earth (DE) consists of fossils of unicellular algae called diatoms, where only the shells remain after the organic materials of the diatoms have disappeared during sedimentation. Diatom shells are deposited on sea or lake floors, are composed of hydrous amorphous silica and have a fine porous structure. DE has been applied industrially as a filter aid, insulating material, and adsorbent due to its features such as porosity, thermal insulation, and heat resistance (Calvert, 1930; Bakr, 2010; Kamigasa, 2002). Most of these products are manufactured by heat treatment. Therefore, an investigation of the structural changes of DE by heat treatment is expected to provide important information regarding the quality stabilization

of these products and the development of new applications that employ DE. It is also important to clarify the crystallization process of DE in the mineralogical field.

It has been reported that diatom shells contained in DE crystallize to cristobalite at above 1100 °C (Shimazu, 1961; Gulturk and Guden, 2011; Zheng et al., 2018). When DE containing calcite (Ibrahim and Selim, 2012) or halite (Escalera et al., 2015) is heated at 1000 and 750 °C, respectively, the diatom shells crystallize to cristobalite. Currently living diatom frustules and glass sponges crystallize to quartz by heat treatment at 800 °C, and then crystallize to cristobalite at 900 and 1200 °C, respectively (Arasuna and Okuno, 2018; Fukushima, 2018). On the other hand, among inorganic amorphous silicas, the crystallization temperature to cristobalite increases in the order of synthetic opal (1200 °C) < silica gel (1300 °C) < silica glass (1400 °C) (Kamiya et al., 2000; Arasuna et al., 2013; Fukushima, 2018). Thus, it

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is clear that the biogenic amorphous silicas have a lower crystallization temperature to cristobalite than inorganic amorphous silicas.

These amorphous silicas have a ring structure of SiO_4 tetrahedra in SiO_4 network structure. Raman spectroscopy can provide information on a ring structure of SiO_4 tetrahedra in amorphous silicas. For inorganic amorphous silicas, 4- and 6-membered rings of SiO_4 tetrahedra are prominent in the SiO_4 network structure of synthetic opal and silica gel and in the structure of silica glass, respectively (Kamiya et al., 2000; Arasuna et al., 2013; Fukushima, 2018). On the other hand, for biogenic amorphous silicas, currently living diatom frustules and glass sponges have mainly 6-membered rings of SiO_4 tetrahedra in the SiO_4 network structure (Arasuna and Okuno, 2018; Fukushima, 2018). For fossilized DE, it has been reported that diatomite has demonstrated to consist of 5-membered rings and various rings larger than 5-membered rings (Cui et al., 2015). Gendron-Badou et al. (2003) used nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy to reveal that fossil diatom frustules and glass sponge spicules exhibit a more condensed and organized silica than living diatom frustules. However, there are very limited reports related to changes in the ring structure by heat treatment of fossilized diatom shells in DE and crystallization temperature to cristobalite.

In this study, we have focused the SiO_4 network structure change and crystallization process on the fossilized diatom shells in DE, which are biogenic amorphous silica. The structural changes and crystallization from the amorphous state by heat treatment up to 1200 °C were investigated using thermogravimetric analyses, powder X-ray diffraction measurements, and IR and Raman spectroscopies. Silica gel and silica glass were also examined to compare the SiO_4 network structural changes of inorganic and biogenic amorphous silica and the difference in crystallization temperature to cristobalite. In addition, these difference of the SiO_4 network structure and crystallization temperature provide information from the perspective of material science, such as lowering the temperature of material synthesis in the development of applications of DE as a silica material. The differences with respect to the SiO_4 network structural change and crystallization temperature to cristobalite between the DEs examined here and various amorphous silicas reported previously are also clarified.

EXPERIMENTAL

Sample preparation

DEs were obtained from the Noto region (Neogene Mio-

cene Iizuka Formation in the city of Suzu), Ishikawa Prefecture, Japan and the Nevada, United States of America (Grade D110, World Minerals, Inc.). The DEs examined after pretreatment are denoted as Noto-DE and Nevada-DE. For Noto-DE, the particles ($>75 \mu\text{m}$) were collected with water using a sieve because Noto-DE includes non-negligible small sized impurities such as clay minerals. The particles ($>75 \mu\text{m}$) were dried at 100 °C using a drying oven and then ground with a mortar. The size of ground particles ranged from a max. 200 to a min. 2 μm . Nevada-DE was used in a commercially available state without pretreatment. That was because the particle size ranged from a max. 40 to a min. 3 μm without pretreatment. Silica gel (Wako Pure Chemical Industries, Ltd) and commercially available fused silica glass (Iwao et al., 2010) were ground with a mortar and used as reference materials. These particle size ranged from a max. 500 to a min. 3 μm and from a max. 200 to a min. 2 μm , respectively. The samples without silica glass were heated in a muffle furnace at 200, 400, 600, 800, 900, 1000, 1100, and 1200 °C for 1 h in an air atmosphere. For the silica glass, only the unheated sample was used as a reference.

X-ray fluorescence (XRF) chemical analyses

The chemical compositions of the unheated Nevada-DE and Noto-DE were determined using a wavelength dispersive X-ray fluorescence spectroscopic analyzer (ZSX Primus, Rigaku Corporation, Japan) with $\text{RhK}\alpha$ radiation at an accelerating voltage of 30–50 kV and a current of 48–80 mA under vacuum conditions with the fundamental parameter method. 0.3 g of the Nevada-DE and Noto-DE and 5 g of cellulose were mixed in a mortar, and the mixed powders were then uniaxially pressed to form a disk with 35 mm in diameter for XRF measurements.

Scanning electron microscopy

Scanning electron microscopy (JSM-7100F, JEOL, Japan) was used for morphological observation of the unheated Nevada-DE and Noto-DE, under an acceleration voltage of 15 kV. The samples were mounted on double-sided carbon tape and coated with Pt-Pd.

Thermogravimetric differential thermal analysis (TG-DTA)

TG and DTA curves of the Nevada-DE, Noto-DE, silica gel, and silica glass were measured up to 1200 °C using a TG-DTA measurement system (TG8120, Rigaku Corporation, Japan). These samples (5–15 mg) were placed in a

platinum pan and heated to 1200 °C with a heating rate of 10 °C min⁻¹ in an air atmosphere.

X-ray powder diffraction (XRD) measurement

X-ray powder diffraction measurements were conducted using a powder X-ray diffractometer (D2PHASER, Bruker AXS) with CuK α radiation at 30 kV and 10 mA in the 2 θ region from 4 to 50° and with sampling steps of 0.05°/2 θ and a counting time of 0.5 s/step. The crystalline phases in the unheated and heated samples were determined for Nevada-DE, Noto-DE, silica gel, and the unheated silica glass based on the measurement data. A suspension containing Nevada-DE was dropped on a slide glass to prepare an oriented-aggregate specimen. The oriented-aggregate specimen was treated with ethylene glycol and heated at 500 °C for 1h to identify clay minerals. The amorphous hallow data extracted from original pattern were used to estimate the first sharp diffraction peak (FSDP) position. For FSDP position, 2 θ values of the maximum values for the extracted hallow data were used.

Attenuated total reflection infrared spectroscopic measurements

Attenuated total reflection infrared spectroscopy (ATR-IR) measurements for the unheated and heated samples of Nevada-DE, Noto-DE, silica gel, and the unheated silica glass were performed using an ATR-IR spectrometer (Nicolet iN10, Thermo Fisher Scientific, Tokyo, Japan) equipped with a diamond crystal. The ATR-IR spectra of these samples were recorded in the range of 525–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Raman spectroscopic measurements

Raman spectra for the unheated and heated samples for Nevada-DE, silica gel, and unheated silica glass were recorded using micro-Raman spectrometer (LabRAM HR800, Horiba Jovin Yvon, Japan). The 514.5 nm (green) line of an Ar⁺ laser light was used to excite Raman scattering, and the Raman light was collected in the backscattering geometry.

RESULTS

XRF analysis

Table 1 shows the chemical compositions of the unheated Nevada-DE and Noto-DE. The Nevada-DE and Noto-DE included 93.2 and 94.0 mass% of SiO₂, respectively. Nevada-DE contained a small amount of Al₂O₃, Fe₂O₃,

Table 1. Chemical composition of Nevada-DE (A) and Noto-DE (B)

Metal oxides	A (mass%)	B (mass%)
SiO ₂	93.17	93.97
TiO ₂	0.22	N.D.
Al ₂ O ₃	4.02	1.11
Fe ₂ O ₃	1.12	2.31
MgO	0.43	0.19
CaO	0.58	0.56
Na ₂ O	0.13	0.50
K ₂ O	0.13	0.41
P ₂ O ₅	0.03	0.13
SO ₃	0.17	0.82
Total	100.00	100.00

N.D., Not detected.

MgO, and CaO, and the amount of Al₂O₃ and MgO was higher than Noto-DE. On the other hand, Noto-DE contained a small amount of SO₃ and Fe₂O₃.

SEM observation

SEM images of the unheated Nevada-DE and Noto-DE are shown in Figure 1. Many diatom shells were observed for each sample. The size of the diatom shells in Nevada-DE was ~ 10–15 μ m, and almost all of the diatom shells were tube-shaped. Nevada-DE was from freshwater diatom, and its genus was *Merosira* (Kawashima and Shiraki, 1941). On the other hand, the size of diatom shells in Noto-DE was ~ 100–150 μ m, with various shapes, such as discoidal, spherical and needle-shaped. Noto-DE was from saltwater diatom, and its genus was mainly *Cosinodiscus* (Ichikawa, 1950). In addition to diatom shells, small amount of sponge spicules and silicoflagellates were also contained in Noto-DE.

TG and DTA analysis

TG and DTA curves of the unheated Nevada-DE, Noto-DE, silica gel, and silica glass are shown in Figure 2. A large weight loss (10.0 mass%) was observed for Nevada-DE from room temperature to 300 °C. Noto-DE, which was mainly composed of diatom shells, exhibited a clearly large weight loss from 200 to 500 °C. It was considered that the dehydration of clay minerals contained in Nevada-DE and the approximately one order smaller diatom shells in Nevada-DE than those in Noto-DE led to faster weight loss. A small weight loss (2.0 mass%) was observed up to 700 °C. A gradual weight loss (2.0 mass%) was observed up to 200 °C for Noto-DE, after which a large weight loss (6.0 mass%) was observed up to 500 °C. No weight loss was observed above 500 °C. On the other

Figure 1. SEM images of Nevada-DE (A) and Noto-DE (B).

hand, a large weight loss (7.5 mass%) was observed for silica gel from room temperature up to 150 °C, followed by a gradual weight loss (6.5 mass%) up to 700 °C. Therefore, the total weight loss of Nevada-DE, Noto-DE, and silica gel were ~ 12.5, 9.7, and 13.2 mass%, respectively. The total weight loss of Noto-DE was smaller than that of Nevada-DE, which indicated that Noto-DE contained less amount of clay minerals than Nevada-DE because it was collected using a sieve (>75 µm) with water. The DTA curves for Nevada-DE and silica gel had a weak broad endothermic peak near 35 °C and a large endothermic peak near 94 °C, respectively. The peak near 35 °C was corresponded to the dehydration of clay minerals contained in Nevada-DE. The peak near 94 °C was corresponded to the dehydration of water adsorbed on silica gel. These endothermic peaks were not observed for Noto-DE. For silica glass, the weight loss and endo- and exothermic peak were not observed.

XRD analysis

Figure 3 shows the XRD patterns for the unheated Neva-

Figure 2. TG (A) and DTA (B) curves for Nevada-DE, Noto-DE, silica gel, and silica glass.

da-DE and Noto-DE and the oriented-aggregate specimens treated with ethylene glycol and heated at 500 °C for 1h. Nevada-DE had a broad peak located at around $2\theta = 21\text{--}22^\circ$ and weak diffraction peaks at $\sim 2\theta = 6.0, 19.9, \text{ and } 35.0^\circ$. The diffraction peak at $\sim 2\theta = 6.0^\circ$ (15.0 Å) shifted to $\sim 2\theta = 5.3^\circ$ (16.7 Å) by ethylene glycol treatment and $\sim 2\theta = 9.2^\circ$ (9.7 Å) by heat treatment at 500 °C, which were due to traces of smectite characterized by ethylene glycol and heat treatment. Noto-DE had mainly an amorphous background and small diffraction peaks of quartz, feldspar, and illite which were due to impurities accumulated in the DE bed. XRD patterns for the heated Nevada-DE, Noto-DE, silica gel, and the

Figure 3. XRD patterns of Nevada-DE and Noto-DE (A) and Nevada-DE after various treatment to identify clay minerals (B). N.T., not treatment; E.G., treated with ethylene glycol; 500 °C, heated to 500 °C for 1h.

unheated silica glass are shown in Figures 4. The XRD patterns for Nevada-DE up to 800 °C showed broad amorphous phase peaks at around $2\theta = 21\text{--}22^\circ$ and weak diffraction peaks at $\sim 2\theta = 19.9^\circ$ from clay minerals. The XRD patterns for the samples heated at 900 and 1000 °C showed only amorphous phases, which indicated the clay minerals were amorphized at 900 °C. At 1100 °C and 1200 °C, the cristobalite phase was observed. The XRD patterns for Noto-DE up to 1000 °C showed broad amorphous phase peaks at around $2\theta = 21\text{--}22^\circ$ and crystalline phase peaks at $\sim 2\theta = 21.0^\circ$ and 26.6° from quartz, and at $\sim 2\theta = 28.0^\circ$ from feldspar. At 1100 and 1200 °C, the

Figure 4. XRD patterns for Nevada-DE (A), Noto-DE (B), and silica gel (C) heated at various temperatures and unheated silica glass. N.T., No treatment.

Figure 5. ATR-IR spectra for Nevada-DE (A), Noto-DE (B), and silica gel (C) heated at various temperatures and unheated silica glass. N.T., No treatment.

cristobalite phase was also observed, as with the Nevada-DE. The XRD patterns for silica gel up to 1100 °C showed broad amorphous phase peaks at around $2\theta = 21-23^\circ$, and at 1200 °C, weak peaks at $\sim 2\theta = 21.9^\circ$ due to cristobalite were observed.

ATR-IR spectroscopic analysis

Figure 5 shows ATR-IR spectra for the heated Nevada-DE, Noto-DE, silica gel, and the unheated silica glass. The ATR-IR bands at 800 and 1020 cm⁻¹ observed in the spectra for all samples were attributed to the Si-O-

Si bending vibration and the Si-O stretching vibration, respectively (Handke and Mozgawa, 1993). For Nevada-DE, the bands at 800 and 1020 cm⁻¹ showed no large thermal change up to 1000 °C. However, at 1100 and 1200 °C, the positions of these bands shifted and became sharp due to the crystallization of cristobalite. A weak band around 1635 cm⁻¹ observed in Nevada-DE, Noto-DE, and silica gel was attributed to the H-O-H bending vibration of molecular water (Benesi and Jones, 1959). These bands disappeared by heating at 600 °C. The weak shoulder at ~ 910 cm⁻¹ also disappeared at 600 °C. For Noto-DE, the ATR-IR spectra in the range of 525-2000

cm⁻¹ were similar to those of Nevada-DE. However, the shoulder at ~920 cm⁻¹ was very weak and disappeared at 400 °C. The ATR-IR spectrum for unheated Nevada-DE in the range of 2800–4000 cm⁻¹ was similar to that of Noto-DE, except for a sharp band at around 3620 cm⁻¹. The sharp band at around 3620 cm⁻¹ and the weak shoulder at about 910 cm⁻¹ observed only in the spectrum for Nevada-DE were attributed to the Al-OH stretching mode of clay minerals such as smectite (Madejová, 2003). These bands for the unheated Nevada-DE disappeared by heating at 600 °C. On the other hand, the broad band at around 2800–3700 cm⁻¹ observed for Nevada-DE, Noto-DE, and silica gel were attributed to the O-H stretching mode of H₂O molecules and silanol groups in the amorphous SiO₂ phase. This band disappeared by heating at 900 °C. The band intensity of the Nevada-DE decreased gradually with the heat-treatment temperature, whereas that for Noto-DE decreased significantly at 400 °C. The ATR-IR spectra for silica gel in the range of 525–2000 cm⁻¹ had three distinct bands at around 800, 950, and 1020 cm⁻¹. The clear band at around 950 cm⁻¹ found in silica gel was attributed to the Si-OH stretching vibration of silanol groups (Almeida et al., 1990). This band at around 950 cm⁻¹ was considered to correspond to the weak shoulder at around 920 cm⁻¹ in the spectra for Noto-DE. This band disappeared by heating at 600 °C, whereas the bands at around 800 and 1020 cm⁻¹ showed no thermal change up to 1000 °C. In contrast, the band at around 1020 cm⁻¹ changed gradually and became similar to that of the silica glass at 1200 °C.

Raman spectroscopic analysis

Figure 6 shows Raman spectra for the heated Nevada-DE and silica gel with the spectrum for the unheated silica glass. The spectrum of Nevada-DE lacks the sharp band around 490 cm⁻¹ observed for silica gel. However, a broad band at around 450 cm⁻¹ was observed, which indicated that the distribution of ring structure was different from silica gel. These results indicated that the ring structure of the Nevada-DE and Noto-DE was composed of 6-membered rings of SiO₄ tetrahedra because the intensity around 450 cm⁻¹ was strong, which could be attributed to the symmetric stretching band of Si-O-Si in the SiO₄ network structure (Galeener and Gessberger, 1983; Sharma et al., 1984). On the other hand, the spectrum for silica gel showed a strong band at around 490 cm⁻¹ and showed that the ring structure of silica gel was the 4-membered rings of SiO₄ tetrahedra (Galeener, 1982a, 1982b; Sykes and Kubicki, 1996). The Raman spectra for Nevada-DE had a broad band centered at around 450, 550, and 630 cm⁻¹ up to 400 °C. The broad bands

Figure 6. Raman spectra for Nevada-DE (A) and silica gel (B) heated at various temperatures and unheated silica glass. N.T., No treatment.

at around 550 and 630 cm⁻¹ were attributed to the hydroxyl translation modes of AlFeOH in the ferruginous smectite (Frost and Klopogge, 2000). The band at around 550 cm⁻¹ was also observed for the currently living diatom frustules (Arasuna and Okuno, 2018), but the details were unknown. The intensities of the Raman bands at around 450, 490, and 600 cm⁻¹ increased with the treatment temperature from 600 °C up to 1000 °C. The small band at around 600 cm⁻¹ was attributed to the 3-membered rings of SiO₄ tetrahedra (Sharma et al., 1981; Galeener, 1982a; Okuno et al., 1999). In contrast, the spectra for silica gel had a relatively sharp band at around 490 cm⁻¹ up to 400 °C, the intensity of which

Table 2. FSDP positions (Q) of X-ray scattering profiles for amorphous silicas

Sample	Q ($\text{\AA}^{-1}$)
Nevada-DE	1.55
Noto-DE	1.55
Silica gel (in this study)	1.62
Silica glass (in this study)	1.50
Diatom frustule (Arasuna and Okuno 2018)	1.59
Glass sponge (Arasuna et al. 2018)	1.60-1.61
Synthetic opal (Arasuna et al. 2013)	1.64
Silica gel (Arasuna and Okuno 2018)	1.63
Silica glass (Shimada et al. 2002)	1.52

Q , $4\pi\sin\theta/\lambda$; λ , the X-ray wavelength.

decreased at 600 °C and then became prominent again at over 1000 °C. Over 1000 °C, the intensity of the broad band centered at around 450 cm^{-1} increased. Furthermore, a band at around 600 cm^{-1} was observed with heat treatment above 400 °C. The Raman spectra of Nevada-DE treated at 1000 °C was similar to those of silica gel heated at 1200 °C and silica glass.

DISCUSSION

SiO_4 network structure change of diatom shells in DE

All XRD profiles for the unheated all samples had broad diffraction peaks at around $2\theta = 21\text{--}22^\circ$. The FSDP position ($Q = 4\pi\sin\theta/\lambda$) can be estimated from XRD data, which assists in evaluating the size of the medium-range structure (Elliott, 1991). The FSDP position for the Nevada-DE and Noto-DE were larger than those of silica glass but smaller than that of silica gel (Table 2), which is consistent with the difference of the FSDP positions for similar samples shown in previous work (Arasuna and Okuno, 2018; Arasuna et al., 2013; Arasuna et al., 2018; Shimada et al., 2002). A small Q value means that there are large voids in the medium-range structure (Gaskell and Wallis, 1996; Gaskell, 2000; Mei et al., 2008). This void shows a ring structure and a configuration formed by SiO_4 tetrahedra in SiO_4 network structure. These results indicate that the voids in medium-range structure of Nevada-DE and Noto-DE may be smaller than that of silica glass but larger than that of silica gel. This is supported by the Raman spectra for these samples. The spectrum for silica gel shows a strong band at around 490 cm^{-1} and the medium-range structure of silica gel is mainly composed of the 4-membered rings of SiO_4 tetrahedra (Kamiya and Nasu, 1998). On the other

Figure 7. FSDP positions for Nevada-DE, Noto-DE, and silica gel as a function of the heating temperature and that for unheated silica glass.

hand, the spectrum for silica glass shows a broad band at around 450 cm^{-1} and the medium-range structure of silica glass is mainly formed by the 6-membered rings (Shimada et al. 2002). Therefore, the medium-range structure of Nevada-DE with a broad Raman band at around 450 cm^{-1} may be mainly composed of the 6-membered rings of SiO_4 tetrahedra like silica glass. The FSDP position of Noto-DE is same to that of Nevada-DE ($Q = 1.55 \text{ \AA}^{-1}$). Therefore the medium-range structure of Noto-DE may be also composed of the 6-membered rings of SiO_4 tetrahedra. From the FSDP position, it is considered that the 6-membered rings of SiO_4 tetrahedra of Nevada-DE and Noto-DE have voids smaller than that of silica glass due to deformation. The FSDP positions ($Q = 1.55 \text{ \AA}^{-1}$) of Nevada-DE and Noto-DE were smaller than those for diatom frustules ($Q = 1.59 \text{ \AA}^{-1}$) and glass sponges ($Q = 1.60\text{--}1.61 \text{ \AA}^{-1}$). This indicates that the size of medium-range structure of Nevada-DE and Noto-DE is larger than those of currently living diatom frustules and glass sponges. The temperature variation of the FSDP position was analyzed for amorphous phases of Nevada-DE, Noto-DE, and silica gel, and the results are presented in Figure 7. For silica gel, the FSDP position ($Q = 1.62 \text{ \AA}^{-1}$) indicates a negative shift of $0.12 \text{ \AA}^{-1}$ with an increase in the temperature up to 1000 °C. In particular, this FSDP position decreases sharply at 800 °C. In contrast, the FSDP positions ($Q = 1.55 \text{ \AA}^{-1}$) for Nevada-DE and Noto-DE indicated almost no temperature variation. These results indicate that silica gel

changes to the SiO₄ network structure containing 6-membered rings by heating at 1000 °C, i.e., the SiO₄ network structure changes from the 4-membered rings of SiO₄ to 6-membered rings (Kamiya and Nasu, 1998). On the other hand, since Nevada-DE and Noto-DE have the amorphous parts corresponding to diatom shells up to 1000 °C from XRD patterns and there is no change in FSDP position by heating, it suggested that the SiO₄ network structure maintains the 6-membered rings of SiO₄ before heating.

Crystallization of amorphous silicas

The XRD patterns for the heated Nevada-DE show a completely amorphous phase at 900 and 1000 °C; therefore, the clay minerals were amorphized at 900 °C. For both the heated Nevada-DE and Noto-DE, the diatom shells crystallized to cristobalite at above 1100 °C. Similarly, some studies have reported that DE is crystallized to cristobalite by heating above 1100 °C (Shimazu, 1961; Gulturk and Guden, 2011; Zheng et al., 2018). These changes are not consistent with the crystallization temperatures of the other amorphous silica materials reported in other previous works. According to the reports of Arasuna et al. (2018) and Fukushima (2018), the diatom frustules and the glass sponges begin to crystallize to quartz at 800 °C and then crystallize to cristobalite at 1200 and 900 °C, respectively. That is, the glass sponges crystallize to cristobalite at a lower temperature than the diatom frustules. In other previous work, synthetic opal showed no crystallization up to 1100 °C and then crystallized to cristobalite at 1200 °C (Arasuna et al., 2013). Silica glass crystallized to cristobalite at 1400 °C (Fukushima, 2018), which is higher than that for synthetic opal. On the other hand, silica gel began to crystallize at 1200 °C as shown in Figure 4. Therefore, it is clear that the various amorphous silicas are crystallized to cristobalite by heat treatment although the crystallization temperatures show a large variation from 900 up to 1400 °C. Furthermore, the biogenic amorphous silicas are crystallized to cristobalite at lower temperatures than that of inorganic amorphous silicas. Silica glass has the highest crystallization temperature among these inorganic amorphous silicas. It is thus considered that silica glass without silanol groups and water molecules requires higher temperature treatment for crystallization to cristobalite. Conversely, it is suggested that the crystallization temperature of silica gel and synthetic opal are lowered due to the reconstruction of the SiO₄ network structure by dehydration of silanol groups and water molecules. This consideration is supported by changes in Raman spectra (Fig. 6) and the FSDP positions (Fig. 7) due to heating of silica gel used in this study. From Raman spectra and the

FSDP positions, SiO₄ network structure of silica gel may be reconstructed from the 4-membered rings of SiO₄ tetrahedra to 6-membered rings at around 800 °C and then, above 1000 °C, increase of 6-membered rings of SiO₄ tetrahedra. However, even at 1200 °C, silica gel shows a clear band at around 490 cm⁻¹ attributed to the 4-membered rings of SiO₄ tetrahedra. For Nevada-DE, the Raman spectra indicate that the SiO₄ network structure may be mainly composed of 6-membered rings of SiO₄ tetrahedra at unheated and 400 °C, and then, above 600 °C, increase of the 6-membered rings of SiO₄ tetrahedra. Therefore, it is considered that the diatom shells in Nevada-DE easily crystallize to cristobalite at a lower temperature than silica gel because the SiO₄ network structure in diatom shells for unheated Nevada-DE is mainly composed the 6-membered rings of SiO₄ tetrahedra such as cristobalite and the 6-membered rings in the SiO₄ network structure increased at a lower temperature than silica gel.

CONCLUSION

The SiO₄ network structural changes and crystallization of diatom shells in Nevada-DE and Noto-DE by heat treatment were investigated using XRF, TG, XRD, ATR-IR, and Raman spectroscopy. From Raman spectra, it is presumed that the SiO₄ network structure of the unheated diatom shells in Nevada-DE are mainly composed of 6-membered rings of SiO₄ tetrahedra. In addition, from Raman spectra of heat treatment samples, the SiO₄ network structure of diatom shells in Nevada-DE is reconstructed to increase the 6-membered rings of SiO₄ tetrahedra and appear the 4- and 3-membered rings with heating, and it was clarified that the SiO₄ network structure is similar to silica glass at 1000 °C. The size of medium-range structure of diatom shells in Nevada-DE and Noto-DE were larger than those of silica glass but smaller than that of silica gel from FSDP positions. Since the FSDP position of Nevada-DE and Noto-DE is the same, the medium-range structure of Noto-DE may also compose of the 6-membered rings of SiO₄ tetrahedra. Among biogenic amorphous silicas, the size of medium-range structure of diatom shells in Nevada-DE and Noto-DE are larger than those of currently living diatom frustules and glass sponges. Biogenic amorphous silicas such as diatom shells in Nevada-DE and Noto-DE are crystallized to cristobalite at lower temperature than that of inorganic amorphous silicas such as silica gel. This reason may be that the SiO₄ network structure for diatom shells in unheated Nevada-DE is mainly composed the 6-membered rings of SiO₄ tetrahedra such as cristobalite and the 6-membered rings in the SiO₄ network structure increased at a lower temperature than silica gel.

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