

Structural changes and properties of diatomaceous earth
by heat treatment and shock compression

(邦訳：珪藻土の加熱および衝撃圧縮による構造変化と特性)

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Abstract

In this dissertation, structural changes for diatom shells contained in diatomaceous earths (DEs) by heat treatment and shock compression have been investigated. Furthermore, properties such as firing shrinkage and humidity control on DE are also investigated. These studies were carried out based on the data obtained by SEM observations, X-ray diffraction measurements, IR and Raman spectroscopies and thermal analyses. The author obtained following research results.

The water molecule and silanol groups in diatom shells are almost dehydrated after heating temperature at 600 °C but remaining in the structure of diatom shells even after shock compression at 25.3 GPa. The diatom shells are crystallized to cristobalite by heat treatment at temperature higher than 1100 °C but not crystallized to cristobalite by shock compression until 25.3 GPa. SiO₄ network structure for diatom shells changes with increasing heat-temperature, and finally its network structure become similar to that of fused silica glass after heating at 1000 °C. But there is almost no change by shock compression. Thus, effect of these structural changes for diatom shells by heat treatment is larger than that by shock compression at up to 25.3 GPa.

The amorphized clay minerals in DE crystallize to wollastonite by reaction with a calcium source, which greatly contributes to the suppression of firing shrinkage. The structural change of clay minerals in DE gives considerable influence on the humidity control property. Therefore, it could be concluded that the structural changes of clay minerals in DE at heat-temperature up to 1000 °C are greatly influence on the properties such as firing shrinkage and humidity control on DE.

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

Despite a lot of experimental results on amorphous silica compounds regarding their network structures before and after heat treatment and their transformation temperatures to cristobalite (Kamiya et al., 2000; Arasuna et al., 2013; Fukushima, 2018), there are very limited number of reports which is relating to changes in the ring structure and their crystallization of fossilized diatom shells in DE with increasing temperature. The knowledges on the structural changes of diatom shells contained in DE by heating will give us important information for various phenomena occurring on the Earth, such as diagenesis and metamorphism of rock.

In this study, heat treatments up to 1200 °C were performed on DEs from Nevada, U.S.A. (Nevada-DE) and Noto region, Ishikawa Prefecture, Japan (Noto-DE). The structural changes of diatom shells were characterized in detail based on the data obtained by using XRF, TG, XRD, ATR-IR, and Raman spectroscopy. Changes in network structure of SiO₄ and crystallization of diatom shells in the DEs by heat treatment were discussed and compared with the structural evolutions of silica gel with temperature. Raman spectrum on unheated Nevada-DE specimen indicated the SiO₄ network structure in diatom shells could be characterized by 6-membered rings of SiO₄ tetrahedra (a broad band at around $\nu = 450 \text{ cm}^{-1}$). Upon heating, 6-membered rings of SiO₄ tetrahedra became rigid and dominant in framework structures of diatom shells for Nevada-DE. In addition, 3- and 4-membered rings of SiO₄ tetrahedra (bands at around $\nu = 600 \text{ cm}^{-1}$ and 490 cm^{-1} , respectively) appeared in SiO₄ network structure with increasing heat-treatment temperature, and finally its network structure became similar to that of fused silica glass after heating at 1000 °C (Fig. 1). The sizes of structural units in a medium-range were

increased in the order, that is silica gel, diatom shells and fused silica glass. The same Q values of first sharp diffraction peak (FSPD) positions for Nevada-DE and Noto-DE indicate that the size of framework structures for diatom shells in both of DEs were virtually identical. The framework structures are namely characterized by presence of 6-membered rings of SiO_4 tetrahedra by comparing the previous studies on the structures of some SiO_2 non crystalline materials (Galeener and Gessberger, 1983; Sharma et al., 1984). Among biogenic amorphous silica compounds, the size of medium-range structural units for diatom shells in Nevada-DE and Noto-DE were larger than those of currently living diatom frustules (Arasuna and Okuno, 2018) and glass sponges (Arasuna et al., 2018). This indicates that the rings in living creatures are the same 6-membered rings as DE, but are more distorted and thus shrunk than those in DEs. Biogenic amorphous silica compounds such as diatom shells in Nevada-DE is crystallized to cristobalite at lower temperature than inorganic amorphous silica compounds such as silica gel (Fig. 2). This is due to similarity among frameworks of biogenic amorphous silica compounds and cristobalite, both are made of 6-membered rings of SiO_4 tetrahedra.

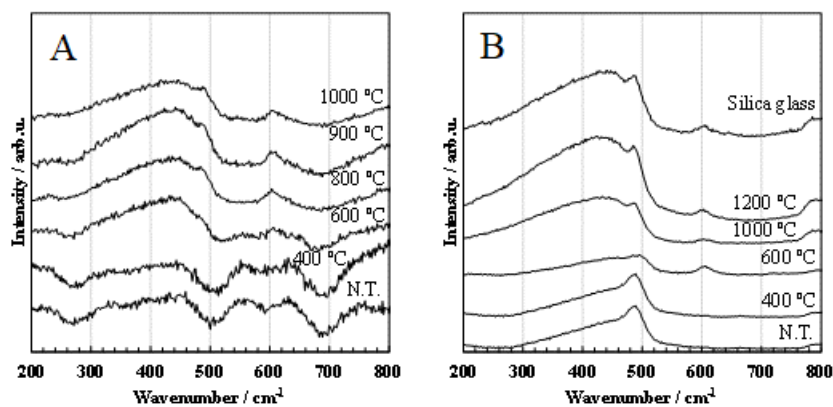


Fig. 1. Raman spectra for Nevada-DE (A) and silica gel (B) heated at various temperatures with that for unheated fused silica glass as reference. N.T.; No heat treatment.

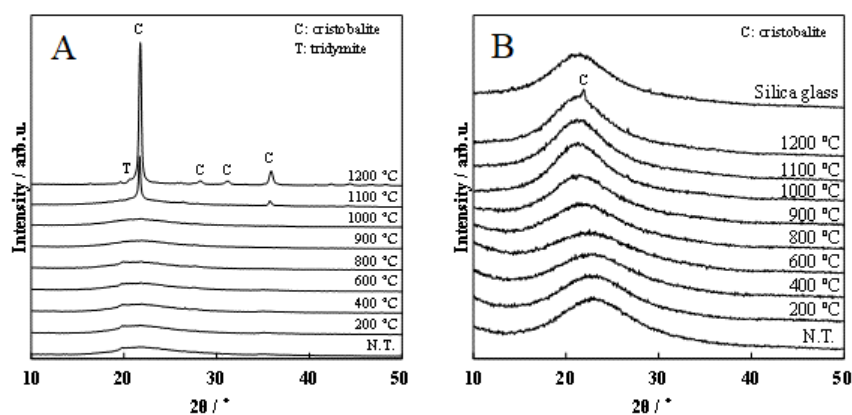


Fig. 2. XRD profiles for Nevada-DE (A) and silica gel (B) heated at various temperatures with that for unheated fused silica glass as reference. N.T.; No heat treatment.

Shock compression of diatomaceous earth

There are many reports on structural changes of anhydrous or hydrous amorphous silica compounds by shock compression (Okuno et al., 1999; Shimada et al., 2002; Inoue et al., 2010; Arasuna et al., 2016). However, shock-induced structural changes of biogenic amorphous silica compounds including DE have not been investigated until now. Investigation of responses from biogenic amorphous silica compounds for shock compression also will give us useful insights on shock transformation of amorphous silica geomaterial such as opal and preparation of new materials from biogenic amorphous silica compounds.

In this study, shock compression experiments up to 25.3 GPa were performed on Nevada-DE. Structural changes of the SiO_4 network in diatom shells in the Nevada-DE by shock compression were discussed. Their structural changes were characterized in detail based on the results obtained by XRD, ATR-IR and Raman spectroscopy. The smectite in Nevada-DE was amorphized after shock compression at 21.5 GPa (Fig. 3).

The effect of shock compression at 21.5 GPa on the sample was equivalent to a heat treatment at 900 °C. This result indicated that an aftershock temperature for shock compression at 21.5 GPa could be close to 900 °C. The silanol groups remained in the structure of diatom shells in Nevada-DE even after shock compression at 25.3 GPa (Fig. 4). The negative shift of Q value on FSDP position for XRD pattern indicated that the size of structural units in a medium-range structure for Nevada-DE samples slightly enlarged after shock compression at pressures higher than 21.5 GPa. This change may be due to relaxation of the distorted framework structure with residual heat after shock compression.

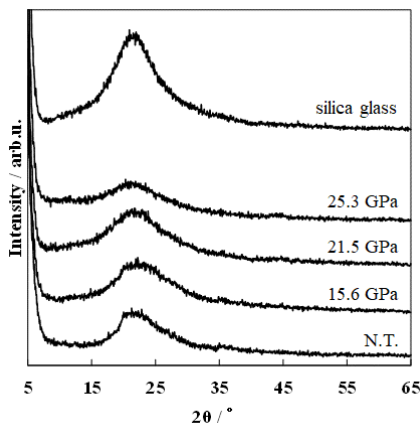


Fig. 3 XRD patterns of Nevada-DE, samples recovered after shock compressions and non-treated silica glass. N.T.; No shock treatment.

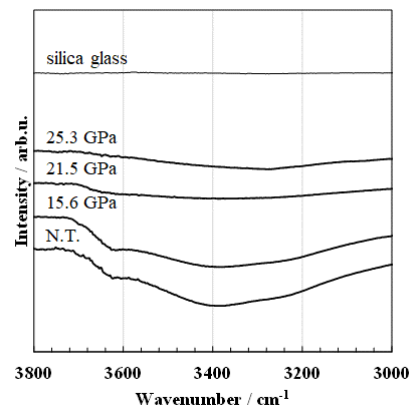


Fig. 4. ATR-IR spectra for Nevada-DE, samples recovered after shock compressions and non-treated silica glass. N.T.; No shock treatment.

Control of heat-induced shrinkage on insulating brick made of diatomaceous earth by doping calcium

The author had developed a new technology for preparing insulating bricks such as the addition of $\text{Ca}(\text{OH})_2$ before calcination and crystallization of CaSO_4 inside the brick

by heat treatment (Sasaki et al., 2011). The bricks thus yielded stand for repeated firing with respect to volume reduction and suppression of SO₂ gas generation. However, a mechanism which realized enhancement of reheat resistivity has not been well understood even now.

In this study, for establishing the technique to stabilize the quality of insulating bricks made of Noto-DE, a mechanism which suppress firing shrinkage in Ca-doped DEs was studied precisely by comparing with those on non-doped DEs from different localities. Two Noto-DE samples were collected from the Wakura layer in Nanao (Noto-DE-W) and Iizuka layers in Suzu (Noto-DE-I), Ishikawa Prefecture, Japan. The other two DE samples were obtained from Akita Prefecture, Japan (Akita-DE) and Nevada, U.S.A. (Nevada-DE). The rate of firing shrinkage for all DEs were different. However, all the Ca-doped DE samples exhibited reduction of firing shrinkage at 1000 °C with reference to non-doped samples. On all the Ca-doped DE samples, enhancement of diffraction intensity from wollastonite and reduction of background intensity were apparent with increasing calcination time (Fig. 5). From elemental maps, the distribution of Ca was not observed in the diatom shells (Fig. 6). This result indicates that diatom shells did not react with calcium sources even after calcination at 1000 °C for 10 h. Wollastonite may be uniformly crystallized in Ca-doped DEs from XRD profiles and elemental maps. The amorphized clay minerals may crystallized to wollastonite by reaction with a calcium source, which greatly contributes to the suppression of firing shrinkage.

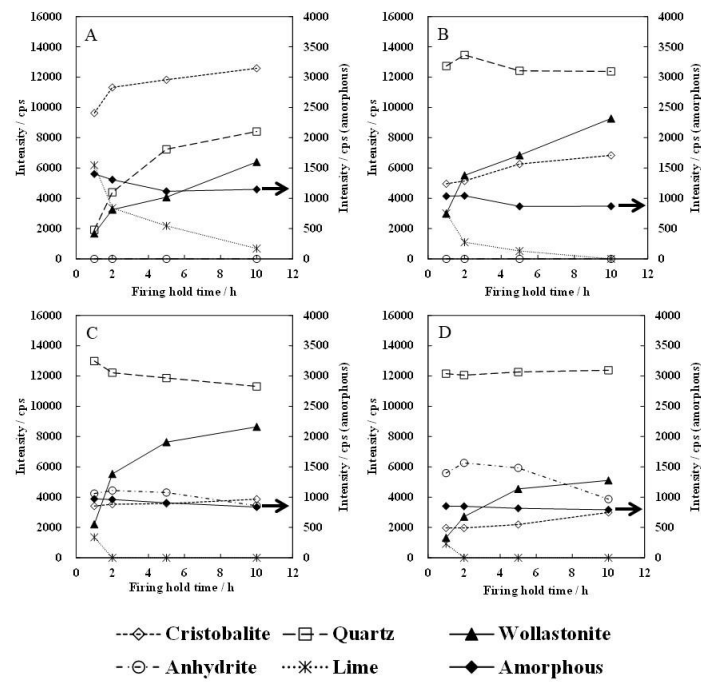


Fig. 5. Changes in XRD peak intensities for crystalline phases of specimens with 20 mass% of Ca(OH)₂ with calcination time at 1000 °C. A: Nevada-DE, B: Akita-DE, C: Noto-DE-I, and D: Noto-DE-W.

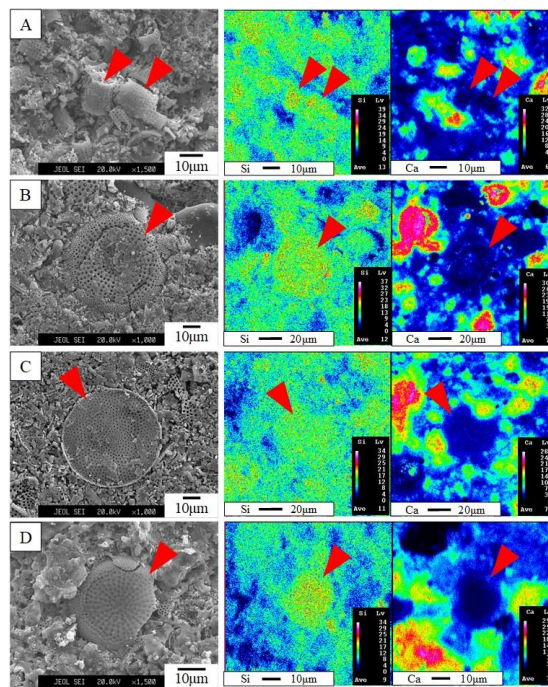


Fig. 6. SEM images and elemental maps of DE samples with 20 mass% of Ca(OH)₂ calcined at 1000 °C for 10 h. A: Nevada-DE, B: Akita-DE, C: Noto-DE-I, and D: Noto-DE-W.

Effect of heat treatment on water vapor adsorption properties of Noto-diatomaceous earth

It is also widely known that clay minerals in DE from Noto region (Noto-DE) contribute to humidity control property of plastered wall, and this property is deteriorated by calcination at 1000 °C for decrease of specific surface area (Miyamoto et al., 1997). However, the relationship between change in crystal structure of clay minerals with temperature and humidity control property of the DE have not been precisely investigated until now.

In this study, changes in the humidity control property of Noto-DE by heat treatment up to 1000 °C were discussed based on the information for crystalline structure changes of clay minerals in Noto-DE. In order to elucidate the heat treatment effects on water vapor adsorption properties of Noto-DE, the specific surface area (SSA) was measured with N₂ and H₂O, and pore size distribution and water vapor adsorption of the samples were also measured. Fractions > 75 μm and < 2 μm in size were fractionated from the samples of Noto-DE and they were calcined at various temperatures up to 1000 °C. Both fractions > 75 μm and < 2 μm showed that the SSA values measured with H₂O were larger than those with N₂. This may be caused by the chemical adsorption action on silanol radical of diatom shells and the interlayer of clay minerals. Concerning samples after particle-size classification, fractions < 2 μm showed the most water vapor adsorption (Fig. 7). This result indicates that the clay minerals that account for ca. 40% of Noto-DE have a great influence on water vapor adsorption properties. Furthermore, the reason why water vapor adsorption of Noto-DE decreased sharply at heat treatment above 800 °C may be due to dehydration and breakdown of smectite (Fig. 8). Therefore it was found that the changes in the humidity control properties of Noto-DE by heating were caused

by the dehydration and breakdown of smectite.

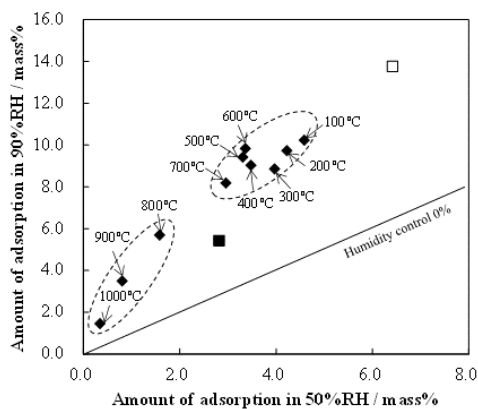


Fig. 7. Relationships between amount of adsorption in 50%RH and 90%RH of Noto-DE calcined at various temperatures (◆) and sieved fractions > 75µm (■) and < 2µm (□).

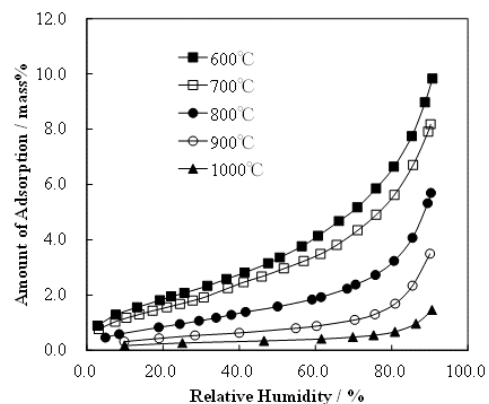


Fig. 8. Isotherms of water vapor adsorption of Noto-DE calcined at various temperatures. (a): 100-500°C, (b): 600-1000°C

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令和 4 年 2 月 4 日

学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

Structural changes and properties of diatomaceous earth by heat treatment and shock compression (邦題：珪藻土の加熱および衝撃圧縮処理による構造変化と特性)

2. 論文提出者 (1) 所 属 自然システム学 専攻

(2) 氏 名 佐々木 直哉

3. 審査結果の要旨（600～650字）

本学位論文について、令和4年1月27日の第一回審査会、及び同日、公聴会を開催した後の第二回審査会での協議の結果、以下の結論を得た。

本論文は、珪藻土の産業的応用に係る性質、特に加熱に対する応答を珪藻殻と粘土鉱物のそれぞれの要素に分解して仔細に追跡し考察しており、得られた知見は物質科学の観点からも産業的応用の見地からも高い意義が認められる。佐々木直哉氏は在学中の成果を参考論文1（焼結体の水蒸気吸着特性の変化、及びその原因）、同2（焼結体の体積減少の抑制とそのメカニズム）、及び同3（珪藻土中の珪藻殻の構造と、その加熱による変化）として報告し、更に珪藻殻の衝撃圧縮に対する挙動を実験的に示している。珪藻土中の珪藻殻に関してはその SiO_4 四面体のネットワーク構造に於いて六員環が卓越すること、及び加熱によるネットワーク構造の連続的な変化と結晶化挙動の違いを明らかにし、ネットワークの完全性と珪藻土焼結体の水蒸気吸着特性との関連、及び焼結体を構成する粘土鉱物の構造と吸湿性との関係もまた示した。焼結体の体積減少抑制技術の開発とそのメカニズム（元素移動の制御と異種結晶の析出による構造強度の保持）の解明は単に珪藻土に留まらず資源の利用を考える際のモデルケースともなりうる。本論文および参考論文2、3は英語で執筆されており、国際的なコミュニケーション能力にも不足はないと判断できる。以上より、本審査委員会は佐々木直哉氏に博士（理学）の学位を授与するに値すると判断した。

4. 審査結果 (1) 判 定 (いずれかに○印) 合格 ・ 不合格

(2) 授与学位 博士（理学）