

The structural changes and water behaviors in hydrous amorphous silica materials under high pressure and temperature

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博士論文要約

The structural changes and water behaviors in hydrous amorphous
silica materials under high pressure and temperature

(高圧力および高温下での含水非晶質珪酸塩物質の構造変化と水の挙動)

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Hydrous amorphous silica minerals including water molecules and silanols (Si-OH) in the structure are easily found on the earth surface and the sea floor. It has been reported widely that the non-crystalline opal, which is one of hydrous amorphous silica minerals, transforms to quartz via opal-C during diagenesis. In addition to this mineral, external skeletons of diatom and radiolarian are also made of hydrous amorphous silica (Okuno et al., 2003). These materials transform to diatomite and chart by deposition on the sea floor and successive metamorphism. Moreover, the water in these materials may be transported to the subduction zone. However, little is known to the structural change and water behavior in hydrous amorphous silica minerals and materials under high pressure and temperature, whereas these are important for the studies of diagenesis of hydrous amorphous silica minerals and materials, and its behavior in subduction zone.

On the other hand, Greenberg (1998) suggested that the comet is mainly formed by the silicate, complex organic refractory and H₂O. Large number of the comet would fall into the primitive earth. Therefore, the comet may bring amino acids and water to the earth from space. Moreover, water in comet may be related with the formation of early ocean. The shock-wave compression experiments of material including water (ice), silicate and amino acid are performed as the analog experiment for compression behaviors of comet on the impact event and provide much important information on the shock transformation of these materials.

In this study, silica gel was used as a model material for the external skeleton of diatom, and comet nucleus. Synthetic opal was used as a model material for the natural non-crystalline opal. High pressure and temperature experiments were conducted for silica gel and synthetic opal in order to elucidate the transformations of the materials under these extreme conditions.

Silica gel used in this study was synthesized by modifying the synthesis procedure reported by Kamiya and Sakka (1980). It was a typical sol-gel method which includes the hydrolysis, dehydration, and condensation processes of TEOS [Si(OC₂H₅)₄]. TEOS, ethanol and acetic anhydride were used for preparing the precursor compound, alcohol solution and catalyst, respectively. A synthetic opal used in this study was prepared based on the procedure reported in Okudera and Hozumi (2003) by modifying Stöber's process. This synthesis procedure includes the hydrolysis, dehydration, and condensation of TEOS in a solution of ethanol solvent with ammonia as a catalyst.

For silica gel, the static compression using multi anvil apparatus up to 10 GPa at room temperature and 100 °C and shock-wave compression experiments using keyed-powder gun up to 31 GPa were conducted. Thermal experiments for synthetic opal and silica gel were conducted by heating up to 1400 °C in an electric furnace. Then, the recovered samples after the high pressure and thermal experiments were analyzed by XRD, TG-DTA, and FTIR, Raman and NMR spectroscopies.

Silica gel and synthetic opal include the water molecules and silanol groups in the structure. The water contents of silica gel and synthetic opal estimated by ¹H MAS NMR and TG analyses are about 20 and 13 wt%, respectively. Kamiya and Nasu (1998) reported that the intermediate range structure of silica gel was mainly composed of four-membered ring of SiO₄ tetrahedra. In consonance with their report, the results of XRD and Raman analyses suggest that the intermediate order range structures of silica gel and opal used in this study are mainly formed by four-membered ring.

After the static compression for silica gel up to 10 GPa at room temperature, unlike silica glass (Hemley et al., 1986), Raman spectra for the compressed samples show the irreversible structural change. These samples show the sharpening of the Raman band around $\nu = 450 \text{ cm}^{-1}$ attributed to a symmetrical Si-O-Si stretching mode (Galeener and Geissberger, 1983; Sharma et al., 1984). ²⁹Si MAS NMR and Raman spectroscopies reveal that the buckling of the network structure under the compressions may occur. Silica gel has the lower polymerized structure with silanol [SiO_x(OH)_{4-x}]. This feature easily leads the compact network structure under compressions and makes it possible to maintain the buckled structure even after release of pressure. Consequently, the compressed samples show the irreversible structural change in contrast to silica glass. Moreover, a large number of adsorbed water molecules are released, although the considerable amount of silanol remains after compressions.

On the other hand, the samples compressed up to 5 GPa under 100 °C show the remarkable structural change despite of relatively low temperature. Under 2 GPa at 100 °C, the four-membered ring in the structure of as-synthesized silica gel is stable and slightly ordered by compression. Moreover, the ordered six-membered ring structure is newly formed. The dehydration and condensation of silanol may occur under the compression even at 2 GPa and 100 °C and lead the formation of the ordered

six-membered ring. Probably, the collapse and reconstruction of the four-membered ring require higher temperature under the compression up to 5 GPa. Under 5 GPa at 100 °C, XRD analysis shows that the compressed sample crystallizes to the coesite structure. This is also supported by the results of Raman and FTIR analyses. The silica gel sample shows the crystallization to coesite by compression under relatively low temperature compared with that of previous report (Zhang et al., 2009 etc.). Furthermore, it should be noted that sample used in this study was non-powder sample. Coesite structure is composed of four-membered rings of SiO₄ tetrahedra (Hemley et al., 1994) such as silica gel, although coesite has well-ordered crystal structure in comparison with that of silica gel. The structural similarity between coesite and silica gel may be very important for the easy crystallization of silica gel to coesite. The stability of the four-membered ring under compressions, and the dehydration and condensation of a large amount of silanol during compression promote the easy crystallization to coesite by compression under relatively low temperature and pressure despite non-powder sample.

The structural changes and the behaviors of water molecules and silanol groups in silica gel by shock compression are summarized as follow.

Up to 20.7 GPa, the almost adsorbed water molecules and silanol groups in compressed samples can remain in silica gel structure. Above this shock pressure, the structure of shock compressed samples changes significantly. Raman spectra show the broadness of the band below $\nu = 480 \text{ cm}^{-1}$, indicating that the polymerization of Si-O-Si network structure and the increase of the larger ring (>four-membered ring) structure. Moreover, above 20.7 GPa, Raman spectra show that the most germinal silanol (2OH bonded to Si) may be dehydrated, although general silanol (1OH bonded to Si) may still remain. The considerable amount of water molecules also starts to be released. The dehydration and condensation of silanol groups form the new Si-O-Si network structure. It is considered that the newly formed network structure may be mainly formed by the six-membered ring of SiO₄ tetrahedra. The high after shock temperature close to 800 °C gives a large influence on these matters. Eventually, with increasing pressures, the intermediate structure of the compressed samples approaches to that of silica glass, of which the average structure is a six-membered ring. However, as compared to the as-prepared silica gel, 60 % of silanol and 20 % of the water molecules remain even

after the shock compression at 27.2 GPa. The residual silanol groups may be attributed to the mutually hydrogen bonded silanol and the silanol hydrogen bonded to water molecules. After the compression at 30.9 GPa, these types of silanol groups and very small amount of water molecules may remain yet and the intermediate structure of the compressed sample is similar to that of silica glass.

The structural evolution and water behavior in synthetic opal and silica gel under heat treatment can be summarized as follows. These results are helpful for the interpretation of the high-pressure experiments.

For both opal and silica gel, the dehydration and condensation of a number of surface silanols form new Si-O-Si linkages as three-membered rings by heat treatment up to 400 °C. However, the quantity of the three-membered ring in the heat-treated silica gel may be lower than opal. Water molecules are released and silanols are completely dehydrated by heat treatment up to 800 °C. The network structure of sample treated at 800 °C has a wide range Si-O-Si angle distribution as observed in silica glass structure. However, the small three- and four-membered rings are still observed. The amount of these small rings decreases by the heat treatment above 1000 °C. It may be due to the reconstruction of the network structure by the thermal effect. Above 1000 °C, the structure of heat-treated silica gel and opal is similar to that of silica glass. By thermal treatment at 1300 °C, the structures of opal and silica gel transform to that of low-cristobalite. However, minor evidence of low-tridymite stacking is observed in the heat-treated opal at 1400 °C.

In conclusion, obtained results may indicate a possibility that the hydrous amorphous silica materials such as the external skeleton of diatom can crystallize into high pressure phase such as coesite easily in the subduction zone. The temperature in the subduction zone becomes higher with increasing depth and is generally higher than experimental condition in this study. The temperature may give larger influence on the dehydration of silanol than pressure. The results of thermal treatments for silica gel and opal suggest that silanol may remain under the subduction zone up to 800 °C. Based on the findings from the shock experiments for silica gel, it is presumed that the water in comet may endure the shock compression and high shock temperature. Silicate minerals in comet may transform to glass like structure, and the water may promote this transformation.

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