

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

メタデータ	言語: eng 出版者: 公開日: 2017-10-05 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/38974

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博士論文

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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Abstract

The structural change and water behavior in synthetic silica gel and opal under high pressure and temperature conditions are investigated. For silica gel, static compression and shock-wave compression experiments were conducted in this study. Thermal treatments by heating up to 1300 °C for silica gel and opal were also conducted. The static compression for silica gel up to 10 GPa at room temperature may cause the buckling of silica gel network structure. Moreover, water molecules in silica gel can be released easily by compression, although the considerable amount of silanol (Si-OH) remains even after compression. The dehydration and polymerization of silanol may require the high temperature condition. Under the compression at 5 GPa and 100 °C, the crystallization of silica gel to coesite occurs easily. The network feature of silica gel and the presence of silanol may promote the easy crystallization to coesite.

After shock temperature for the shock-wave compressions of silica gel may be relatively high even at 20.7 GPa of the shock pressure and give a great influence on the silica gel structure. Based on the result of thermal treatments for silica gel samples, the shock temperature may be close to 800 °C at this pressure. Above 20.7 GPa, the intermediate structure of compressed samples becomes greater due to the thermal effect. The dehydration and polymerization of silanol may occur and lead the formation of new Si-O-Si network structure, which contains larger ring (>four-membered ring) of SiO₄ tetrahedra.

Under the heat treatments for synthetic silica gel and opal, the upsizing of intermediate structure and the dehydration of water molecules and silanol occur in the range of 400-800 °C. At 1300 °C, the samples crystallize into low-cristobalite with minor quantity of low-tridymite.

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. For example, chalcedony, agate and opal are well known hydrous silica minerals. Especially, hydrous amorphous silica minerals, such as non-crystalline opal can include a great number of water molecules and silanols. It has been reported widely that the non-crystalline opal denoted as opal-A transforms to quartz via opal-C during diagenesis. In addition to these silica minerals, external skeletons of diatom and radiolarian are also made of hydrous amorphous silica. These materials transform to diatomite and chart by deposition on the sea floor and successive metamorphism. Moreover, the water in these hydrous materials may be transported to the subduction zone. However, little is known to the structural change and water behavior in hydrous amorphous minerals under high pressure and temperature, whereas these are important for the studies of diagenesis of hydrous mineral and its behavior in subduction zone.

On the other hand, Greenberg (1998) suggested that the comet is 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 nucleolus. Synthetic opal was used as a model material for the natural opal-A and other natural hydrous silica minerals. High pressure and temperature experiments were conducted for silica gel and synthetic opal in order to elucidate the transformations of these materials under these extreme conditions.

Silica gel used in this study was synthesized by 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 1300 °C in a 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. Based on the XRD and Raman analyses, the intermediate order range structures of silica gel and synthetic opal are mainly formed by four-membered ring structure of SiO₄ tetrahedra.

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. The compressed 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). The buckling of the network structure under the compression 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 Si-OH remains after compressions.

On the other hand, the samples compressed under 100 °C show the considerable 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 silanol groups may be dehydrated under the compression even at 2 GPa

and 100 °C. Therefore, the dehydration and condensation of silanol may lead the formation of the ordered six-membered ring. Probably, the collapse and reconstruction of the four-membered ring require higher temperature. Under 5 GPa at 100 °C, XRD analyses show that the compressed sample crystallizes to the coesite structure. This is also supported by results of Raman and FTIR analyses. The silica gel sample shows the crystallization to coesite by compression under relatively low temperature and short duration compared with that of previous report (Zhang et al., 2009 etc.). Furthermore, it is first report for the easy crystallization to coesite from non-powder sample. Coesite structure is composed of four-membered rings of SiO₄ tetrahedra such as silica gel (Hemley et al., 1994), 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 a large amount of silanol may also promote the easy crystallization to coesite by compression under relatively low temperature 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 of a number of surface silanols by heat effect and polymerization to form new Si-O-Si linkages as three-membered rings by heat treatment up to 400 °C are observed in this study. However, the quantity of the three-membered ring in the heat-treated silica gel may be lower than opal. At heat treatment up to 800 °C, water molecules are released and silanols are completely dehydrated. It may lead the formation of the network structure. This network contains a wide range Si-O-Si angle distribution as observed in silica glass structure, although small three- and four-membered rings are still relatively abundant. At heat treatment above 1000 °C, the structures of opal and silica gel approach that of silica glass. In addition, the amount of small rings decreases. This structural change may be due to the reconstruction of the network structure by the thermal effect. Above 1300 °C, the structures of opal and silica gel change to that of low-cristobalite. However, minor evidence of low-tridymite stacking is observed in heat-treated opal at 1400 °C.

In conclusion, obtained results may indicate a possibility that the hydrous amorphous silica minerals and 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. Based on the result of thermal treatments for silica gel and opal, 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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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。）

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

（和訳）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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3. 審査結果の要旨（600～650字）

○ 本学位論文について、平成26年1月30日に、第1回審査会を開催し審査方針等について検討した。同日、公聴会を開催した後、第2回審査会を開き、協議の結果、以下の結論を得た。

本論文は、含水非晶質珪酸塩物質のシリカゲル及びオパールを合成し、得られた試料についてマルチアンビル高圧力装置による静水圧縮実験、及び一段式火薬銃による衝撃圧縮実験並びに加熱実験を行い、高圧・高温下におけるナノスケールの構造変化とそれに伴う水の詳細な挙動を明らかにしたものである。本研究で得られた含水非晶質シリカの高圧・高温下での構造変化と、そこでの水の役割についての研究成果は全く新しい知見を含み、地球の上部マントルでの物質変化と水の役割や彗星の地球衝突時の含水物質の変化について重要で新しい情報を与えるものである。特に、高圧力下での含水シリカの構造変化については、X線回折測定、ラマン分光測定、NMR測定など多彩な手法により得られた情報から、非常に精密な解析を行っているほか、水の存在下でシリカゲルが比較的低い温度・圧力条件で石英の高圧相であるユーサイトに変化することを見出している。これらの研究は地球科学分野のみならず物質科学の分野の発展に大きく寄与すると期待できる。なお、成果の一部は既に英文の国際誌に掲載されている他、海外での国際会議においても研究発表を行い、国際的なコミュニケーション能力も十分である。よって、本審査委員会は本論文の成果は、荒砂 茜氏に博士（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）