

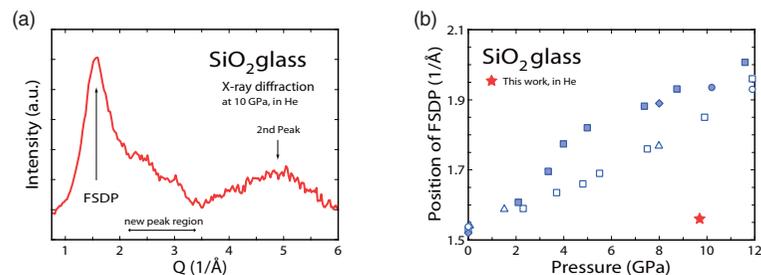
## Helium Prevents Compaction of Voids in Silica Glass under High Pressure

**S**iO<sub>2</sub> glass has a network structure with a significant amount of interstitial voids. X-ray diffraction measurements show that the pressure-induced shift of the first sharp diffraction peak of SiO<sub>2</sub> glass in helium is significantly smaller than normal, suggesting that voids are prevented from contracting because helium atoms penetrate into them. The results of volume and Raman scattering measurements are consistent with those of X-ray diffraction measurements. These results may affect discussions on the Earth's evolution as well as interpretations of various high-pressure experiments, and also lead to the creation of new materials.

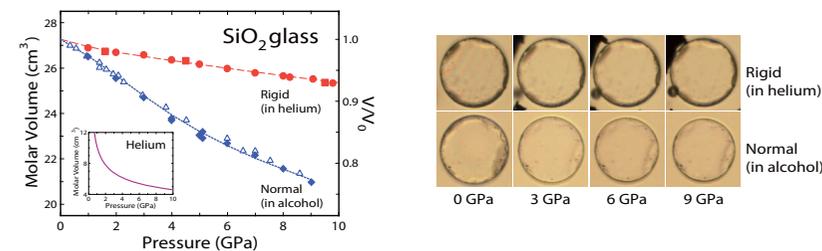
SiO<sub>2</sub> is an archetypal oxide as well as an archetypal glass-forming material, and is also the most abundant component of terrestrial rocks. Therefore, SiO<sub>2</sub> glass has been studied extensively in various fields of physical sciences. SiO<sub>2</sub> glass is compressible among silicates (or oxides) because its structure has a significant amount of interstitial voids. Helium is monatomic and the smallest molecule, and therefore is used as a light inert gas. It is also widely used as the ideal pressure medium in high-pressure experiments. Its isotopic ratio is useful as a tracer of the Earth's evolution. Here we report an anomalous behavior of SiO<sub>2</sub> glass in helium under high pressure [1].

X-ray diffraction measurements were carried out for a sample compressed in a diamond-anvil cell by using an angle-dispersive method with 25-keV monochromatic X-rays and an imaging plate detector at BL-18C. The X-ray diffraction pattern of SiO<sub>2</sub> glass in helium obtained at 10 GPa is shown in Fig. 1(a). This pattern is significantly different from normal patterns. As shown

in Fig. 1(b), the pressure-induced shift of the first sharp diffraction peak (FSDP) in helium is significantly smaller than those in other mediums and without mediums. The FSDP is associated with the presence of intermediate-range order and is considered to arise from the periodicity of ordering of the rings consisting of SiO<sub>4</sub> tetrahedra. At pressures below 20 GPa, SiO<sub>2</sub> glass has a network structure consisting of SiO<sub>4</sub> tetrahedra. The SiO<sub>4</sub> tetrahedra are highly incompressible, and the high compressibility of SiO<sub>2</sub> glass is ascribed to changes in the intermediate-range order, i.e., compaction of voids. Therefore, this small shift of the FSDP is considered to be caused by occupation of voids by helium atoms. As shown in Fig. 1(a), an indication of a peak is also observed at around 2.2–3.4 Å. In this region, no peak is observed at ambient pressure, and a new peak appears at high pressures. However, the new peak has not been observed so far at about 2 GPa, suggesting that the structure of SiO<sub>2</sub> glass in helium at 10 GPa is not identical to the normal structure at 1–2 GPa.



**Figure 1**  
(a) The X-ray diffraction pattern of SiO<sub>2</sub> glass in helium measured at 10 GPa. An indication of a new peak is observed between 2.2–3.4 Å<sup>-1</sup>. No major changes in the second peak at around 5 Å<sup>-1</sup> are observed as normal. (b) Pressure dependence of the position of the FSDP of SiO<sub>2</sub> glass. The FSDP position in helium (red star) is significantly different from those in previous studies. The blue open and filled symbols represent the FSDP position at room temperature and at high temperatures or under conditions where the structure and/or deviatoric stresses have been relaxed, respectively, reported in the literature. Since helium is in a liquid state at 10 GPa, the FSDP position was not affected by deviatoric stresses.



**Figure 2**  
Pressure dependence of the volume of SiO<sub>2</sub> glass. The red and blue filled symbols represent our data in helium and methanol-ethanol, respectively. The blue open symbols and dotted line represent the data in methanol-ethanol in the literature. The photographs compare the change in the size of the bulk sample compressed in the two mediums. While the samples are almost the same size, about 80 μm in diameter, at 0 GPa, the sample in methanol-ethanol is obviously smaller than that in helium at 9 GPa.

The volume change ( $V/V_0$ ) was determined by measuring the change in size of the bulk sample. As shown in Fig. 2, the volume change of SiO<sub>2</sub> glass in helium is much smaller than normal. This low compressibility of SiO<sub>2</sub> glass in helium is consistent with the small shift of the FSDP. The result of Raman scattering measurements is also consistent with those of X-ray diffraction and volume measurements. From the volumes of SiO<sub>2</sub> glass and helium in Fig. 2, the helium solubility in SiO<sub>2</sub> glass is estimated to be between 1.0 and 2.3 mol per mole of SiO<sub>2</sub> glass at 10 GPa. The maximum solubility of helium in SiO<sub>2</sub> glass has so far been estimated to be 0.1 mol per mole of SiO<sub>2</sub> glass (at 1–2 GPa), based on measurements up to about 0.1 GPa. Moreover, gas solubilities are expected to decrease drastically at higher pressures due to compaction of voids. These well-accepted models, however, cannot explain our volume measurements.

Our results may affect discussions on the Earth's evolution. The fact that helium solubility in SiO<sub>2</sub> glass at high pressures is completely different from the estimation based on the data at low pressures suggests

the necessity of reconsidering conventional models on degassing from the mantle and other relevant events in the Earth's history. Our results also suggest the possibility that a helium medium may affect the compression behavior of materials with voids. When helium atoms occupy these voids, the materials are compressed not only from outside but also from inside. This is very different from normal compression. Therefore, in addition to the effects on compressibilities, applying pressure in helium could be an interesting way to synthesize novel phases.

### REFERENCE

- [1] T. Sato, N. Funamori and T. Yagi, *Nature Communications* 2 (2011) 345.

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