Oxygen *K*-edge X-Ray Raman Scattering Study of $MgSiO_3$ Glass at High Pressure

$MgSiO_3$-rich silicate melts can serve the model system for the primary components of the Hadean magma ocean, playing essential roles in the chemical differentiation of the early Earth. Silicate melts at the top of the transition zone and the core-mantle boundary have significant influences on the dynamics and properties of Earth's interior. Diverse macroscopic properties of silicate melts in Earth's interior, such as density and crystal-melt partitioning, depend on their short-range local structures at high pressures and temperatures. In spite of the essential roles of silicate melts in many geophysical and chemical problems, their nature under the conditions of Earth's interior including the densification mechanisms and the atomistic origins of the macroscopic properties at high pressures is not well understood. This is mostly because of their inherent structural disorder and the lack of suitable experimental probes of atomic structure of melts at high pressures.

Formation of tricluster (oxygen triply coordinated by framework cations, such as Al and Si) is known to be one of the dominant factors affecting the melt properties at high pressure. The presence of tricluster can account for the anomalous pressure-induced changes in viscosity and oxygen diffusivity and may significantly enhance the partitioning coefficient of an element between crystals and Mg-silicate melts in Earth's interior and probably explain the low solubility of noble gases in the melt at high pressure. The formation of five- and sixfolded silicon ($^{[5,6]}$Si) in the highly depolymerized $MgSiO_3$ glass is expected to be associated with the formation of the oxygen tricluster, considering similar densification behavior of Si with the fully polymerized silicates. However, experimental evidence for its formation in the silicate melts and glasses at high pressure is lacking. Synchrotron X-ray Raman scattering (also known as inelastic X-ray scattering) with diamond anvil cells (DACs) provides detailed information on the pressure-induced electronic bonding changes for low-z elements in amorphous oxides. Oxygen *K*-edge X-ray Raman scattering is currently the only available *in situ* experimental technique to directly reveal the pressure-induced electronic bonding changes around oxygen atoms in oxide glasses. We explore the local atomic structures of $MgSiO_3$ glass (as a precursor to Mg-silicate melts) using high-pressure X-ray Raman spectroscopy up to 39 GPa where high-pressure oxygen *K*-edge features suggest the formation of tricluster oxygens (oxygen coordinated with three Si frameworks; O) above 20 GPa [1].

While detailed experimental setups can be found in our recent report [1], $MgSiO_3$ glass was loaded into the sample chamber of a Be gasket in a DAC. The X-ray Raman spectra were collected at beamline **BL12XU** of the SPring-8, beamline 13ID-C of Geo Soil Enviro Consortium for Advanced Radiation Sources, and beamline 16ID-C of the High Pressure Collaborative Access Team of the Advanced Photon Source. Figure 1 presents the oxygen *K*-edge spectra of $MgSiO_3$ glass where a dominant feature at 538–539 eV shows negligible changes in the pressure range between 1 atm and approximately 12 GPa. Above 20 GPa, the spectra, however, shows a distinct feature at ~544–545 eV, wherein the spectral features gradually shift to higher energies with increasing pressure. The occurrence of the spectral feature near 545 eV at high pressures may stem from a variety of pressure-induced structural changes in the $MgSiO_3$ glass, such as the formation of the $^{[3]}$O tricluster, an increase in the Mg-O distance, reduction in NBO, and formation of oxygen linking $^{[4]}$Si and highly coordinated silicon, such as $^{[4]}$Si–O–$^{[5,6]}$Si and $^{[6]}$Si–O–$^{[6]}$Si. By comparing these features with those for the known crystalline $MgSiO_3$ and SiO_2 polymorphs with varying oxygen configurations and topology (i.e., bond angle and length), most of the features relevant to the local oxygen configurations observed for the crystalline phases at high pressure, including both the specific bond angles, length effect of crystals, edge-sharing oxygen (537 and 541 eV), and $^{[6]}$Si–O–$^{[6]}$Si (543 eV), cannot explain the significant changes observed for the glasses at high pressures. In particular, pressure-induced changes in the Mg–O distance or the formation of $^{[4]}$Si–O–$^{[5,6]}$Si because of the reduction in NBO can only partially contribute to the occurrence of the spectral features at 545 eV. We suggest that the feature at 545 eV in the $MgSiO_3$ glass at pressures above 20 GPa corresponds to the formation of the triply coordinated oxygen and changes in the short- to medium-range structures that are associated with the formation of the triply coordinated oxygen (i.e., formation of a three-member ring, an increase in bond length, and a decrease in bond angle). The schematic atomic configuration for the oxygen triclusters is also shown in the inset of Fig. 1.

The current results suggest the formation of the oxygen triclusters and associated changes in the

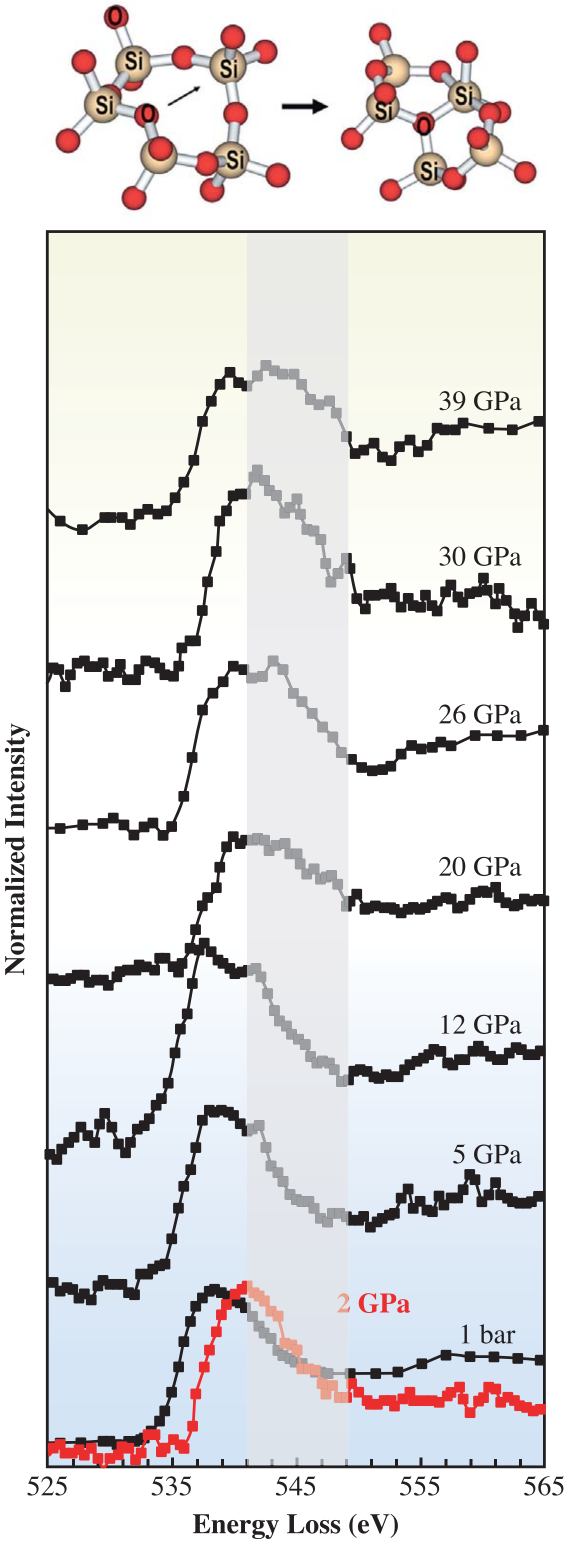

Fig. 1. Oxygen *K*-edge X-ray Raman spectra for $MgSiO_3$ glasses at high pressures [plotted as energy loss (incident energy−elastic energy) *vs.* normalized scattered intensity]. Grey area represents energy range from 543 eV to 551 eV. The schematic mechanism for the formation of the oxygen tricluster is also shown on top of the spectra. Red and yellow spheres refer to oxygen and silicon atoms, respectively.

atomic configuration in short-to-medium range in the $MgSiO_3$ glass at high pressure. These pressure-induced densification certainly affects the thermodynamic (e.g., density, molar volume, and crystal-melt partitioning) and transport properties of silicate melts (e.g., viscosity and diffusivity) in the Earth's interior. The formation of oxygen triclusters can be an efficient densification mechanism in the $MgSiO_3$ melt and may explain the atomistic origin of the high-density Mg-silicate melts at the core-mantle boundary [2,3]. As Changes in the local electronic structure and composition of silicate melts are believed to promote the partitioning of elements between crystalline phases and melts in the Earth's mantle [4,5]. The increase in the fraction of the oxygen triclusters with smaller member rings results in a reduced free volume needed to host elements that are more incompatible. That is, the triclustered oxygens increase the crystal-melt partitioning coefficient of elements, such as radioactive nuclides.

Sung Keun Lee

School of Earth and Environmental Sciences,
Seoul National University, Korea

E-mail: sungklee@snu.ac.kr

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