

# Pressure-induced changes in local electronic structures of SiO<sub>2</sub> and MgSiO<sub>3</sub> polymorphs: Insights from ab initio calculations of O *K*-edge energy-loss near-edge structure spectroscopy

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## ABSTRACT

Despite its important geophysical implications, direct probing of the local electronic structure of mantle minerals, such as MgSiO<sub>3</sub> perovskite and post-perovskite is experimentally challenging. Recent advances in ab initio calculations have allowed us to explore the details of the local electronic bonding structure around oxygen in MgSiO<sub>3</sub> polymorphs in Earth's interior. Here, we calculate the O *K*-edge energy-loss near-edge structure (ELNES) spectra for SiO<sub>2</sub> and MgSiO<sub>3</sub> polymorphs (i.e.,  $\alpha$ -quartz, stishovite, enstatite, ilmenite-type MgSiO<sub>3</sub>, MgSiO<sub>3</sub> perovskite, and post-perovskite) using ab initio calculations based on the full-potential linearized planewave (FP-LAPW) method. The calculated O *K*-edge ELNES spectra for SiO<sub>2</sub> and MgSiO<sub>3</sub> polymorphs show characteristic oxygen *K*-edge features caused by distinctive local atomic configurations and topology around oxygen, and are in good agreement with previous experimental O *K*-edge X-ray Raman scattering (XRS) results. The O *K*-edge ELNES spectra for  $\alpha$ -quartz and enstatite show similar edge features at ~538 eV, which is characteristic of corner-sharing oxygen sites (<sup>4</sup>Si-O-<sup>4</sup>Si). The spectra for stishovite and ilmenite-type MgSiO<sub>3</sub> show edge features with double peaks at ~537–538 and ~541–543 eV due to an electronic excitation from an oxygen in edge-sharing topology. The spectrum for MgSiO<sub>3</sub> perovskite shows a broad peak spanning from ~538 to ~543 eV, which results from corner-sharing oxygen with two six-coordinated silicon (<sup>6</sup>Si-O-<sup>6</sup>Si). The calculated O *K*-edge ELNES spectrum for MgSiO<sub>3</sub> post-perovskite shows a predicted main feature at ~543–545 eV, approximately 3 eV higher than that of MgSiO<sub>3</sub> perovskite. These O *K*-edge features systematically shift to higher energy with increasing degree of densification in atomic arrangement in the polymorphs (from enstatite, ilmenite, perovskite, to post-perovskite), indicating an increase in the energy of unoccupied oxygen 2*p*-state with pressure. The calculated O *K*-edge spectra also show the effect of densification on the changes in the edge features for the crystallographically distinct oxygen sites: the features for the corner-sharing oxygen move to higher energy from enstatite, perovskite, to post-perovskite. A drastic peak shift for edge-sharing O atoms in ilmenite-MgSiO<sub>3</sub> and post-perovskite is also observed. These results confirm that the oxygen *K*-edge features at ~540–550 eV for MgSiO<sub>3</sub> glass at pressures above ~20 GPa can be due to densification of the atomic configurations around oxygen in melt networks associated with enhanced proximity between oxygen atoms. The current methods also shed light on a unique opportunity to probe the pressure-induced electronic bonding transitions and topology in diverse simple and complex oxides in Earth's interior using ab initio calculations of O *K*-edge ELNES spectra.

**Keywords:** MgSiO<sub>3</sub> polymorphs, X-ray Raman scattering, energy-loss near-edge structure, high pressure, ab initio calculations