

Provenance of gem corundum: A global LIBS study

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Laser-Induced breakdown spectroscopy (LIBS) is a minimally destructive analytical technique that provides a rich geochemical fingerprint to use in determining gem provenance. The provenance of gem corundums is investigated using LIBS analyses in Ar using a 1064 nm Nd-Yag Laser. Resulting spectra were interpreted using a multivariate data analysis technique, Principal Component Analysis (PCA). Rubies and sapphires from three general tectonic regions are compared: (1) Gondwana belt represented by samples from Sri Lanka, Southern India (Mysore), Tanzania, and Madagascar, (2) Himalayan belt represented by samples from Afghanistan, Pakistan, Vietnam, and Myanmar, and (3) other continents represented by samples from North America (Wyoming, Montana, and North Carolina, USA), northwestern Russia, and Australia. LIBS spectra of these samples will be used to determine variability within (1) a mine/locality, (2) a geographic region, (3) a tectonic region, (4) geologic occurrence. Biotite gneiss, fuschite with and without zoisite, marble, and phlogopite schist are the matrix assemblages that will be used in analyzing different geologic occurrences. Preliminary results on a small sample set demonstrate that LIBS spectra effectively distinguish between gem corundums from India, Myanmar, Australia, and Sri Lanka.

The pressure-induced structural changes in silicate glasses at high pressure: Insights from solid-state NMR and First-principle calculations

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Recent advances in solid-state NMR and first-principle calculations allow us to explore the previously unknown details of local atomic structure and electronic environments of silicate glasses at high pressure. Here, we report recent progress that we have made on the effect of Na content on the pressure-induced structural changes in partially depolymerized aluminosilicate glasses using 2-dimensional triple-quantum magic-angle spinning (3QMAS) NMR spectroscopy. We also explored the pressure-induced changes in local electronic bonding structure of diverse silicates using the first-principle calculations to achieve better insight into the experimental inelastic x-ray scattering (IXS) for silicate glasses.

The ²⁷Al and ¹⁷O MAS and 2D 3QMAS NMR spectra for peralkaline Na-aluminosilicate glasses quenched from melts at high pressure show that the degree of polymerization increases with increasing pressure from 1 atm to 8 GPa but decreases with Na content as evidenced by a decrease in Na-O-¹⁴Si and a subsequent increase in ¹⁴Si-O-¹⁵, ⁶Al fraction with increasing pressure. Whereas the proportion of high energy cluster, ¹⁴Al-O-¹⁴Al, decreases with increasing pressure, its fraction is non-negligible at 8 GPa, implying stability of bridging oxygen cluster at high pressure should be redefined. The ²⁷Al and ¹⁷O quadrupolar coupling constants of atomic clusters in the glasses increase non-linearly with pressure, suggesting an increase in topological disorder [1]. The calculated oxygen K-edge electronic excitation spectra for silicates at high pressure show the distinct oxygen K-edge features for diverse oxygen environments in silicates. These results suggest that the previous assignment of a distinctive oxygen K-edge feature at 545 eV in the IXS spectrum for Mg-silicates as tricluster at high pressure above 20 GPa is likely to be correct [2].

- [1] Lee, S.K. (2004) *J. Phys. Chem. B* **108**(19), 5889–5900.
[2] Lee, S. K. (2008) *PNAS* **105**(23), 7925–7929.