

TRACKING GLASS STRUCTURE IN IDPS WITH O-XANES. Z. Gainsforth^{1,†}, A. L. Butterworth¹, C. E. Jilly-Rehak¹, M. A. Marcus², A. J. Westphal¹, ¹Space Sciences Laboratory, University of California, Berkeley, CA 94720, ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, [†]e-mail: zackg@ssl.berkeley.edu.

Introduction: Amorphous silicates can be formed and/or altered via different mechanisms (melting, condensation, irradiation, corrosion, collision). Different mechanisms may leave signature chemical compositions, and/or imprints in the bonding environments of specific atomic species. For example, different oxygen fugacities could be recorded as Fe oxidation, or silica polymerization could vary with formation temperature and mechanism. X-ray Absorption Near-Edge Spectroscopy (XANES) is a powerful technique for studying chemical bonding and atomic environments in amorphous systems. Here we use XANES at the oxygen K-edge to study silicates in interplanetary dust particles (IDPs), combining experimental with modeled spectra. For amorphous silicates within equilibrated aggregates (EAs) [1] and Glass with Embedded Metals and Sulfides (GEMS) [2], O-K XANES promises to address several questions: In principle, it should be able to differentiate between phases with medium-range order from those without any order which could distinguish between highly unequilibrated amorphous phases (irradiated, corroded) from more equilibrated glasses (melt formation). It may be possible to detect and study the presence of H in the silicate through the O-H bonds which would be useful for identifying alteration in a nebular environment, such as solar wind implantation. Finally, just as Si-K XANES has been used to constrain the presence of silicone oil in interplanetary dust particles (IDPs)[3], O-XANES can detect silicone oil contamination in IDPs, and has been used to distinguish aerogel contamination in samples returned by the Stardust mission [4]. Such contamination can be difficult to detect using other methods. The primary difficulty in using O-K XANES is that every oxygen atom contributes to the spectrum. While this means that the O-XANES is potentially very information rich, it also means that interpretation of the spectrum requires simultaneous modeling of all oxygen coordination environments present in the sample.

Methods: We carried out density functional theory (DFT) calculations using the Molecular Foundry (MF) Vulcan and Nano compute clusters on the Lawrence Berkeley Laboratory (LBL) supercluster. We simulated oxygen K-edge XANES using the XSPECTRA package [5] within the Quantum Espresso (QE) DFT package [6]. We used the excited core hole (XCH) approximation where a 1s electron is moved to the valence band [7] to simulate the interaction between the excited electron and the positively charged core hole. We created the XCH pseudopotential using the atomic package [9] and used the PBE exchange-correlation functional [8]. We simulated forsterite and enstatite spectra by summing together spectra for each O atom computed individually. Starting from a relaxed structure we replaced one O atom with the XCH pseudopotential while keeping an unexcited pseudopotential for all other O atoms. The computation was then repeated for every symmetrically inequivalent O atom in a 2x2x1 supercell which provided a simulation box of ≈ 100 atoms and ≈ 1 nm on an edge. We

tested spectral convergence with regard to k-point sampling, supercell size and energy cutoffs. An energy scaling of $\approx 10\%$ was applied to theoretical spectra since we did not calculate electron self-energy.

To simulate amorphous silicate with forsterite and enstatite composition, we modeled glass in a molecular dynamic (MD) simulation using the an established recipe of heating to 5000K and rapid cooling [10]. We used a cooling rate of 470K/ns, which is slower than typical for MD glasses. We carried out simulations using the LAMMPS MD package [11] and interatomic potentials for silicates [12].

To check the validity of the single particle approximation for O-XANES in silicates, we also calculated the spectrum of an individual O atom in forsterite using the Bethe-Salpeter equation and found only minor differences. Therefore, multi-electron interactions are likely to be of minor importance and the improved accuracy to be gained by transitioning to a quantum field theory approach is not justified for this system given the increase in computation time. All simulations were done within the dipole approximation. Since pre-edge features are often caused by quadrupole interactions or bands created by transition metals, or hydrogen, we do not expect our modeling to capture any pre-edge features of the O-K spectrum, but leave that for future work. Experimental spectra were acquired from IDP L2071 Cluster 17 "Nessie" using beamlines 11.0.2 and 5.3.2 at the Advanced Light Source at LBL. Identification of olivine, orthopyroxene and GEMS were verified by EDS, diffraction and imaging using the TitanX TEM at the Molecular Foundry at LBL.

Results: Figure 1 shows experimental O-XANES spectra for Fo₉₀ and En₈₂ from an EA and two GEMS, all from Nessie. The GEMS spectra are not identical. One GEMS is attached to an EA and shows a feature at 548 eV whereas the other GEMS is not attached to an EA and has a smoother spectrum. The broad peak from 550-570 eV peaks at 558 eV for the GEMS attached to the EA whereas the standalone GEMS peaks at 560 eV. The GEMS attached to the EA has Si/Mg ≈ 1 while the standalone GEMS has Si/Mg ≈ 3 .

Figure 2 shows the experimental O-K XANES for Fo₉₀ and En₈₂, with theoretical calculations for forsterite and enstatite. The calculations do a good job of reproducing the structure between 545 to 560 eV. Olivine has a ledge on the side of the main peak at 544 eV, as well as peaks at 548, 553 and 557 eV. Pyroxene shows two broader peaks at 549 and 559 eV. However, the 535 to 545 eV region is not as well-reproduced.

Figure 3 shows the experimental O-K XANES for the two GEMS compared to the theoretical spectra. In the case of the standalone GEMS (bottom) the fit is very good. However, in the case of the GEMS which is attached to the equilibrated aggregate, neither the Fo₁₀₀ nor En₁₀₀ glass simulations capture the feature at 548 eV.

Discussion: Since the standalone GEMS is well-modeled

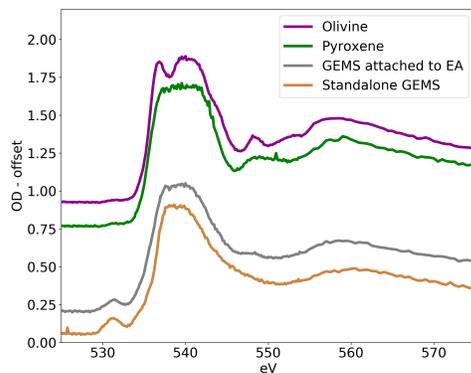


Figure 1: Experimental O-K XANES from an olivine, orthopyroxene (top) and from two GEMS (bottom). The GEMS with the 548 eV feature is attached to an equilibrated aggregate.

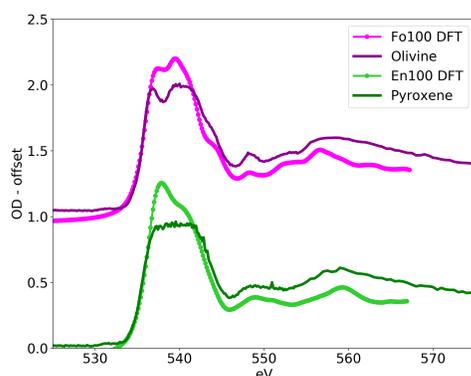


Figure 2: Experimental O-XANES spectra for olivine and pyroxene from an equilibrated aggregate compared with theoretical spectra generated by DFT simulation.

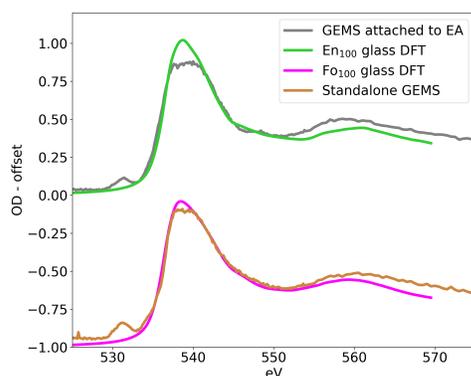


Figure 3: Experimental O-XANES spectra for two GEMS compared with theoretical spectra generated by molecular dynamics and DFT simulation.

with a glass structure of forsterite composition, we claim that

this is a good representation of the silicate structure. However, in the MD simulation, the glass was cooled at a rate that is far faster than realistic cooling rates, so our simulation can be considered as a limiting case for rapid cooling. Because the simulated glass with olivine composition was not identical to the simulated glass with pyroxene composition it should be possible to distinguish glass characteristics even at this cooling rate. However, the GEMS attached to the EA showed structure that was not captured by either theoretical structure and therefore has a different structure, as yet unknown. Since the experimental spectrum shows a well characterized peak, it is likely that it is more ordered than the standalone GEMS.

Interestingly, our amorphous models were closer to the experimental spectra of GEMS than our crystalline models were to forsterite and pyroxene. We explored several reasons that could cause this. The most abundant element in the glass aside from Mg, Si and O is Fe. We produced Fo_{90} and found that the spectrum does change, but the difference was smaller than we expected. In future work we hope to explore the influence of other common elements found in silicates such as Al and Ca. As noted above, the Bethe-Salpeter equation (BSE), did not greatly improve the spectra. However, the BSE still does not account for electron self-energy which may improve the results. Additionally, it is known that the thermal deviation of atoms from their crystallographic centers due to lattice vibrations can have an impact on the XANES spectrum. The fact that the glass simulations were so much more accurate, yet were modeled in the same way suggests we should calculate spectra from crystalline structures where atoms have been thermally displaced or where defects are present.

It will also be important to try other glass structures in the future. We should attempt to create glass structures that plausibly describe condensation, irradiation, and corrosion. It will also be important to simulate glass structures for more slowly cooled glasses.

Conclusion: We find that not all GEMS have equivalent glass structures. A GEMS attached to an equilibrated aggregate shows evidence for silicate ordering which is not present in another GEMS that is not associated with an EA. Further work is needed to determine whether the ordering in GEMS is associated with EAs. The standalone GEMS exhibits extremely disordered silicate structure and is well matched by the limiting case of glass formed by extremely fast cooling.

Acknowledgments: ALS and the Foundry are supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

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