

XAFS on Hf in silicate glasses and minerals

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High-field-strength elements (HFSE), like Zr and Hf, are important trace elements that provide important information about magmatic processes and mass transfer in the Earth's interior. The formation of silicate melts in the Earth's crust and the upper mantle and their interaction with the surrounding host rocks are important processes for the evolution of the lithosphere. The geochemical distribution of trace elements between minerals, silicate melts and aqueous solution is controlled by their structural incorporation in the phases at equilibrium. While the effect of the structure and composition of crystalline phases on the chemical partitioning is understood quite well, the effect of the melt composition and structure is far less well known. Here, we investigated the effect of silicate melt composition on the local environment of Hf. XAFS measurements at the L₃-edge of Hf in quenched melts of compositions that differ strongly in composition, and structure. In addition, a couple of Hf-bearing minerals with known crystal structure were measured in order to test the simulation of XANES spectra by FEFF9.0 [1].

The EXAFS spectra were collected at beamline C using a Si (311) double-crystal monochromator. Spectra were recorded in fluorescence mode.

Glass compositions reported on here are NS3 (Na₂Si₃O₇), and albite (NaAlSi₃O₈). Glasses were doped with 8000 ppm and 2 wt% of Hf. K³-weighted EXAFS spectra and their Fourier transforms are plotted in figure 1 for the two glasses. The spectra indicate already differences for the local structural environment between the studied compositions. The amplitude of the EXAFS and consequently, the first maximum of the Fourier transform (FT) is much higher for NS3 (partially depolymerised glass). Fitting of the EXAFS using the harmonic approximation yields a Hf-O distance of 2.046 ± 0.006 Å and 6 neighbors for the NS3 glass and only 1.999 ± 0.007 Å and 4 neighbors for albite. For NS3, significant contribution by multiple scattering indicates a regular octahedral coordination. For albite, the unrealistic low number of neighbors and short Hf-O indicate significant anharmonic effects due to a high degree of static disorder for Hf. First attempts to fit asymmetric pair-distribution functions show considerable improvement for the structural parameters. The observed difference between the two samples is consistent with their difference in structural properties. Large cations such as Hf prefer bonding to non-bridging oxygens, which are (almost) not present in the fully polymerized albite glass [2, 3].

XANES spectra of model compounds are shown in figure 2. Compounds shown are armstrongite CaZrSi₆O₁₅·3(H₂O), eudialyte Na₄Ca₁₅Ce_{0.5}Fe_{0.6}Mn_{0.3}Y_{0.1}ZrSi₃O₂₂(OH)Cl_{0.5} and wadeite K₂ZrSi₃O₉ that contain Hf as a minor component. Hf replaces Zr in these minerals and is 6 fold coordinated. Spectra of all three compounds show a very strong white line with split peak at the maximum. At higher energies, the spectra of the minerals differ slightly probably owing to the difference in composition and structure. Spectra simulated based on structural data from the literature using FEFF9 describe the spectral features reasonably well, especially for wadeite. Discrepancies may be related to the simplifications implicit to FEFF or due to the fact that the structural data taken from the literature do not match the measured sample.

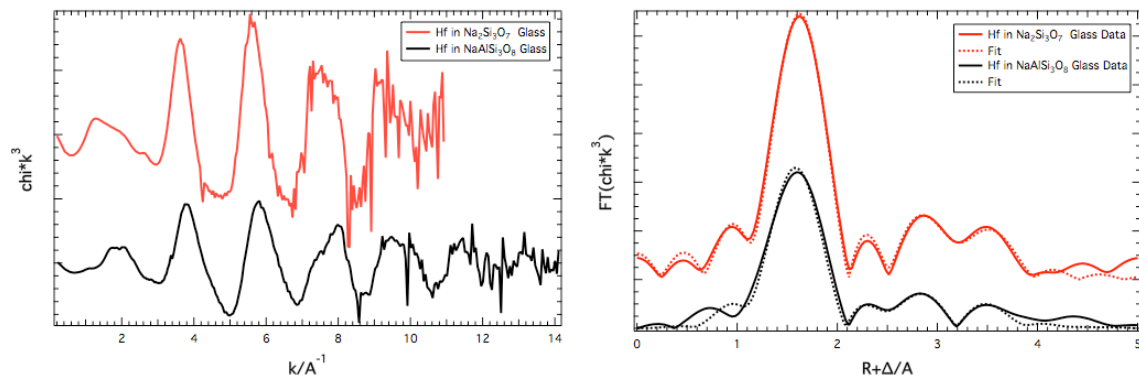


Figure 1: k^3 -weighted EXAFS and Fourier Transform of Hf in NS3 and albite line glass taken at the L_3 -edge.

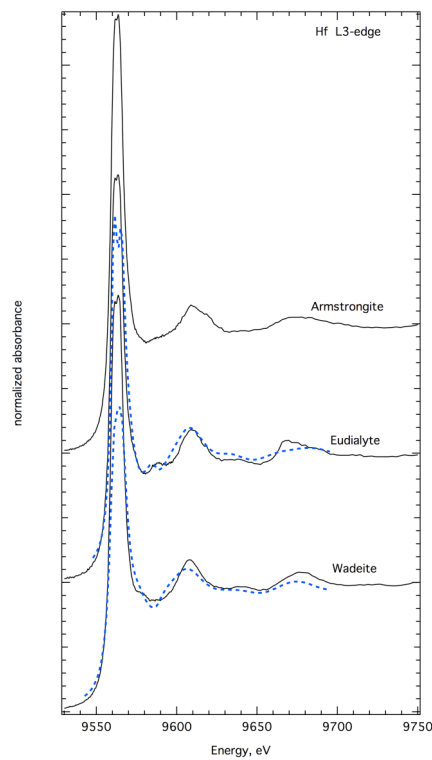


Figure 2: XANES of armstrongite ($\text{CaZrSi}_6\text{O}_{15} \cdot 3(\text{H}_2\text{O})$), eudialyte $\text{Na}_4\text{Ca}_{15}\text{Ce}_{0.5}\text{Fe}_{0.6}\text{Mn}_{0.3}\text{Y}_{0.1}\text{ZrSi}_3\text{O}_{22}(\text{OH})\text{Cl}_{0.5}$ and wadeite ($\text{K}_2\text{ZrSi}_3\text{O}_9$). Dashed lines indicate spectra simulated using FEFF9.

References

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- [2] Farges F et al. (1991) *Geochimica et Cosmochimica Acta*, **55**, 1563-1574
- [3] Farges F, Rossano S (2000) *European Journal of Mineralogy*, **12**, 1093-1107