

Zr K-edge EXAFS on silicate glasses and natural minerals

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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, especially at active plate boundaries. High-field-strength elements (HFSE), like Zr, are important trace elements that provide important information about melt formation and mass transfer in the Earth's interior. Important steps for the HFSE cycling are the processes related to subduction zones, where interaction of solids and silicate melts with aqueous fluids plays an important role. It has been suggested that silicate components, which are dissolved in aqueous fluids at high pressure and temperature may be responsible for the mobilisation of HFSE-bearing minerals such as zircon in these systems ([1], [2]). Therefore, we started to study the influence of silicate components dissolved in aqueous fluids on the solubility of zircon at high P and T. In parallel, the complexation mechanism of Zr in these fluids is studied by XAFS. The authors of [1], [2] suggested that Zr might be incorporated in these fluids as part of polymeric silicate complexes. To provide a reference for XAFS spectra collected on fluids at high P and T (performed at the ESRF), we investigated here how changes in the silicate melt composition affect the local environment of Zr. In this contribution, we report on results of XAFS measurements at the K-edge of Zr in quenched melts of those compositions that are used in the experiments at high P & T. In addition, a couple of Zr-bearing minerals with known crystal structure were measured.

Glass compositions reported on here are NS2 ($\text{Na}_2\text{Si}_2\text{O}_5$), nepheline (NaSiO_4), albite ($\text{NaAlSi}_3\text{O}_8$). Glasses were doped with 2000 ppm of Zr. The EXAFS spectra were collected at beamline C using a Si (311) double-crystal monochromator. Minerals were either powdered and pressed into pellets or measured as polycrystalline aggregates that were cut into thin slices. Depending on the total Zr content spectra were recorded in transmission or fluorescence mode. The fluorescence signal was collected using a Lytle detector [3].

k^3 -weighted EXAFS spectra and their Fourier transforms are plotted in Figure 1 for glasses and Figure 2 for minerals. The spectra of the glasses show good counting statistics, even in the higher k -regions. 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 highest for NS2 (depolymerized glass). The position of this maximum for NS2 is also slightly shifted to higher distances in comparison to albite and nepheline glasses. Fitting of the backward Fourier transform of the first maximum gives a Zr – O distance of $2.087 \pm 0.01 \text{ \AA}$ for the NS2 glass and $2.083 \pm 0.01 \text{ \AA}$ for nepheline. The result for Zr in albite glass is $2.085 \pm 0.01 \text{ \AA}$, which is consistent with previous work ([4],[5]) taken for the same glass composition where Zr – O distances were determined at $2.085 \pm 0.03 \text{ \AA}$. The fit results also indicate a stronger distortion of the coordination polyhedron or larger degree of disorder for the polymerized glass compositions. In addition, spectra of the glasses indicate that differences are also present in the second coordination shell.

In general, the positions of these maxima of the glasses are quite similar to those found for elpidite and wadeite. In these compounds Zr is 6-fold coordinated in a highly distorted polyhedron and shows average Zr – O distances of 2.070 \AA and 2.079 \AA [6],[7].

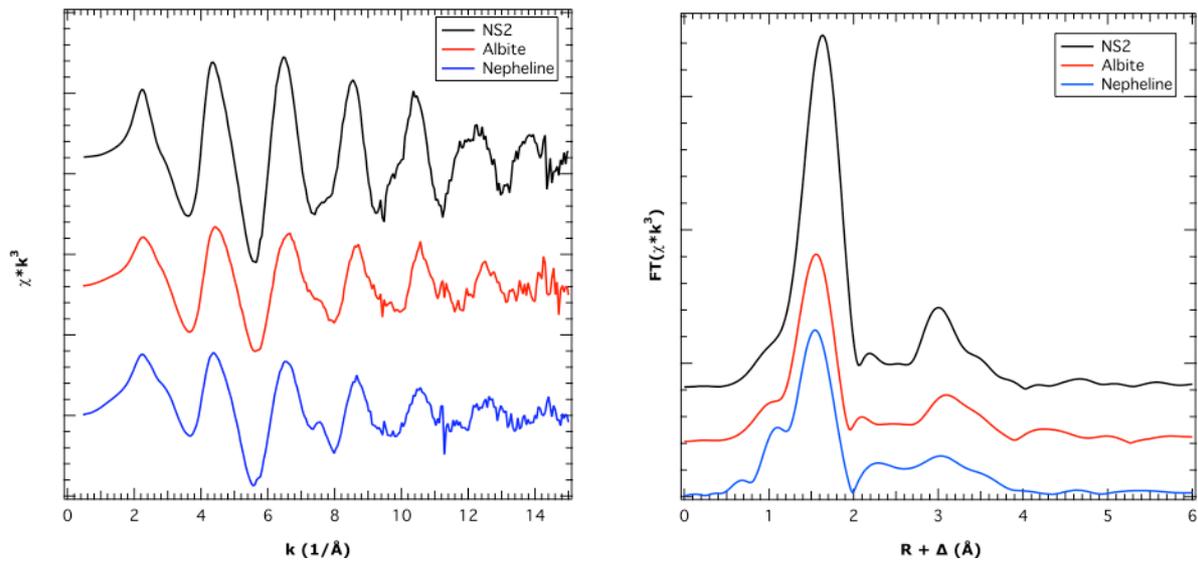


Figure 1: k^3 -weighted EXAFS and Fourier Transform of Zr in NS2, albite and nepheline glass taken at the K-edge (2000 ppm Zr).

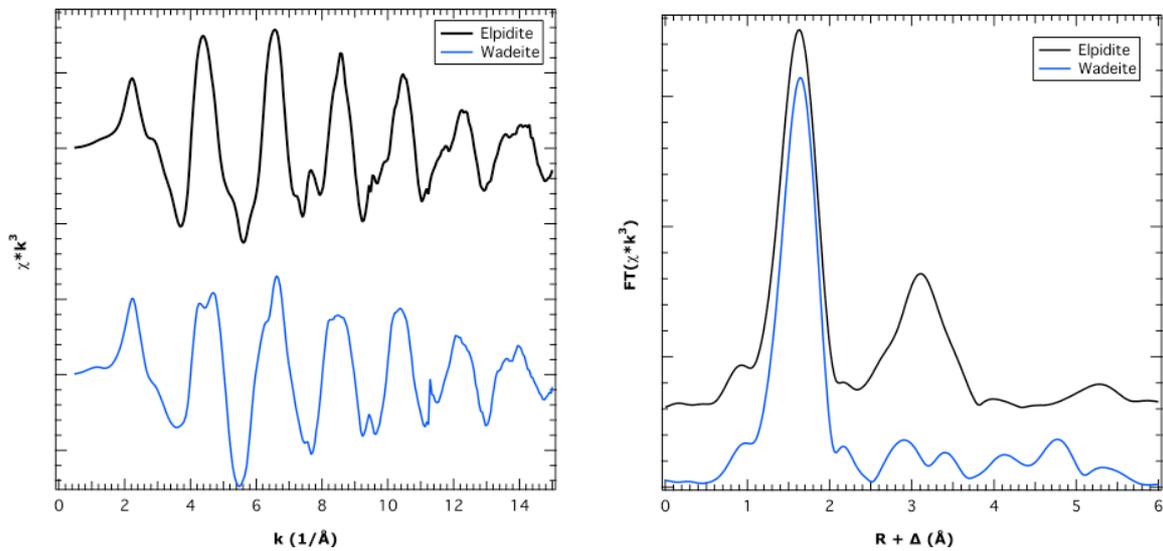


Figure 2: k^3 -weighted EXAFS and Fourier Transform of Zr in elpidite and wadeite crystals taken at the K-edge (wadeite ~ 23wt% Zr; elpidite ~ 15wt% Zr).

References

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