Local structure of yttrium in aluminosilicate glasses

S. Simon[1], M. Wilke[1], S. Klemme[2], R. Chernikov[3]

[1] Deutsches GeoForschungsZentrum (GFZ), Telegrafenberg, 14473 Potsdam, Germany

[2] Institut für Mineralogie, Westfälische Wilhelms-Universität, Corrensstr. 24, 48149 Münster, Germany

[3] HASYLAB at DESY, Notkestr. 85, 22607 Hamburg, Germany

Trace elements are important indicators in magmatic and metamorphic rock on Earth, Moon and the terrestrial planets. It is generally accepted that the partitioning of trace elements (TE) is controlled by T, P, crystal chemistry and melt composition (e.g. [1]). Particularly, the trace element partition coefficients of Prowatke and Klemme's [2] between melt and titanite, which varied over several orders of magnitude, suggest a strong control of the melt composition. Ponader and Brown [3] already reported that the coordination of rare earth elements (REE) in quenched melts changes with the degree of polymerization of the melts. However a direct correlation between element coordination and partitioning of TE was not attempted. The scope of this study is to investigate the local structure of Y in aluminosilicate glasses.

The studied melt compositions were taken from [2] and vary in the aluminum saturation index (ASI, molar ratio of $Al_2O_3/(Na_2O+K_2O+CaO)$) from 0.115 to 0.768. The glasses were synthesized from oxides and carbonates and doped with 5000 ppm Y. EXAFS spectra at the Y K-edge (17038 eV) were collected at beamline C in fluorescence mode. A Si(111) fixed-exit two-crystal monochromator was used. The fluorescence signal was detected using a Stern-Heald type detector filled with Kr [3] or a 7-element SDD detector [4]. The spectra were analyzed using the software Athena and Artemis [4]. Amplitudes and phase shift were calculated using Feff6 and checked on crystalline compounds with known structural parameters (Y_2O_3, $Y_3Al_5O_{12}$ and $YN_3O_9 *6H_2O$). Due to large static disorder and non-Gaussian pair distributions in melts and glasses a histogram fit based on an asymmetric gamma-like distribution function was used to model the Y-O pair correlation of the first coordination shell in the glasses.

The k^3-weighted EXAFS spectra of all glasses and the corresponding Fourier-transforms (FT) are shown in Fig. 1 together with the resulting fit. The EXAFS amplitude decreases considerably from ASI200 to ASI280. The position of the first maximum of the FT, which corresponds to the Y-O correlations of the first coordination shell, plots at nearly the same position for all samples (2.26 Å). The first maximum, however, shows a considerable decrease in the magnitude and significant broadening from ASI200 to ASI280. The second maximum of the FT corresponds to pair correlations of the second coordination shell. The analysis of the EXAFS data shows an increase in the coordination number for Y from 6 to 8 with increasing ASI and thus polymerization of the melt. Along with this an increase of the average Y-O distance by 0.12 Å is observed, which is also associated with a considerable increase in the asymmetry and width of the Y-O pair distribution, as displayed in the pair distribution function determined by the fit (Fig. 2). We were able to show that the local structure of Y in aluminosilicate melts changes with the ASI of the melt composition. Changes in ASI will result in a change of the polymerization of the tetrahedral network of silicate melts. The lower amount of non-bridging oxygens in highly polymerized silicate melts forces Y into a higher coordination in order to meet local charge-balance requirements.
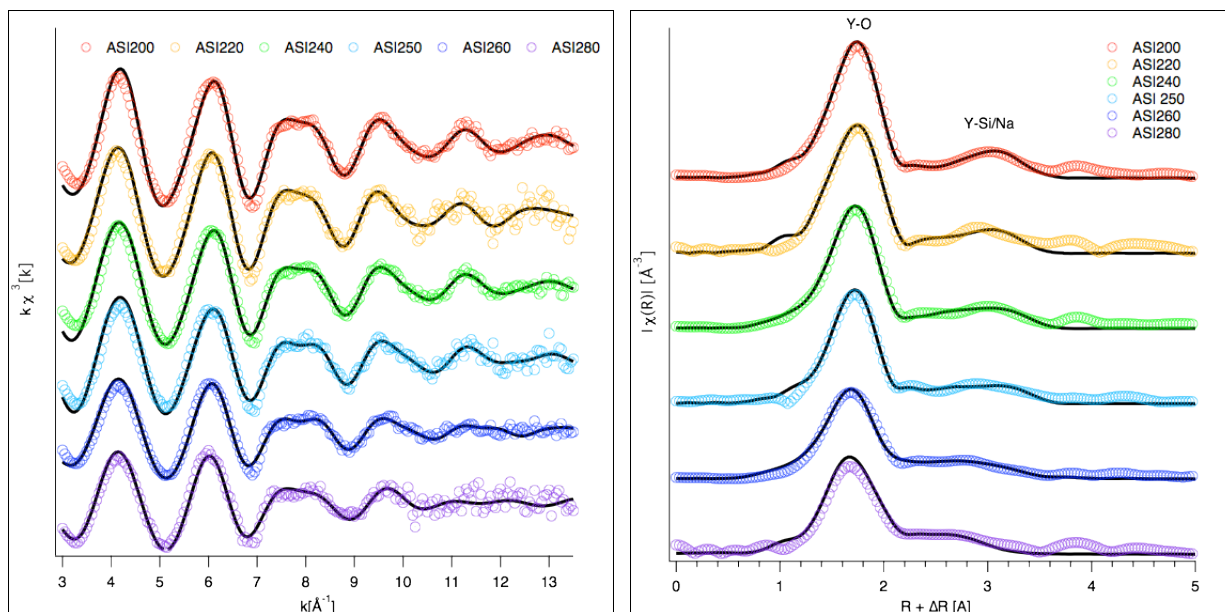
Figure 1: k^3-weighted EXAFS (left) and Fourier-transform (right) of Y at the K-edge in silicate glass (5000 ppm Y). Markers indicate data points and solid lines the fits. Peaks in the FT are labeled for the corresponding atomic pair correlations. Peak positions in the FT are uncorrected for backscattering phase-shifts.
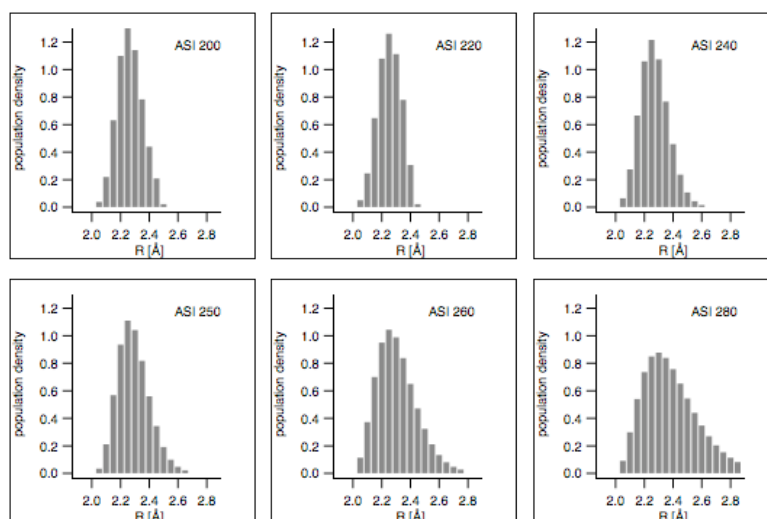

Figure 2: Y-O PDF for the first coordination shell determined by the fit of the EXAFS. The PDF show an increase of asymmetry and width with increasing ASI of the melt composition.

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