

Local Structures around Si, Al and Na in Hydrated Silicate Glasses

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Abstract. XANES spectra were collected at the Si-, Al-, and Na K-edge in hydrous silicate glasses to understand the effect of water on the local structure around these cations. Around network forming Si and Al, no drastic changes are observed. Around Na, the dissolution of water creates more ordered environments in Al-bearing glasses and less ordered environment in Al-free glasses. *Ab-initio* XANES calculations were undertaken to understand the structural origins for these features. Based on these results, a bond valence model was refined that considers not only the present XANES experiments and models but also NMR information. The double percolation model refined explains, among others, the explosive properties of water-bearing hydrous melts, at the origin of a number of cataclysmic eruptions in subduction zones.

Keywords: Si, Al, Na, XANES, FEFF, molecular dynamics, bond valence, rheology, volcanoes

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INTRODUCTION

Before erupting, volcanic melts are potentially highly explosive when they are highly hydrous [1]. This is because water dramatically affects the physical and chemical properties of silicate melts [2]. In melts, water is present as both hydroxyl groups and molecular water. Nuclear magnetic resonance (NMR) spectroscopy studies of hydrous Al-bearing silicate glasses suggests that the spectra are unaffected by the presence of water. Thus, water does not appear to depolymerize these melts, in contrast to Raman scattering findings [1]. Therefore, information from X-ray absorption near edge structure (XANES) spectroscopy of Si, Al and Na is of interest.

EXPERIMENT

High-pressure (500 MPa) glasses were synthesized from homogenized dry glasses, using an internally heated pressure vessel [2]. The glasses includes NS3 ($\text{Na}_2\text{Si}_3\text{O}_7$), ALB ($\text{NaAlSi}_3\text{O}_8$) and a more complex

“haplorhyolite” ($\text{Qz}_{21}\text{Ab}_{16}\text{Or}_{63}$ in which Qz, Ab and Or are SiO_2 , $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 , respectively). Na-, Al- and Si K-edge XANES spectra were collected on the SA-32 beamline (LURE, Orsay, France; operating at 0.8 GeV and 400-200 mA). For Na, Al and Si K-edges, we used a double crystal monochromator constituted by beryl (1010), quartz (100) and InSb (111), respectively. The energy resolution is 0.7 eV at the Si K-edge and 0.3 eV at the Na-, and Al-K edges. Counting time of 1 s. were used over 0.2 eV steps (0.1 eV in the pre-edge region), using a total electron yield detector.

RESULTS

Figures 1a and 1b show the normalized Si and Al K-edge XANES spectra collected for the glass samples. For each edge, the XANES spectra do not show significant influence of the dissolved water on the local structure around these network formers. The XANES of the

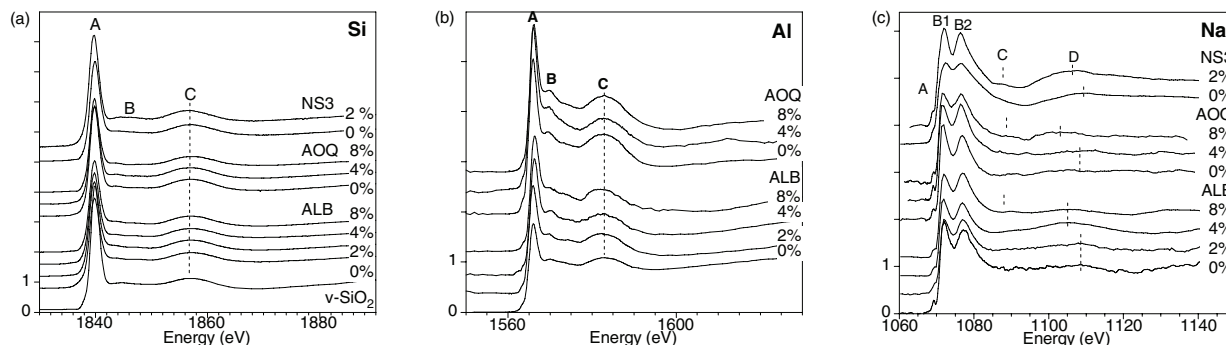


FIGURE 1. Si K- (left), Al-K- (middle) and Na K-edge (right) XANES spectra for the NS3, ALB and AOQ densified glasses. The percentages shown correspond to the total water dissolved in the melts prior their quench.

hydrated glasses are similar to these for the anhydrous glasses (Si and Al are tetrahedrally coordinated). Figure 1c shows the normalized Na K-edge XANES spectra collected for NS3, ALB and AOQ. Their XANES spectra are composed by a doublet (features B1 and B2), a shoulder (feature C) and the first EXAFS oscillation (feature D). At high water contents, feature D is shifted to lower energies. Also, features B and C are more clearly defined. In the less hydrous ALB and AOQ (≤ 2 wt. % water), feature B1 is higher than B2 as compared to their more hydrous counterparts. Feature C2 is slightly more defined in the most hydrous glasses. We note that 2 wt. % water are enough to modify the Na K-edge XANES spectrum for NS3, whereas higher water amounts are needed to obtain similar changes in the hydrous polymerized glasses (ALB and AOQ). Insets of the pre-edge feature (feature “A” in Fig. 1c) are shown on Figs. 2a-c. In NS3, the pre-edge feature for sodium increasing in intensity (and becomes broader) with increasing water. The reverse trend is observed for ALB and AOQ (Figs. 2b and c).

Crystalline Albite

In order to assign robustly the present Na K-edge XANES spectra, *ab-initio* XANES calculations were

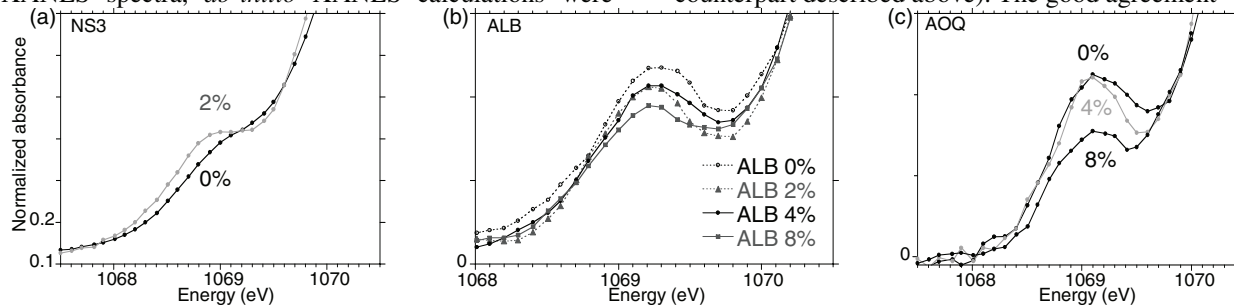


FIGURE 2. Normalized Na K-edge pre-edge features collected for the high-pressure (5 kbars) glasses of that study.

undertaken using FEFF8.2 [3]. In order to provide a fully consistent approach, the Si, Al and Na K-edges for crystalline albite were modeled considering the same FEFF conditions. We choose to model the XANES for crystalline albite because it is relatively close to these measured in its glassy counterpart (ALB). Figures 3a-c show the obtained modeled XANES. To achieve these, the Z+1 approximation [4] and Hedin-Lunqvist potentials for $\text{NaAlSi}_2\text{O}_6$ gave the best results. The agreement between experiment and model is fair despite the same conditions were used for all simulations. These calculations confirm that, at the Al-, and Si K-edges, feature B is related to the medium range environment around Si and Al, whereas feature C is related to the first neighbors. At the Na K-edge, the doublet of the edge crest is then dominantly related to first-, and next-nearest neighbors, in contrast to previous assignments [4].

Glassy Albite

Molecular dynamics (using BKS potentials [5-6]) were undertaken to provide a structural model for an albitic glass. A selected cluster refined around Na is shown on Figure 4, which was then simulated using FEFF8.2 (same conditions as for the crystalline counterpart described above). The good agreement

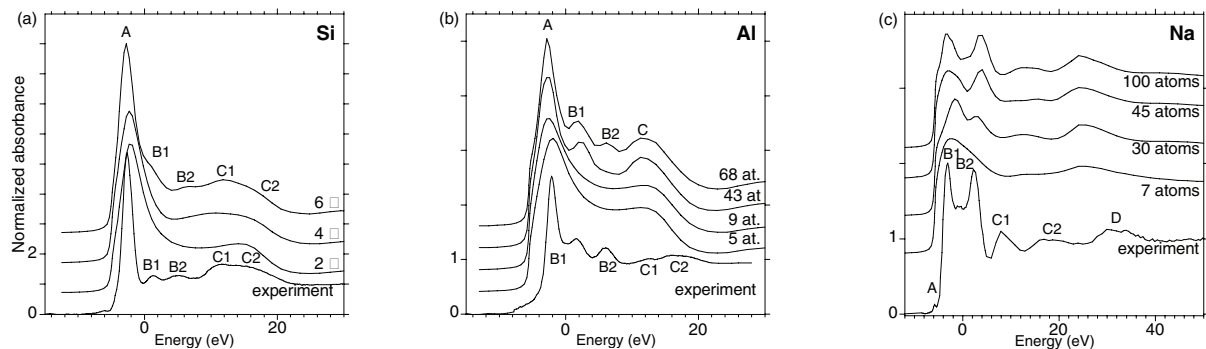


FIGURE 3. FEFF8.2 simulated Si (left), Al (middle) and Na (right) K-edge XANES spectra for crystalline albite model. For each edge, the experiment is shown at the bottom, while clusters with variable cutting distance (or number of neighbors) are shown.

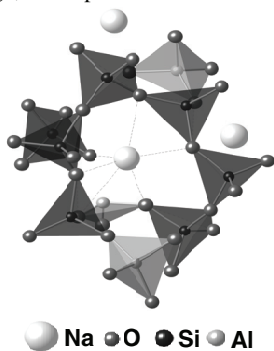


FIGURE 4. Example of a cluster around Na (#916 out of 1216) in an albitic glass, modeled by molecular dynamics (BMH potentials) [7].

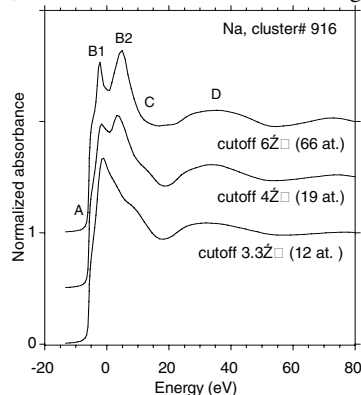


FIGURE 5. *Ab initio* Na K-edge XANES spectra (FEFF8) for the cluster illustrated in Fig. 5.

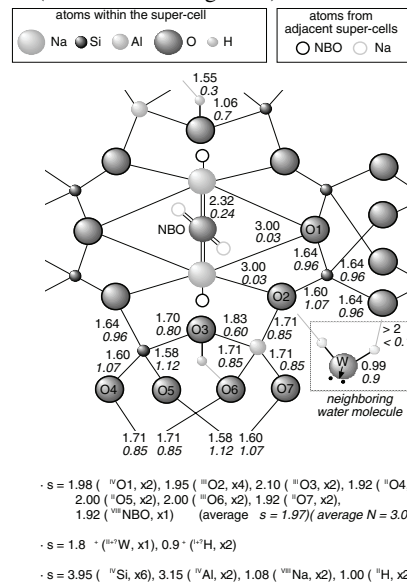


FIGURE 6 (right). Bond valence model based on XAFS and NMR information. Bond valence sums (Σs) for most ions are given.

between the experiment (Fig. 1c) and the model (Fig. 5) suggests that the local structure around Na in anhydrous ALB arises dominantly from oxygen first neighbors. Na next-nearest neighbors contribute little to the XANES spectra. Based on these constraints, a bond valence model [5] for an hydrous ALB was refined, using 2 moles of albite and one mole of water (Fig. 6). The model was iteratively refined to verify both the present XANES information and previous NMR (^{18}O , ^{29}Si , ^{27}Al and ^{23}Na) spectroscopy data [1,8-10]. The refined model does not infer tetrahedral depolymerization due to the introduction of water (which bonds through protonated bridging oxygens, in agreement with NMR simulations [8]). The refined model suggests that a hydrous polymerized melt is a double percolative network, with a “silicate subnetwork” and a “supercritical water subnetwork”. This double percolation model explains well the lower viscosities of such melts (presence of protons bridges,

among others) and their explosive character (presence of a highly compressible hydrous subnetwork).

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