XAFS study on the Zr local structures in tektites and natural glasses

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The local structures of tektites and natural glasses were studied by Zr K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements in order to obtain quantitative data on the Zr–O (bonding) distances and coordination numbers for the glasses. Zr⁴⁺ ions have different coordination environments. The structure of glass (tektite, impact-related glass, fulgurite, and volcanic glasses) is affected by the temperature during the glass-formation process. Differences in the formation processes for natural glasses result in different local structures for the zirconium ions.

All tektites can be classified as being of the same type and as having 7-fold coordination Zr ions. The Zr–O distances in tektite glasses are 2.198–2.215 Å, and their XANES spectra are similar, too. Impact-related glasses can be classified into different types and are formed under different physical and geological processes at the impact event. Volcanic glasses, impact-related glasses, and fulgurite glasses have several local Zr structures with 6- and 7-fold coordinated Zr ions. It can thus be concluded that local structures of Zr in natural glasses are closely related to the formation temperature and quenching conditions of the glasses. The Zr XAFS spectra of natural glasses can be used to identify the natural glasses.

Keywords: Local structure of Zr, Tektites, Impact glasses, EXAFS, XANES

INTRODUCTION

Several kinds of glasses are formed naturally by various geological activities. For instance, tektites and impact glasses are produced by impact events (Alvarez et al., 1980). Further, volcanic activities can result in volcanic glasses such as obsidian and pitch stone. These natural glasses are formed by different physical processes, which should lead variety of local structure in glass structures (Stebbins and McMillan, 1989; Paris et al., 1994; Mysen and Neuvile, 1995; Yarger et al., 1995). It is likely that a giant meteorite crashed on Earth, catapulting materials in the Earth’s surface into outer space, where they solidified. The solidified materials eventually fell back to Earth. Tektites were formed by this series of processes (Wang et al., 2011). On the other hand, impact glasses were formed by materials that did not catapult into space; this process was similar to the formation of coherent impact melt rocks, which are found in the craters observed in crystalline targets (Osiniski et al., 2005). Lightning strikes on sandy soil produce fulgurites. The local structure analyses of titanium, iron, aluminum and calcium are studied on various natural glasses and tektites (Farges and Brown, 1997; Neuvile et al., 2004; Wang et al., 2011; Tobase et al., 2013). It is known that tektites exhibit a characteristic XANES spectrum that is distinguishable from those of other natural glasses.

Mountjoy et al. (2000) have reported that the Zr K-edge XANES spectra of crystal phases have different patterns, which can be classified into three types on the basis of the main absorption edge. These include two double-peak profile patterns, one with a tetrahedral (lower-energy-side peak taller than the higher-energy-side peak) coordination environment and one with an octahedral (higher-energy-side peak taller than the lower-energy–side peak) coordination environment and a single peak for sites with 7-fold coordination. The pre-edge peak of

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The Zr K-edge XANES spectra correspond to p–d mixing; this has been determined from density of states calculations for crystalline ZrO₂ (Mountjoy et al., 2000). The structure of glass is affected by the pressure and temperature during the glass-formation process (Stebbins and McMillan, 1989; Paris et al., 1994; Mysen and Neuville, 1995; Yarger et al., 1995). Analyses of the local titanium, iron, aluminum, and calcium structures have shown that the local structures of tektites and other glasses are influenced by their formation conditions (Farges and Brown, 1997; Neuville et al., 2004; Wang et al., 2011; Tobase et al., 2013). However, the Zr K-edge XANES spectra of only a few natural glasses and tektites have been reported, even though this technique is suitable for analyzing Zr local environments. Zircon is a valuable mineral for determining geological age. The main constituent element of zircon is zirconium. The local zirconium structures of tektites and impact-related glasses can be useful for obtaining information on the physical conditions and formation processes (or pressure and temperature histories) of these glasses. Thus, in this study, we investigated the XANES and extended X-ray absorption fine structure (EXAFS) studies of the local structure around Zr for tektite samples from six strewn fields and impact-related glasses, in order to obtain comprehensive data on the related impact events.

**SAMPLES AND EXPERIMENT**

The tektite specimens were from different strewn fields (Table 1): hainanite, indochinite, philippinite, and australite were obtained from an Australian strewn field while moldavite was procured from a European strewn field. Kofelsite, suevite, Darwin glass, and Libyan Desert glass are impact-related glasses. The volcanic glasses were pitchstone and obsidian. The Si and Zr contents of these samples were 56.45–97.1% and 79.0–246.7 ppm, respectively. These values were determined by SEM/EDS and XRF measurements, respectively. The diameters of the tested samples were 7–15 mm. The crystalline phases of zircon, SiZrO₃, and PbZrO₃ were used as references.

The Zr K-edge XAFS measurements were performed at beamline BL-NW10A, which is equipped with a Si (311) double-crystal monochromator, of the Institute of Materials and Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. The storage ring is operated at an electron energy of 6.5 GeV and ring current of 400.3–401.0 mA. The size of the synchrotron X-ray beam is 1 × 2 mm. The Zr K-edge spectra were recorded in the fluorescence mode using a Lytle-type detector for energies of 17.6–18.8 keV in steps from 0.723 to 14.466 eV and for counting times of 2 to 15 s. The EXAFS function, \( \chi(k) \), was extracted from the measured spectra using the standard procedure (Maeda, 1987). The calculated \( \chi(k) \) values were normalized using MacMaster coefficients, in keeping with Lytle et al. (1989). For quantitative analyses, we employed Fourier filtering and performed a nonlinear least-squares fit on the \( \chi(k) \) values (Maeda 1987). We also calculated the values of a few structural parameters of the glass samples, such as the Zr–O distances and the coordination numbers. We used the EXAFS formula as it pertains to the single-scattering theory with cumulant expansion up to the fourth-order term (Ishii, 1992):

\[
\chi(k) = \sum N_\theta \left\{ \frac{N_\theta}{k R_{\text{ab}}} f_\theta(k/\eta) \left[ \exp \left[ -2 R_{\text{ab}}/(k/\eta) \right] \right] \times \exp \left[ -2 \sigma_\xi k^2 + (2/3)\sigma_\eta k^4 \sin \left[ 2kR_{\text{ab}} - (2k/\xi R_{\text{ab}}) \right] \times \left[ 1 + 2R_{\text{ab}}/(k/\eta) \right] \sin \left[ 4/3(\sigma_\xi k^3 + \psi_{\text{ab}}(k)) \right] \right] \right\},
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>SiO₂(%)</th>
<th>ZrO₂(ppm)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moldavite</td>
<td>Rodmilice Bohemia, Czech Republic</td>
<td>78.6-82.6</td>
<td>135.4-136.1</td>
<td>Green</td>
</tr>
<tr>
<td>Australite</td>
<td>Mount Dare, Nothren most Area, South Australia</td>
<td>70.4-77.2</td>
<td>205.8</td>
<td>Black</td>
</tr>
<tr>
<td>Philippinite</td>
<td>Pagrayanan, Isabela Province, Luzou, Philippines</td>
<td>67.2-74.9</td>
<td>150.3</td>
<td>Black</td>
</tr>
<tr>
<td>Hainanite</td>
<td>Hainan Province, China</td>
<td>72.77</td>
<td>126.6</td>
<td>Black</td>
</tr>
<tr>
<td>Indochinite</td>
<td>Khorat Plateau, Nakhon Ratrasima Province, Thailand</td>
<td>72.9-74.9</td>
<td>144.1</td>
<td>Black</td>
</tr>
<tr>
<td>Köfelsite</td>
<td>Öztal near Köfels, Tirol, Austria</td>
<td>58.4-61.5</td>
<td>87.9</td>
<td>Black</td>
</tr>
<tr>
<td>Darwin glass</td>
<td>Mount Darwin Crater, Tasmania, Australia</td>
<td>81.8-82.2</td>
<td>246.7</td>
<td>Green</td>
</tr>
<tr>
<td>Libyan Desert Glass (LDG)</td>
<td>Libyan Desert, Libya</td>
<td>94.2-95.6</td>
<td>137.6</td>
<td>Grey</td>
</tr>
<tr>
<td>Suevite</td>
<td>Nördlinger Ries Crater, Bayern, Germany</td>
<td>56.45-59.54</td>
<td>79</td>
<td>Black</td>
</tr>
<tr>
<td>Obsidian</td>
<td>Hokkaido, Japan</td>
<td>68.2-69.1</td>
<td>236.82</td>
<td>Black</td>
</tr>
<tr>
<td>Pitchstone</td>
<td>Seto Inland Sea Volcanic regions, Aichi, Japan</td>
<td>70.8-73.2</td>
<td>98.5</td>
<td>Grey</td>
</tr>
<tr>
<td>Fulgurite</td>
<td>Sahara, Morocco</td>
<td>95.3-97.1</td>
<td>113.5</td>
<td>Grey</td>
</tr>
</tbody>
</table>

Table 1. Locations, SiO₂, ZrO₂ compositions and colors of the studied tektites and natural glasses
where $N_B$ is the coordination number of the scattering atom B at a distance $R_{AB}$ from the absorbing atom A, $|f_B(k; \pi)|$ is the backscattering amplitude of photoelectrons, and $\Psi_{AB}(k)$ is the phase shift function. The values of the functions $|f_B(k; \pi)|$ and $\Psi_{AB}(k)$ were calculated using the FEFF3 program (Rehr et al., 1991). Here, $\sigma_n$ denotes the nth cumulant. The mean free path, $\lambda$, of the photoelectrons was assumed to be dependent on the wavenumber, $\lambda(k) = k/\eta$, where $\eta$ is a constant. The XAFS data were analyzed using the XAFS93 program, which has been described by Yoshiasa et al. (1997). Single–shell fitting was performed for each nearest-neighbor distance. Because the third- and fourth-order terms in the cumulant expansion were negligibly small, the final refinement was performed by using the harmonic model; the structural parameters $R_{AB}$, $\sigma_2$, $\eta$; and the $\Delta E_0$ values. Here, $\Delta E_0$ is the difference between the theoretical and experimental threshold energies. The reliability of the fitting parameters corresponding to the experimental and calculated EXAFS functions, which is given by

$$ R = \sum |k^2 \chi(k)_{exp} - k^2 \chi(k)_{calc}|/|k^2 \chi(k)_{exp}| $$

was less than 0.0036. Figure 1 shows a $k^2 \chi(k)$ signal, the Fourier transformations of the $Zr$ K-edge EXAFS spectra, and the observed and calculated $\chi(k)$ spectra.

**RESULTS**

**XANES spectra of tektites and natural glasses**

The XANES spectra of zirconium in the studied tektites and natural glasses are shown in Figure 2. Large double peaks (peak A and peak B) were observed for energies greater than the threshold energy. The position of one of these peaks (peak A) for köfelsite, which occurs at 18.002 keV, is shown by the dotted line. Another high

Figure 1. (a) Observed Zr K-edge XAFS spectra. (b) The EXAFS $k^3 \chi(k)$ oscillation of australite in the range $3.0 < k < 11.5$ Å$^{-1}$. (c) Its Fourier transform.

Figure 2. Experimental Zr K-edge XANES spectra of the studied tektites and natural glasses. Peak A at 18.002 keV (shown for comparison) is represented by the dotted line, while peak B at 18.014 keV is represented by the dashed line. The pre-edge peak at 17.989 keV is represented by the solid line.
was located at 18.014 keV for the type III, IV, and V glasses. The heights of the peak B increased in order from III to V. It was found that the tektite (type IV) and impact–related glasses (type I and type III) exhibited unique XANES spectra, which were distinguishable from those of the volcanic glasses (type V). The photon energy of peak A of the type V glasses was slightly lower than that of peak A of the type IV glasses. According to previous studies (Mountjoy et al., 2000; Farges et al., 1996), the presence of a pre–edge feature in the spectra of the type III glasses implies a 7– to 8–fold coordination with specific local symmetry.

Figure 3 shows a comparison of the observed XANES spectra near the Zr K–edge of the tektites, impact–related glasses, and natural glasses, which contained the zirconium compounds ZrSiO₄, zircon, PbZrO₃, and SrZrO₃. The main absorption edge (peak A) for zircon was located at 18.002 keV. The main absorption edge (peak B) for SrZrO₃ and PbZrO₃ was located at 18.011 keV. The spectra of the type I and II glasses contained similar zircon–related features. On the other hand, the patterns corresponding to obsidian in the spectra of the type V glasses were similar to those of SrZrO₃, in which Zr occupies an octahedral site. The spectra of the type I glasses and zircon, in which Zr occupies eight–coordinated sites, exhibited the highest peak at approximately 18.002 keV (peak A) and a second peak at approximately 18.014 keV (peak B). The height of peak B is usually greater than that of peak A in the case of PbZrO₃ and SrZrO₃, in which Zr occupies six– and seven–coordinate sites.

Radial distribution function and local structure

The EXAFS $k^3\chi(k)$ functions were transformed into radial distribution functions (RDF) for the Zr K–edges of the two tektites, three natural glasses, and two reference compounds, as shown in Figure 4. The RDFs of the Zr atoms in australite and indochinite were similar. This indicated

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**Figure 3.** Zr K–edge XANES spectra of the studied tektites and natural glasses and those of reference compounds. (a) Zircon has the highest A peak, at 18.002 keV. (b) PbZrO₃ and SrZrO₃ have the highest B peak, at 18.014 keV.

**Figure 4.** Fourier transforms of the Zr K–edge EXAFS oscillation functions, $k^3\chi(k)$. No phase–shift corrections were made. The first nearest peaks correspond to Zr–O bonds.
Table 2. Structural parameters determined by XAFS

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type</th>
<th>Coordination number</th>
<th>Zr-O distance (Å)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircon</td>
<td></td>
<td>8</td>
<td>2.226 (6)</td>
<td>0.26</td>
</tr>
<tr>
<td>Suevite</td>
<td>I</td>
<td>7.7</td>
<td>2.218 (4)</td>
<td>3.62</td>
</tr>
<tr>
<td>LDG</td>
<td>III</td>
<td>7.5</td>
<td>2.214 (4)</td>
<td>0.81</td>
</tr>
<tr>
<td>Australite</td>
<td>IV</td>
<td>7.5</td>
<td>2.215 (5)</td>
<td>0.14</td>
</tr>
<tr>
<td>Indochinite</td>
<td>IV</td>
<td>7</td>
<td>2.198 (3)</td>
<td>0.69</td>
</tr>
<tr>
<td>Obsidian</td>
<td>V</td>
<td>6.5</td>
<td>2.171 (2)</td>
<td>0.47</td>
</tr>
<tr>
<td>SrZrO$_3$</td>
<td></td>
<td>6</td>
<td>2.141 (3)</td>
<td>0.28</td>
</tr>
</tbody>
</table>

The expected bonding distances of six-, seven, and eight-coordinated Zr-O based on the Shannon ionic radii.

DISCUSSION

As the precursor of tektites is primarily of terrestrial origin (Urey, 1955), their chemical compositions are almost identical, with the SiO$_2$ and ZrO$_2$ contents being 67.2–82.6 wt% and 126.6–205.8 ppm, respectively (Table 1). These concentrations correspond to those seen in rhyolitic rocks. Farges and Brown (1997) suggested that volatile elements such as F, Cl, and H$_2$O do not have a significant effect on the coordination chemistry of Ti in silicate glasses. Thus, it can be presumed that the chemical composition is barely affected by variations in the structure and that it is the different physical conditions during the impact events such as the temperature and quenching speed that result in differences in the Zr local structures. There are several reasons for the existence of different types of local structures. By comparing the various crystalline phases, it can be seen that the shapes of the XANES spectra of the glasses are related to the corresponding Zr coordinated environment. The shape of the main peak for zircon corresponds to 8-fold coordinated Zr ions, and those of the peaks related to SrZrO$_3$ correspond to 7- and 6-fold coordinated Zr ions (Fig. 3 and Table 2). Further, it can be seen that the Zr local structure in volcanic glasses (obsidian and pitchstone, type V) has a coordination number of 6–6.5, which is similar to that for SrZrO$_3$.

The shapes of the main peaks for köfelsite and suevite (impact-related glasses, type I) were similar to that of the peak for zircon. These data indicated that type I glasses have local Zr environments similar to that in zircon. Zircon is a common component of igneous rocks and is a primary crystallization mineral with a high melting temperature. The crystalline phase in the type I glasses could not be detected by X-ray diffraction analysis. However, it is assumed that either zircon does undergoes crystallization, since its cooling rate is low, or that it does not melt fully, because the temperature is not high for long enough during the impact event. We can therefore conclude that the cause of the zircon like-local structure is the latter process, owing to the occurrence of type I glasses. The XANES spectrum of fulgurite is also similar to that of zircon. These data also indicated that fulgurite has a Zr local structure similar to that of zircon. This means that fulgurite is formed by a special process. The peak temperature of lightning is 1900–2300 K (Sakai et al., 2008). Lightning forms fulgurite instantaneously. Therefore, fulgurite experiences a high temperature for a very short time. The period of formation of fulgurite is shorter than that of other natural glasses. It is for this reason that fulgurite has a special local structure similar to that of zircon.

Mountjoy et al. (2000) reported that the presence of a clear pre-edge peak and a broad main peak in the XANES spectra imply poor orbital symmetry. The XANES spectra of Libyan Desert glass and Darwin glass (impact-related glasses, type III) have clear, uniquely shaped pre-edge and broad main peaks. The local Zr structure in type III glasses may have lower orbital symmetry with an approximately 7-fold coordination number.

All tektites can be classified as being of the same type (type IV). The Zr-O distances of type IV glasses are 2.198–2.215 Å, and their XANES spectra have similar shapes. This indicates that tektites have similar local Zr structures with 7-fold coordination Zr ions. However, when one focuses on the shapes of the XANES spectra, there are small differences between those of australite and philippinite.
Further, impact-related glasses can be classified into different types (type I: köfelsite, suevite; type III: Libyan desert glass and Darwin glass). Impact-related glasses are formed under different geological processes during the impact event and experience different physical environments. The Zr content of type I glasses (79.0–87.9) is higher than that of type III glasses (137.6–246.7). In contrast to XANES spectra of the other types of the glasses, those of types III, IV, and V had similar main peaks (A and B). The height of the main peak B of type IV glasses was lower than that for the type V glasses, while that of the type III glasses was lower than that for the type IV glasses. Finally, volcanic glasses can be classified as type V, while tektites can be classified as type IV and impact glasses (Libyan Desert glass and Darwin glass) can be classified as type III. The glass structure is affected by the pressure and temperature existing during the glass formation process (Stebbins and McMillan, 1989; Paris et al., 1994; Myseen and Neuvilee, 1995; Yarger et al., 1995). Tektites and impact glasses are produced by impact events, and experience high temperature and pressure. Volcanic glass experiences high temperature. Pitchstone and obsidian exhibit compositions identical to that of rhyolitic glass. The temperature of rhyolite magma is 700–900 °C. Koeberl (1997) reported that baddeleyite occurs in Libyan Desert glass and requires temperatures of 1500–2000 °C. The occurrence of baddeleyite in Libyan Desert glass indicates that impact glasses experience very high temperatures (greater than 1500–2000 °C). The formation temperature of type III glasses is higher than that for type V glasses. Further, tektites experience extremely high temperatures at the instant of impact. Melosh and Ivanov (1999) stated that silicates at the site of impact can reach an instantaneous temperature of 50000 °C, remaining at 5000–10000 °C for tens of seconds. Although the tektite formation process is still in dispute, regardless of whether tektites are formed by the quenching of the plasma state or melt, they possess extremely higher temperature history than volcanic glasses. Type II and III glasses have 7-fold coordinated Zr ions, while type IV glasses have 6-fold coordinated Zr ions. With respect to the local structures of type III, IV, and V glasses, the coordination number of Zr has a positive correlation with the temperature. With regard to the density of type II-IV glasses, obsidian has an average density of 2.36 g/cm³ (Stevenson et al., 1996), while the average density of tektite is 2.4 g/cm³ (Dunlap et al., 1998). Further, that of Darwin glass is 2.45–2.55 g/cm³ (Fudali and Ford, 1979). Thus, the density also has a positive correlation with the coordination number. Therefore, it can be surmised that the density of glasses is closely related to their local Zr structure.

CONCLUDING REMARKS

The local structures of Zr in tektites and natural glasses were studied using Zr K-edge XAFS measurements. On the basis of the XANES spectra, Zr-O distance, coordination number, and radial distribution function, determined by EXAFS analysis, we could classify the studied tektites and natural glasses into five types. These were type I (köfelsite and suevite), with a Zr coordination number of 7.7 and Zr-O distance of 2.21 Å; type II (fulgurite), which had a special structure similar to that of zircon; type III (Libyan Desert glass and Darwin glass), with a Zr coordination number of 7.5 and Zr-O distance of 2.214 Å; type IV (tektite), with a Zr coordination number of 7–7.5 and Zr-O distance of 2.198–2.215 Å; and type V (pitchstone and obsidian), with a Zr coordination number of 6.5 and Zr-O distance of 2.171 Å. The XANES spectra of types I and II have features similar to those in the spectra of zircon. On the other hand, types III, IV, and V are similar to SrZrO₃. Finally, type III is different from the other types. The XANES spectrum of type III has a pre-edge at 17.987 keV. The local Zr structures of the glasses are closely related to their formation temperatures and their density. Further, the formation temperature has a positive correlation with the coordination number. Finally, the density of the glasses also has a positive correlation with the coordination number.

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