Local structure of Titanium in natural glasses probed by X-ray absorption fine structure

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Abstract. Synchrotron radiation has been used to collect titanium K-edge absorption spectra of a suite of natural glasses (tektites, impact glasses, fault rocks and volcanic glasses). XANES and XAFS analysis provided the qualitative and quantitative information of Ti oxidation state, Ti-O distance and site geometry. Tektites possess four-, five-, six-coordinated Ti, whereas fault rock-pseudotachylite, volcanic glasses and impact glass only presented five- and six-coordinated Ti. This study indicated that different petrogenesis of natural glasses has different local structures of titanium.

1. Introduction
In natural, several kinds of glasses are formed by various geological actives. Tektites and impact glasses are produced by impact event (Alvarez et al., 1980); volcanic actives formed volcanic glass; and plate boundary active produced fault rocks. These natural glasses experienced different extreme environments, which should lead changing of local structure (Stebbins & McMillan, 1989; Paris et al., 1994; Mysen & Neuville, 1995; Yarger et al., 1995). We studied Ti local structure of tektite (2011). This present study completed natural glasses results.

2. Experiment
The specimens are tektites: hainanite, indochinite, philippinite, australite, bediasite and moldavite; impact glass-impactite, suevite and köfelsite; volcanic glasses- Darwin glass, perlite, obsidian, Kilauea volcanic glasses; and fault rock- pseudotachylite. In order to analysis the local structure of Ti in natural glasses, we used the XAFS methods. The XAFS measurement of Ti local structure was preformed with a Si (111) double crystal monochromator at the beam line BL-9C of the Photon Factory in National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. Spectra near Ti K-edge were collected in transmission and fluorescence mode at the room temperature. Analysis of XAFS data were performed by XAFS93 and MBF93 programs. (Maeda, 1987; Yoshiasa et al., 1997)

3. Result and discussion
Experimental Ti-K edge XANES spectra of typical tektites are shown in Fig.1A. The highest peak position of moldavite-green at 4984.7eV is shown by dotted line for comparison. The pre-edge peak heights at 4967.3eV change with coordinated environments. The detailed XANES spectra of tektites from three strawnfield were explained by Wang et al., 2011. These spectra are divided into three types
according to pre-edge and XANES shape: Type I, indochinite; Type II, hainanite-core, hainanite-rim, philippinite and Type III, moldavite-green. The normalized intensity at 4984.7eV is regard as 100% in moldavite-green. The pre-edge peak heights at 4967.3eV for Type I, II and III are 59-49%, 49-47%, 14%, respectively. The white line peak and shoulder heights at 4984.7eV for Type I, II and III are around 86%, 90% and 100%, respectively. Meanwhile, the crest energy at 4984.7eV in moldavite-green is more intense than other tektites.

**Figure 1.** XANE spectra near the Ti K-edge for typical tektites (A) (Wang 2011), impact glasses (B) and volcanic glasses and fault rock-pseudotachylite (C).

Fig.1B shows XANES spectra of impact glasses. Darwin glass, suevite, and köfelsite have a large pre-edge peak with shoulder. Pre-edge intensities of these three samples are 25.7%, 15.7% and 11.4%. This feature is comparable with tektite Type II and III. Impactite possesses pre-edge, which contains a main peak and two subordinate peaks. The back of XANES regions of these glasses is similar with moldavite-green, which has intense crest edge around 4984eV. The variation of XANES feature in impact glass suggested the relaxation is diverse. The various relaxations are caused by the environment when impact glasses are formed. Temperature and annealing time are most important conditions for relaxation.

Fig.1C shows XANES spectra of volcanic glasses and fault rock-pseudotachylite. Kilauea volcanic glass is an exception of this group, and only possesses a large pre-edge peak with shoulder. In addition, it has a wider crest (4984eV) than other volcanic glasses. Chemistry composition of Kilauea volcanic glasses, which contains 50.89wt% SiO$_2$ and 2.55wt% TiO$_2$, is distinguishing; it is similar with basalt. But other samples are similar with rhyolite (SiO$_2$ ≥ 70wt %). Their different forming processes are suggested that the Kilauea volcanic glass is distinguishable from other volcanic glasses by XANES pattern. Fault rock-pseudotachylite has a similar XANES spectrum with normal volcanic glasses but possesses a bit broader crest.

![Image of XANES spectra](image)

**Figure 2.** Observed Ti K-edge EXAFS $k^3\chi(k)$ oscillation of a tektite

The EXAFS $k^3\chi(k)$ functions (Fig.2) were transformed into the radial distribution functions (RDF) for Ti K-edge, as shown in Fig.3. In Fig.3A, the RDF of Ti atom in Type I- indochinite, Type II- hainanite-rim, hainanite-core, and philippinite are similar and Type III- moldavite-green is discriminated from others. In Fig.3B, Suevite shows the same feature with Type II tektites; impactite, darwin glass, and köfelsite also show the same feature with Type III tektite. The mainly peak located
around 1.5 Å and it is the same position with moldavite-green. It indicates that impact glasses have two kinds of local atomic environment around the Ti atom. In Fig. 3C, Kilauea volcanic glass and perlite show the same feature with Type II tektites; obsidian and pseudotachylite show the same feature with Type III tektite. The impact glasses, volcanic glasses, and fault rock are almost having the same structure with Type II and Type III tektites.

Figure 3. Fourier transforms of the Ti K-edge EXAFS oscillation function \( k^3 \chi(k) \). No phase shift corrections are made. In A (Wang 2011), The first nearest peaks corresponding Ti-O bonds increase with increasing coordination number of Ti in tektite (arrows). Three types of tektites can be recognized. Impact glass has the main peak position, which between Type II and Type III tektites. In B and C, all non impact related glasses possess the mainly peak that located around 1.5 Å.

In order to obtain the further information on structure parameter, we figured out the parameter fitting with analytical EAXFS formula expressed by cumulant expansion up to third order terms in tektites and natural glasses. The obtained structural parameters are summarized in Table 1.

Table 1. The structure parameters determined by EXAFS and TiO₂ composition for natural glasses. The expected bonding distances of 4-, 5- and 6- coordinated Ti-O based on the Shannon Ionic Radii: Ti(4-coordinated)-O=1.80 Å; Ti (5-coordinated)-O=1.89 Å; Ti (6-coordinated)-O=1.99 Å. Uncertainties in the last decimal place are shown in parentheses.

| Sample name              | \( \sigma^2(\text{Å}) \) | Coordination number | Ti-O distance(Å) | R-factor (%) | TiO₂(wt%) |
|--------------------------|-----------------------------|---------------------|------------------|--------------|-----------|
| indochinite              | 0.009(1)                    | 4                   | 1.812(5)         | 4.3          | 0.8       |
| hainanite-core           | 0.005(1)                    | 4 and 5             | 1.868(4)         | 0.3          | 0.87      |
| hainanite-rim            | 0.006(1)                    | 5                   | 1.888(6)         | 0.1          | 0.87      |
| philippinite             | 0.003(1)                    | 5 and 6             | 1.921(5)         | 2.7          | 0.81      |
| moldavite-green          | 0.003(1)                    | 6                   | 2.001(4)         | 3.5          | 0.11      |
| suevite                  | 0.001(0)                    | 5                   | 1.887(2)         | 2.5          | 0.64      |
| Kilauea volcanic glass   | 0.002(2)                    | 5                   | 1.900(1)         | 0.330        | 2.55      |
| perlite                  | 0.000(0)                    | 5                   | 1.902(1)         | 0.46         | 0.9       |
| pseudotachylite          | 0.005(0)                    | 5 and 6             | 1.950(2)         | 2.3          | 0.78      |
| impactite                | 0.002(0)                    | 5 and 6             | 1.952(2)         | 0.22         | -         |
| Darwin glass             | 0.005(0)                    | 5 and 6             | 1.963(4)         | 0.17         | 0.63      |
| obsidian                 | 0.000(0)                    | 5 and 6             | 1.969(2)         | 0.94         | 0.76      |
| köfelsite                | 0.006(0)                    | 6                   | 1.983(3)         | 2.1          | 0.66      |

Based on the local Ti-O distances, coordination numbers, and radial distribution function determined by EXAFS analysis, we can classify the tektites into three types. Indochinite is classified in Type I, where Ti occupy 4-coordinated (tetrahedral site) and Ti-O distances are 1.812-1.835 Å. Hainanite-rim, hainanite-core, and philippinite are in Type II, where Ti occupy 5-coordinated site (trigonal bi-pyramidal or tetragonal pyramidal site) and Ti-O distances are 1.868-1.921 Å. Moldavite-green is in Type III, where Ti occupy the 6-coordinated site (octahedral site) and Ti-O distance is 2.00-1.96 Å. Impact glasses, fault rocks and volcanic glasses have fewer variety structure than tektites.
Only 5- and 6-coordinated titanium existed with Ti-O distance of 1.89-1.90 Å, 1.95-1.98 Å. Titanium in natural glasses are from 0.11-2.55 wt%, the composition does not influence the local structure.

Farges, F. and Brown, G.E. (1997) discussed the pre-edge intensity gradually decreased by 4-, 5-, and 6- coordination Ti. Fig. 4 shows the relationship between Ti-O distance, pre-edge, and crest intensity in all tektites and natural glasses. The pre-edge feature corresponded to the previous study. In addition, the crest intensity trends to higher with increasing of Ti-O distance. It is very easy to identify the tektites and natural glasses.

4. Summary
Analysis of local structure is helping to compare formation conditions of natural glasses and distinguish them. Tektite possessed 4-, 5-, 6-coordinated Ti. All of them had a single pre-edge peak with different normalized heights. But fault rock-pseudotachylite, volcanic glasses and impact glasses, such as impactite possessed fewer variety local structures and tektites, only presented 5- and 6-coordinated Ti with Ti-O distances of 1.89-1.90 Å, 1.95-1.98 Å, and their XANES pre-edge features are similar with TiO₂ anatase, which has a main peak and two subordinate peaks. The variation of XANES feature in impact glass suggested the relaxation is diverse. The various relaxations are caused by the environment when impact glasses are formed. Temperature and annealing time are most important conditions for relaxation. This study indicated that different petrogenesis of natural glasses has different local structures of titanium. Tektite flew from atmosphere to outer space and once more returned to the earth, in this process, tektite rapidly experienced changes of annealing time, temperature and pressure. But fault rock- pseudotachylite and volcanic glasses experienced only a single tremendous change of temperature or pressure. Impact glasses are close to impact crater, so changes of temperature and pressure are limited and slowly. This reason leads the local structure of tektite is more various than other natural glasses and the four-coordinated Ti are unique in natural glasses.

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