Local Structures of Ti in Natural Silicate Glasses by XAFS Measurements

The local structure of Ti in silicate glass is known to depend on the formation and quenching conditions. We performed X-ray absorption fine structure experiments of Ti on natural glasses and Cretaceous-Paleogene boundary sediments at BL-9C. The relationship between the pre-edge position and the average Ti-O distance was found to provide detailed Ti local structural information as guided by the Ti-bearing crystals including Ti^{3+} species. This relationship implies that tektites and impact glasses were formed by various impact and quenching processes as well as different chemical conditions.

Impact glasses and tektites are silicate glasses formed by hypervelocity impact on rocks and soils on the Earth's surface, followed by rapid quenching in the atmosphere. The minimum impact velocity to produce a significant amount of melts by an impact is considered to be 12 km/s on the Earth. Natural impact-induced glasses display unique shapes, structures, and chemistry depending on the formation conditions and cooling rates. The impact sites have been identified geologically in most cases. Studies on sediments related to meteorite impacts at the Cretaceous-Paleogene (K-Pg) boundary provide important information on mass extinctions and the subsequent environmental changes. However, laboratory experiments are required to determine the detailed structural changes in glasses that experienced various impact processes before solidification.

X-ray absorption fine structure (XAFS) spectroscopy, which is an effective technique for investigating glass structures in detail, is divided into two types: X-ray absorption near-edge structure (XANES), which is known to be sensitive to the local environment around Ti (e.g. coordination number, *CN*, and valence state) in silicate glasses [1-4], and extended X-ray absorption fine structure (EXAFS), which is used to determine the average Ti-O distance [5-7].

Ti *K*-edge XAFS measurements were performed by the fluorescence method with Si (111) monochromator at the beamline BL-9C. The copper pre-edge peak position at 12.7185 keV was used for the energy calibration. The following natural glasses were selected: tektites (hainanite (t1), indochinite (t2), philippinite (t3), australite (t4), bediasite (t5), moldavite-green (t6) and
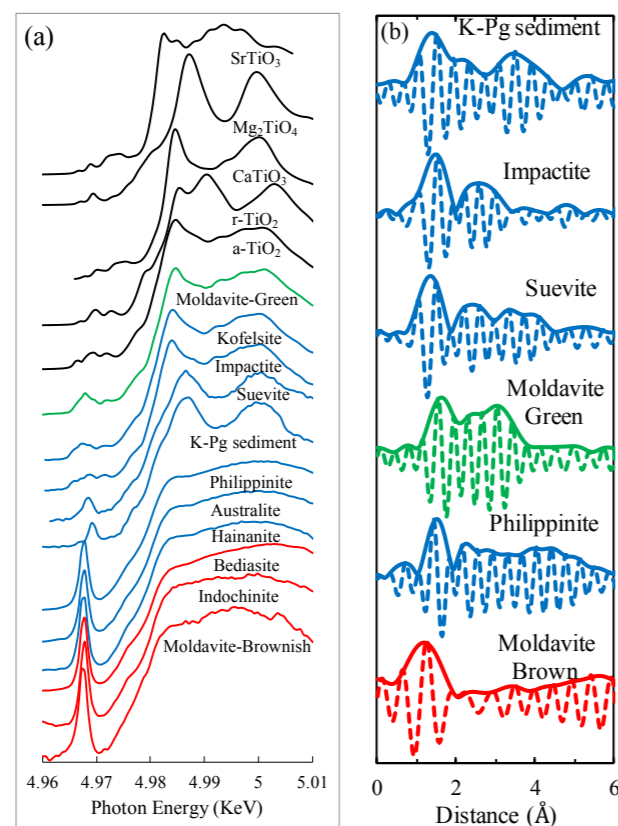

Figure 1: XANES spectra (a) and EXAFS spectra (b) of natural glasses. The reference materials with 6-coordinated Ti are plotted together.
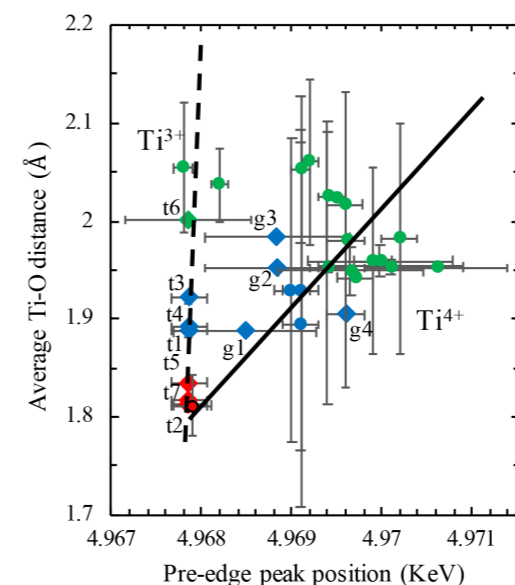

Figure 2: Relationship between the Ti *K* pre-edge position and the average Ti-O distance of natural glasses (t1-7 and g1-4; diamonds) and reference materials (circles). The red, blue and green colors represent the coordination number of 4, 5 and 6, respectively. The solid and dotted lines represent the trends of reference crystals and tektites, respectively.

-brownish (t7), whose colors depend on the composition [8]), impact glasses (suevite (g1), impactite (g2) and kofelsite (g3)) and K-Pg boundary sediment (g4). Simultaneously we measured TiO_2 (anatase and rutile), $CaTiO_3$, Mg_2TiO_4, and $SrTiO_3$ for reference. XAFS data were analyzed by XAFS93 and MBF93 programs [9].

The XANES and EXAFS spectra of Ti in the samples are shown in **Figs. 1(a)** and **1(b)**, respectively. The XANES spectra of reference compounds have various patterns, while those of the glasses are similar. However, there are two groups in terms of the pre-edge features: samples t1–t5 and t7 show narrow and high intensity, and samples t6 and g1–g4 show broad and relatively low intensity. The *CN* of Ti in the glass was estimated in previous studies by the Ti *K* pre-edge position and Ti-O distance for known reference compounds, classified into red (*CN* = 4: samples t2, t5, and t7), blue (*CN* = 5: samples t1, t3, t4, and g1-4), and green (*CN* = 6: sample t6) [3-6]. This is in contrast with the fact that TiO_2 has *CN* = 6 under ambient conditions. **Figure 2** shows different trends between the tektites and the reference crystals in the relationship between the pre-edge energy and average Ti-O distance of the samples in the present study.

Previous studies suggested that tektites with Ti *CN* = 4 were formed at high temperatures and low pressures while those with Ti *CN* = 6 were quenched at

low temperatures and high pressures [1, 2]. Ti *CN* = 5 in synthetic silicate glasses has been known at ambient pressure. *CN* of Ti in glass may be affected by chemical composition [10] and cooling speed [11]. The pre-edge positions of tektites may be affected by the valence state of Ti [4]. The pattern of Ti of K-Pg sediment is similar to those of K-Pg glasses, but the pre-edge features differ slightly. The pre-edge features and main peaks of impact glasses, K-Pg sediment and moldavite-green are similar to that of TiO_2-anatase. This similarity might be explained by the fact that Ti-polyhedron in glass is crystallized to anatase structure by a slow cooling speed or diagenesis [7]. In order to understand the detailed structural change of Ti local structure in silicate glasses, we carried out shock recovery experiments on a tektite. The data obtained by Ti XAFS match the trend of the reference crystal but not that of tektite in **Fig. 2**. This result indicates that natural tektites were formed under special quenching and oxidation conditions. The present study proves a clear relationship between the Ti *K* pre-edge energy position and the average Ti-O distance. This relationship may help clarify the tektite formation and quenching processes.

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T. Tobase[1], T. Sekine[1] and A. Yoshiasa[2] ([1]HPSTAR, [2]Kumamoto Univ.)