Local structure of Zn in Cretaceous-Tertiary boundary clay from Stevns Klint

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The local structure around zinc atoms in Cretaceous-Tertiary (K-T) boundary clay from Stevns Klint, Denmark, was studied by Zn K-edge XAFS spectroscopy. XAFS measurements were performed at the BL-12C and BL-9C beamlines at the Photon Factory in the High Energy Accelerator Research Organization (KEK), Japan. The local structure around Zn in the K-T clay resembles the framework structure of the tetrahedral ZnO₄ site in the zinc silicate willemite, judging from first shell Zn-O and second shell Zn-cation distances [1.953(3) and 3.51(2) Å, respectively], X-ray absorption near edge structure (XANES) spectra, and radial structure function. The Debye-Waller factor σ^2 of the K-T clay sample is similar to those for the tetrahedral sites in crystalline phases, where Zn occupies mainly tetrahedral sites. The local structure of Zn in the K-T clay is peculiar and differs from that found in many clay minerals.

Keywords: XAFS, Local structure of Zn, K-T boundary clay, EXAFS, XANES

INTRODUCTION

The Cretaceous-Tertiary (hereafter, K-T) mass extinctions, which occurred 65.5 million years ago, have generally been considered to be a result of a meteorite impact, since Ir anomalies at the K-T boundary clay were found by Alvarez et al. (1980). K-T boundary clay is also enriched in other trace metals including Zn (Christensen et al., 1973; Strong, 1985; Schmitz et al., 1992). By comparing data from six K-T boundary sites, Strong et al. (1992) revealed that the boundary clay is also enriched in Cr, Co, Ni, Cu, Zn, As, and Sb on a global scale in addition to being enriched in Ir. They considered that the clay's high content of Cr and Ni was meteoritic in origin, and that the Cu, Zn, As, and Sb content was derived from the impact ejecta from terrestrial sources. The impact-target rocks of the impact site are considered to be a suitable origin for the Cu, Zn, As, and Sb content. The Zn content in the K-T boundary clay is larger than 300 ppm and reaches a maximum of 800 ppm (Strong et al., 1992; Premovic et al.,

2008). Because absolute concentrations are far higher than would be provided directly from terrestrial and meteoritic sources, enrichment was presumed. Based on geochemical considerations, Premovic et al. (2008) proposed that the predominant source of enhanced concentration of Zn was probably the impact-ejecta fallout deposited on the hinterland of nearby soil, which was subsequently leached by the impact-induced-acidic surface waters. They also suggested that Zn²⁺ resides in the exchangeable Mg²⁺ interlayer sites of the main clay mineral smectite.

It is important to know whether Zn forms a crystal phase and how Zn is concentrated in mineral phases under various conditions. Many researchers have been interested in the occupying sites of Zn in clay minerals (Manceau et al., 2000; Schlegel et al., 2001; Juillot et al., 2006). Zinc ions in crystal phases have been found in both tetrahedral and octahedral coordination environments with first-neighbor oxygen atoms. The coordination environment changes with physical and chemical conditions such as temperature (Wang et al., 2011) and pH (Roberts et al., 2003) at the time of formation. For example, tetrahedral coordination of Zn can be formed under higher tempera-

ture or higher pH conditions. X-ray absorption fine structure (XAFS) analyses provide information about the chemical state and coordination environment around Zn atoms and help identify of the main concentration phase. We have published the chemical state and local structure of arsenic in the K-T clay and clarified that As occupies the tetrahedral AsO_4 site in ferrihydrite (Sakai et al., 2007). In order to obtain detailed information on the local structures in the K-T boundary clay, in this study, we determined the local Zn-O distances and Debye-Waller factor σ^2 for Zn in the K-T boundary clay by EXAFS analyses.

EXPERIMENTAL AND ANALYTICAL METHODS

The specimen of K-T boundary clay is from Stevns Klint in Denmark (Sakai et al., 2007). The measurement was performed at a red clay layer located in the lowermost K-T clay. Zn content in the specimen was determined to be several hundred ppm by SEIKO, SEA2001 XRF measurement. In order to investigate the local structure around zinc atoms in the K-T boundary clay, we first prepared several references of natural Zn minerals from the National Science Museum, Tokyo, such as willemite (Zn_2SiO_4), adamite [$\text{Zn}_2(\text{AsO}_4)(\text{OH})$], smithonite (ZnCO_3), descloizite [$\text{PbZnVO}_4(\text{OH})$], hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$), franklinite [$(\text{Zn}, \text{Mn}, \text{Fe})_3\text{O}_4$], gahnite (ZnAl_2O_4), scholzite [$\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$], zincite (ZnO), and wurtzite (hexagonal ZnS), where the idealized chemical formula is shown in the parenthesis. All XAFS measurements were performed with a Si(111) double crystal monochromator at BL-12C and BL-9C branch lines of the Photon Factory in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The mirror for focusing and strengthening X-ray intensity was installed at the upstream side. The energy calibration of X-rays was performed by setting the copper metal pre-edge absorption peak to 8.9788 keV. Spectra near the Zn *K*-edge were collected in transmission mode and fluorescence mode using the Lytle-type and 19-element solid-state detectors (SSD) at room temperature.

Analyses of XAFS data were performed using the XAFS93 program (Maeda, 1987). The EXAFS interference function, $\chi(k)$ was extracted from the measured absorption spectrum using a standard procedure (Maeda, 1987; Yoshiasa et al., 1999a, 1999b). The radial structural function was obtained by the Fourier transform over the k range of 2.5–11.5 $\text{\AA}^{-1}$ for reference minerals and of 2.5–9.5 $\text{\AA}^{-1}$ for the K-T clay. In the quantitative analysis for the K-T clay sample, willemite, adamite, gahnite, hardystonite, and zincite, we carried out the Fourier filtering technique and a nonlinear least-squares structure parame-

ters fitting method with an analytical EXAFS formula expressed by cumulant expansion up to third order terms (Yoshiasa et al., 2000). The EXAFS oscillation for the first and second shells were obtained by the Fourier transform in the range $1.0 \text{ \AA} \leq R \leq 2.0 \text{ \AA}$ and $2.6 \text{ \AA} \leq R \leq 3.2 \text{ \AA}$, respectively. Coordination numbers for the first shell were fixed to $N = 4.0$ or 6.0 and neighboring atoms were set to only oxygen atoms during the analysis, based on the known crystal structures of willemite, adamite, gahnite, hardystonite and zincite (Louisnathan, 1969; Cooley and Reed, 1972; Hawthorne, 1976; Klaska et al., 1978; Albertson et al., 1987). The second shell distance for the K-T clay was determined assuming that the coordination number is eight and the neighboring atoms are silicon. The third-order term was negligibly small in these minerals and in the K-T clay. The reliability indexes, R , between the experimental and calculated EXAFS function, were less than 0.022.

Figure 1. Experimental Zn *K*-edge XANES spectra for reference zinc minerals and K-T clay.

RESULTS AND DISCUSSION

Zn *K*-edge XANES spectrum features and radial structure in K-T clay

The Zn *K*-edge XANES spectrum of the K-T clay sample is compared with those of reference zinc minerals (Fig. 1). There is almost no chemical shift in the threshold E_0 energies among these Zn^{2+} oxide minerals. In the K-T boundary clay, the E_0 energy of Zn agrees well with the values of the Zn^{2+} oxide minerals. The spectrum of the K-T clay reveals similar features to those of willemite, adamite and smithonite, in which zinc is in a divalent state. The main peak in the XANES spectrum of the K-T clay is similar in shape to that of willemite, although the shape of the spectra is different around 9.68 keV.

The EXAFS interference function was transformed into the radial structure function (RSF) for zinc *K*-edge of six specimens, namely willemite, adamite, gahnite, hardystonite, zincite, and K-T clay sample, as shown in Figure 2. The RSF for the K-T clay sample is similar in shape to that for willemite. It indicates that they have a similar local atomic environment around Zn atoms, although the distances between a Zn atom and cation is slightly elongated (the second peak at 2.8–3.0 Å in Fig. 2). Willemite is a silicate mineral with a framework structure consisting of ZnO_4 and SiO_4 tetrahedra. Hence, the XANES spectra and RSF for Zn atoms indicate that Zn in the K-T clay occupies a tetrahedral ZnO_4 site in a willemite-like framework structure.

Local Zn-O distance and EXAFS Debye-Waller factor σ^2

The local Zn-O distances and Debye-Waller factor σ^2 derived from least-squares fit to Fourier-filtered EXAFS spectra are summarized in Table 1. The Zn-O interatomic distance for the K-T clay sample is 1.953(3) Å, which is similar to the distances for willemite, 1.961(6) Å; gahnite, 1.966(4) Å; hardystonite, 1.962(3) Å; and zincite, 1.969(3) Å. The magnitude of σ^2 is influenced by coordination environment and it becomes smaller with decreasing bonding distance in general (Yoshiasa et al., 1997; Yoshiasa et al., 2000). The magnitude of σ^2 in the tetrahedral site is smaller than that in the octahedral site (Table 1). In case Zn was physically absorbed on the surface, the Debye-Waller factor usually shows a greater value than that for crystal phases (Dalba and Fornasini, 1997; Ouyang et al., 2010). In the present study, the Debye-Waller factor σ^2 of the K-T clay sample is similar to those for tetrahedral sites in crystalline phases, indicating that Zn occupies mainly a tetrahedral site in crystalline phases.

Zinc ions in crystal phases have been found in both tetrahedral and octahedral coordination environments with first-neighbor oxygen atoms. In previous studies, the local structural environments of Zn^{2+} in phyllosilicate and other layered structures were investigated by EXAFS experiments (Manceau et al., 2000; Schlegel et al., 2001; Juillot et al., 2006). First shell Zn-O and second shell Zn-cation distances in phyllosilicates and layered structures were typically 2.04–2.08 Å and 3.08–3.32 Å, respectively (Schlegel et al., 2001; Juillot et al., 2006). Zn ions in phyllosilicate including smectite are commonly located in octahedral sites. Although Premovic et al. (2008) assumed that Zn resides in the exchangeable Mg^{2+} interlayer sites of the smectite in the K-T boundary, the assumption is not

Figure 2. Fourier transforms of the zinc *K*-edge EXAFS oscillation function for reference zinc minerals and K-T clay. The absolute and imaginary parts of the Fourier transforms of EXAFS spectra were shown. No phase shift correction was applied.

Table 1. The structure parameters determined by EXAFS and diffraction methods

Sample	σ^2 (Å ²)	Coordination Number	Zn-O distance by EXAFS (Å)	Zn-O distance by diffraction (Å)
K-T boundary clays	0.0041(2)	4	1.953(3)	—
Willemite	0.0067(7)	4	1.961(6)	1.941-1.979 (Klaska, et al. 1978)
Adamite	0.0103(5)	6	2.103(6)	2.010-2.131 (Hawthorne, 1976)
Gahnite	0.0070(3)	4	1.966(4)	1.948-1.958 (Cooley and Reed, 1972)
Hardystonite	0.0055(2)	4	1.962(3)	1.937 (Louisnathan, 1969)
Zincite	0.0049(2)	4	1.969(3)	1.970-1.981 (Albertson et al., 1987)

The distances by diffraction experiments represent the mean value of ions occupying a crystallographically equivalent site because the natural minerals form a solid-solution.

in agreement with our results, indicating that Zn occupies a tetrahedral ZnO₄ site in a framework structure.

The local structure of Zn in the K-T clay is peculiar. Environmental change after a meteorite impact may be anticipated by understanding how the unique local structure of Zn occurs in the K-T clay. It is known that Zn forms both tetrahedral and octahedral coordination sorption complexes on oxide surfaces and in precipitate depending on pH condition (Roberts et al., 2003). The tetrahedral Zn-O distance in the complexes synthesized under higher pH conditions was typically 1.92-1.93 Å. Though detailed structures of these complexes are not known, complexes synthesized under higher pH conditions may have a framework structure or a framework-like cluster with ZnO₄ tetrahedra. This may imply that precipitation of Zn silicate oxide took place under high pH conditions such as in seawater. The local structure around Zn in the K-T clay resembles that of the Zn site in willemite, judging from first shell Zn-O and second shell Zn-cation distances [1.953(3) and 3.51(2) Å, respectively], XANES spectra (Fig. 1) and RSF (Fig. 2). After precipitation formation, the local structure of Zn in a crystal phase which resembled willemite might have formed by diagenesis.

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