

# XAFS Study of As in K-T Boundary Clays

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**Abstract.** Local structure around arsenic atoms in K-T boundary clays was studied by As K-edge XAFS spectroscopy. The threshold  $E_0$  energy of As and the characterization of the white peak of XANES spectra agree well with the values of As(+5) minerals like  $\text{Zn}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCu}(\text{AsO}_4)(\text{OH})$  according to the comparison with several types of arsenic minerals. This indicates that arsenic is in a high oxidation state As(+5) and occupies the  $\text{AsO}_4$  tetrahedral site of a mineral in K-T boundary clays.

**Keywords:** As in K-T boundary clay, XAFS of As minerals, Local structure of As, Chemical species of As.

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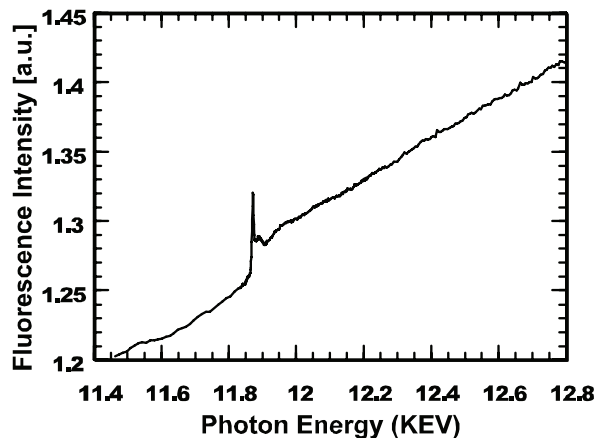
## INTRODUCTION

K-T boundary clays were formed inbetween the Cretaceous (Kreide) and Tertiary geological times. As they are composed of black clays, they stand out clearly. These clays contain relatively high Pt-group element concentration including iridium [1]. Additionally, arsenic anomalies have also been detected in some K-T boundary clays [2]. These concentrations may provide various kinds of information on the asteroid impact and mass extinction at the end of the Cretaceous.

## EXPERIMENTAL

The specimen of K-T boundary clays is from Stevns Klint in Denmark. In order to study the local structure around As atoms in K-T boundary clay, we prepared several reference natural arsenic minerals such as, natural arsenic (As), nickeline (NiAs), enargite ( $\text{Cu}_3\text{AsS}_4$ ), arsenopyrite ( $\text{FeAsS}$ ), conichalcite  $\{\text{CaCu}(\text{AsO}_4)(\text{OH})\}$ , ferrihydrite and legrandite  $\{\text{Zn}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}\}$ . The ferrihydrite was ( $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ) from the Horobetsu mine, Hokkaido, Japan that strongly sorbs to arsenic (+5) as arsenate ( $\text{AsO}_4$ )<sup>3-</sup>. All XAFS measurements were performed with a Si(111) double crystal monochromater at BL-

12C and BL-9C branch lines of the Photon Factory in the National Laboratory for High Physics (KEK), Tsukuba, Japan. Spectra near the As K-edge were collected in transmission mode and fluorescence mode using Lytle-type or 19-elements solid-state detectors (SSD) at room temperature. Analyses of XAFS data were performed by using XAFS93 and MBF93 programs [3].



**FIGURE 1.** XAFS spectra near the As K-edge for K-T boundary clays.

## RESULTS AND DISCUSSION

The fluorescence XAFS spectrum near the As K-edge for K-T boundary clays are shown in Fig. 1. and the unsmoothed background subtracted normalized EXAFS data for all samples studied are shown in Fig. 2. In Fig. 3 the observed XANES spectrum near the As K-edge of the K-T clay sample is compared to those of reference arsenic minerals.

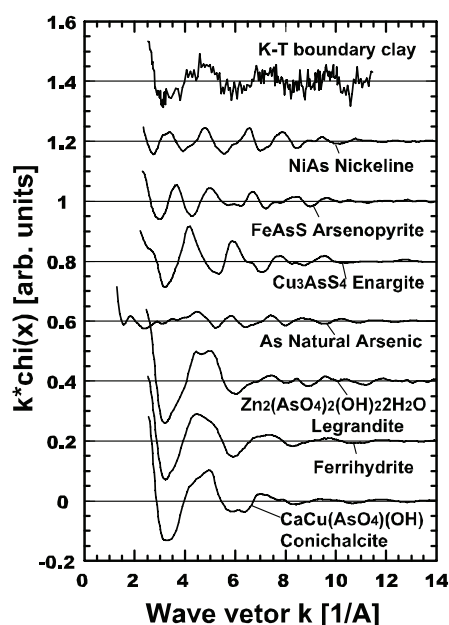


FIGURE 2. Unsmoothed background-subtracted normalized EXAFS data for all samples studied.

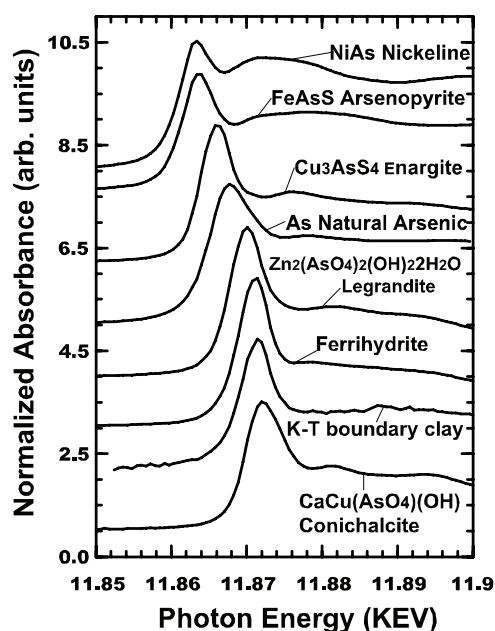


FIGURE 3. XANES spectra near the As K-edge for reference arsenic minerals and K-T clay.

In the XANES spectra, the threshold  $E_0$  energy (the absorption edge) shifts to higher values with increasing arsenic oxidation state. However the absorption edge for As(+5) oxide, legrandite, is at lower energy than that of the corresponding As(+5) oxide, conichalcite. The shift is attributed to difference of the composing atoms. The oxidation state of As in the K-T clay sample is estimated as As(+5) because the absorption edge approximately corresponds to that of legrandite, ferrihydrite and conichalcite.

The  $k^3\chi(k)$  function was transformed into the radial structure function (RSF) for the As K-edge of four samples, ferrihydrite, conichalcite, legrandite and K-T clay as shown in Fig. 3. As seen from Fig. 3, the RSF for the As atoms in the K-T boundary clay sample, conichalcite and ferrihydrite are very similar, although the peak positions are slightly shifted and the shape of the EXAFS spectra is slightly different (Fig. 2). It indicates that the compounds have a similar local atomic environmental around the As atoms, but that their extended structures are not equivalent.

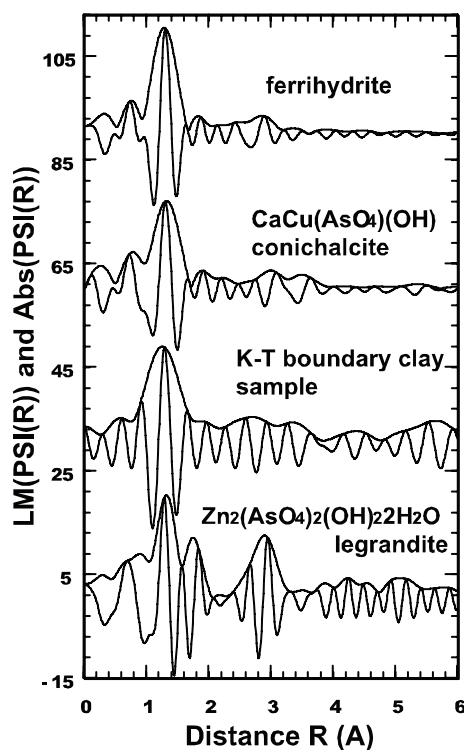


FIGURE 4. Fourier transforms of the As K-edge XAFS oscillation function  $k^3\chi(k)$  spectra in the range of  $3.0 < k < 13.0 \text{ \AA}^{-1}$  for ferrihydrite, conichalcite ( $3.0 < k < 13.0 \text{ \AA}^{-1}$ ), K-T clay sample ( $2.5 < k < 11.5 \text{ \AA}^{-1}$ ) and legrandite ( $3.0 < k < 15.0 \text{ \AA}^{-1}$ ). No phase shift corrections are made.

In order to obtain further information on the structure parameters of the local structures and to compare them around the As atoms, we carried out

**TABLE 1.** The structural parameters determined by EXAFS and diffraction methods.

| Sample name       | $\sigma^2$ ( $\text{\AA}^2$ ) | Coordination Number | As-O distance by EXAFS ( $\text{\AA}$ ) | R factor (%) | As-O distance by diffraction ( $\text{\AA}$ ) |
|-------------------|-------------------------------|---------------------|-----------------------------------------|--------------|-----------------------------------------------|
| K-T boundary clay | 0.0014(10)                    | 4                   | 1.682(3)                                | 3.0          | -                                             |
| Conichalcite      | 0.0017(1)                     | 4                   | 1.716(0)                                | 3.5          | 1.679(5)-1.714(4)                             |
| Legrandite        | 0.0020(1)                     | 4                   | 1.679(1)                                | 3.5          | 1.67(1) - 1.70(1)                             |
| Ferrihydrite      | 0.0019(3)                     | 4                   | 1.703(3)                                | 3.1          | -                                             |

parameter fitting with the analytical EXAFS formula expressed by cumulant expansion up to third order terms in the K-T clay sample, conichalcite, legrandite and ferrihydrite.

In the parameter fitting analysis, coordination number and atoms were constrained to  $N = 4.0$  and oxygen atoms, respectively, because As atoms have tetrahedral 4-fold coordination ( $\text{AsO}_4$ ) in ferrihydrite, conichalcite and legrandite [4-6]. The obtained structural parameters are summarized in Table. 1. The third-order term was negligible. The As-O interatomic distance of the K-T clay sample is 1.682  $\text{\AA}$ , which approximately coincides with result of conichalcite, 1.716(0)  $\text{\AA}$ , legrandite, 1.679(0)  $\text{\AA}$  and ferrihydrite, 1.703(3)  $\text{\AA}$ . In addition, the Debye-Waller factor for the K-T clay sample is similar to those of conichalcite, legrandite and ferrihydrite. If As were adsorbed on the surface or co-precipitated in the K-T clay sample, the Debye-Waller factor and a shape of the obtained XANES spectrum would differ greatly from those of the other reference minerals. The obtained information and the existence of a second nearest neighbor shell for the K-T clay sample indicate that the As atoms occupy  $\text{As(5+)O}_4$  tetrahedral sites of trace single-phase arsenic mineral in the K-T clay sample. At the present stage, we predict that the reason for this, from several implications like oxidation state, is associated with the high temperature at asteroid impact, with

weathering after the impact, and with diagenesis caused by sedimentation. To reveal the reason, XAFS study of meteorites and oceanic basalts, including other concentrated elements, is necessary to precisely determine the chemical states. Additionally, clarification of the main arsenic phase in K-T clays contributes to the study of K-T boundary phenomena.

## ACKNOWLEDGMENTS

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## REFERENCES

1. L. W. Alvarez, *Science* **208**, 1095-1108 (1980).
2. B. Schmitz, *Geochim. Cosmo. Acta* **56**, 1695-1703 (1992).
3. H. Maeda, *J. Phys. Soc. Jpn.* **56**, 2777 (1987).
4. M. M. Qurashi and W. H. Barnes, *Can. Mineral.* 561-577 (1963).
5. W. J. Mclean *et al.*, *Am. Mineral.* **56**, 1147-1154 (1971).
6. D. M. Sherman and S. R. Randall, *Geochimica Acta*, **67**, 22, 4223-4230 (2003).