Materials Science

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Local structure of As in arsenic concentrated K-T boundary clay

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Introduction

K-T boundary was formed in-between geologic time, Cretaceous (Kreide) and Tertiary, which is composed black clays, stands out clearly. These clays contain relatively high Pt-group element concentration including Iridium. Additionally, arsenic anomaly has also detected in some K-T boundary clays. These concentrations may have various kinds of information in 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 (Cu_3AsS_4), arsenopyrite (FeAsS), conichalcite {$CaCu(AsO_4)(OH)$}, ferrihydrite and legrandite {$Zn_2(AsO_4)_2(OH)_2\ 2H_2O$}. The Ferrihydrite ($Fe_2O_3{\cdot}0.5H_2O$) from Horobetsu mine, Hokkaido, Japan that strongly sorbs to arsenic (+5) as the arsenate $(AsO_4)^{3-}$. All XAFS measurements were performed with a Si(111) double crystal monochromater at BL-12C and BL-9C blanch lines of Photon Factory. Spectra near the As K-edge were collected in transmission mode and fluorescence mode using a Lytle-type or 19-elements solid-state detectors (SSD) at room temperature. Analyses of XAFS data were performed by using XAFS93 and MBF93 programs.

Results and Discussion

In Fig. 1, observed XANES spectra near the As K-edge of the K-T clay sample are compared to those of reference arsenic minerals. In XANES spectra, threshold E0 energies (the absorption edge) shift to higher side with increasing arsenic oxidation state. The oxidation state of As of K-T clay sample is estimated As(+5) because the absorption edge approximately corresponds with that of legrandite, ferrihydrite and conichalcite. As seen from Fig. 2, the radial structure function for As atoms of K-T boundary clay sample, conichalcite and ferrihydrite are very similar. The As-O inter-atomic distance of K-T clay sample is 1.682 Åwhich approximately coincides with result of conichalcite, 1.716(0Å, legrandite, 1.679(0)Å and ferrihydrite, 1.703(3)Å. As atoms occupy $As^{+5}O_4$ tetrahedral sites of trace single-phase arsenic mineral in K-T clay sample. At the present stage, we predict that the reason associate with several implication like oxidation with high temperature at asteroid impact, with weathering after the impact, with diagenesis caused by sedimentation [1].

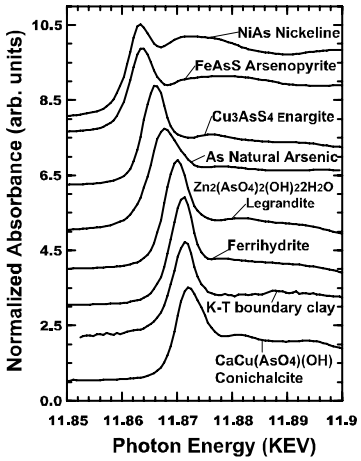

Figure 1. XANES spectra near the As K-edge for reference arsenic minerals and K-T clay.

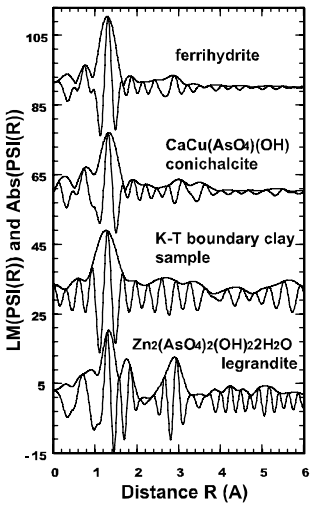

Figure 2. Fourier transforms of the As K-edge XAFS oscillation function $k^3\chi(k)$ spectra for ferrihydrite, conichalcite, K-T clay sample and legrandite. No phase shift corrections are made.

References

[1] S. Sakai et al. The American Institute of Physics,Conf. Proc. 882, 274 (2007)

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