

Blocking Effect of Natural Organic Matter on the Adsorption of Cesium in Particulate Matter Recovered from the Pripyat River in Chernobyl

Cesium (Cs) is adsorbed into the interlayer of clay minerals as an inner-sphere complex. Natural organic matter (NOM) in the environment can inhibit the adsorption of Cs by an NOM covering on the clay minerals. This blocking effect of NOM can increase the dissolved fraction of Cs in river water, leading to an increase of Cs incorporation in the ecosystem. The blocking effect, however, has not been shown by direct observation of natural samples. Using scanning transmission X-ray microscopy (STXM), we confirmed a coating of humic substances on clay minerals in particulate matter obtained from the Pripyat River, and revealed that the blocking effect occurs in natural samples.

The behavior of radioactive cesium (RCs) emitted by nuclear power plant accidents [1, 2] differed between the Abukuma (Fukushima) and Pripyat (Chernobyl) Rivers. Previous studies showed that more than 70% of Cs was dissolved in the Pripyat River [3]. Conversely, Cs in particulate matter (PM) accounted for more than 70% of total Cs in the Abukuma River (dissolved fraction was less than 30%) [4]. Although Cs is generally adsorbed into the interlayer of clay minerals as an inner-sphere complex [5], laboratory adsorption experiments suggested that the different RCs behavior between Chernobyl and Fukushima may be related to the blocking effect by the coating of natural organic matter (NOM) on clay minerals [6]. This blocking effect of NOM, however, has not been shown by direct observation of natural samples in terms of morphological images and characterization of NOM responsible for the effect. Therefore, the aim of this study was to investigate the blocking effect in the environment (especially at Chernobyl) including characterization of the blocking organic matter.

In the Pripyat River, water sample was filtered initially by a membrane filter to recover river PM (> 0.45 μm). Dissolved organic carbon (DOC) content was 18 mg/L in the Pripyat River, which is 10 times higher than that in the Abukuma River (= 0.9–1.3 mg/L).

We examined Cs L_{III} -edge EXAFS to study Cs species adsorbed on PM collected from the Pripyat River and on the PM treated by hydrogen peroxide (H_2O_2) to decompose organic matter [6]. The samples for Cs-EXAFS were prepared as follows: a PM sample was equilibrated with 0.76 mol/L CsCl, washed repeatedly with Milli-Q water to remove the excess CsCl solution, and then sealed in polyethylene bags [6]. The EXAFS spectra of the Cs on PM were measured at BL-9A and BL-12C.

Figure 1(b) shows radial structural functions (RSF; phase shift uncorrected) of Cs L_{III} -edge EXAFS spectra for Cs adsorbed on Chernobyl PM before and after the removal of NOM [7]. As references, spectra of hydrated Cs^+ in water and Cs adsorbed on clay minerals are shown. The first and second peaks at $R+\Delta R = 2.3\text{--}2.7 \text{ \AA}$ and $3.3\text{--}3.7 \text{ \AA}$ are ascribed to Cs bonding to oxygen in hydrated water and the direct bonding of Cs to a siloxane layer in a 2:1 phyllosilicate mineral, respectively. As to the PM from Chernobyl, the RSF for the original sample exhibits a larger first peak than the second one. On the other hand, the magnitude of the second peak became similar to that of the first peak after the removal of NOM. These results suggest that PM has the potential to form an inner-sphere complex with Cs, the contri-

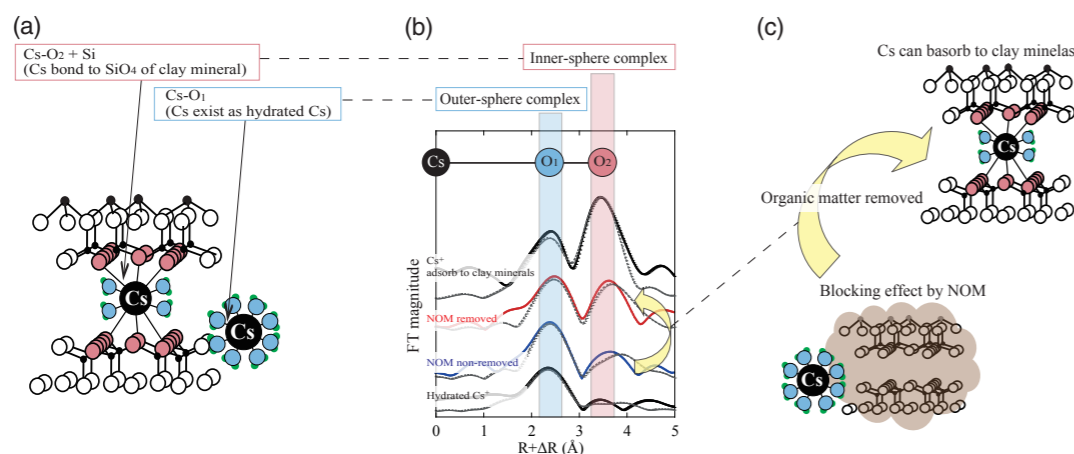


Figure 1: (a) Cs adsorption model of inner-sphere and outer-sphere complex. (b) RSF of Cs L_{III} -edge EXAFS of Cs adsorption on clay minerals, NOM removed sample, NOM non-removed sample, and hydrated Cs. (c) The model of the blocking effect, and relationship between organic matter and Cs adsorption behavior.

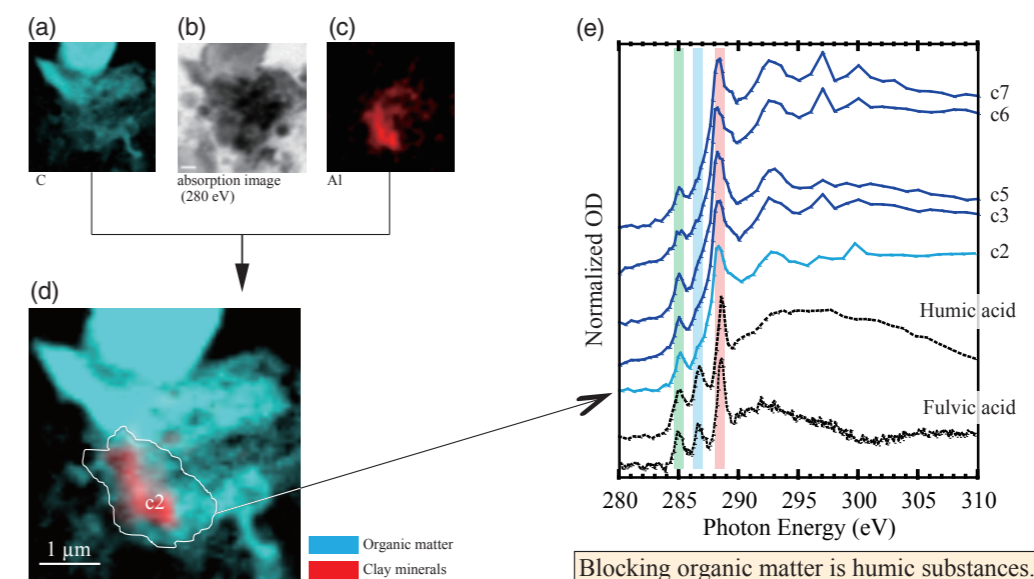


Figure 2: (a), (b), and (c) are the carbon image, absorption image at 280 eV as the morphological image, and aluminum image, respectively. (d) Composite image of (a) and (c), clearly showed that organic matter covering the clay minerals. (e) C-XANES extracted from the area of interest in (d) and that of other PM, which revealed that the blocking organic matter is humic substances. The first, second, and third peak indicate aromatic, phenolic or ketonic, and carboxylic carbon, respectively.

tribution of which is larger in the sample after the removal of organic matter [6]. The second peak, however, was attenuated for Cs adsorbed on the original PM, which suggests that the NOM inhibits the formation of the inner-sphere complex because of the blocking effect. The coating of NOM results in the reduction of K_d (solid-water distribution coefficient), or the decrease of Cs adsorption onto the PM [7].

Subsequently, association of NOM and clay minerals in the PM and characterization of NOM were conducted by scanning transmission X-ray microscopy (STXM) coupled with C K -edge XANES for the area of interest within the STXM image [7] using a compact STXM [8], newly developed at BL-13A. Figure 2 shows the absorption image at 280 eV as a morphological image of PM [7]. Figure 2 (d) clearly shows that organic matter covered the clay minerals, and carbon K -edge XANES [Fig. 2(e)] indicated that humic substances, mainly composed of humic and fulvic acids [9, 10], were the main components that induced the blocking effect in the Pripyat River.

Based on these Cs EXAFS and C XANES results, it is confirmed that the blocking effect can occur in the Pripyat River, which is caused by the covering of humic substances on clay minerals [7]. It was also found that K_d of Cs decreases with the increase of organic content in the PM, possibly due to the blocking effect. Hence, we conclude that the association of NOM and clay minerals can control the distribution of RCs into the aque-

ous phase, which in turn governs its incorporation into aquatic ecosystems.

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BEAMLINES

BL-9A, BL-12C, and BL-13A

H. Suga^{1,2}, Q. H. Fan³, Y. Takeichi^{2,4}, K. Tanaka¹, H. Kondo¹, A. Sakaguchi⁵, N. Inami², K. Mase^{2,4}, K. Ono^{2,4}, and Y. Takahashi^{2,6} (¹Hiroshima Univ., ²KEK-IMSS-PF, ³Chinese Academy of Sciences, ⁴SOKENDAI, ⁵Univ. of Tsukuba, ⁶The Univ. of Tokyo)