

# Chemical State Analysis of Trace-level Alkali Metals Sorbed in Micaceous Oxide by Total Reflection X-ray Photoelectron Spectroscopy

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## 1 Introduction

After the accident of Fukushima Daiichi Nuclear Power Station in March 2011, it has become clear that radioactive cesium is strongly sorbed in micaceous oxides of clay minerals. In order to clarify the adsorption-desorption behavior of radioactive cesium in micaceous oxides, the chemical bonding states of cesium and the other alkali metals sorbed in micaceous oxides have been investigated. Since the number of atoms in radioactive <sup>137</sup>Cs (or <sup>134</sup>Cs) is extremely small, we specially focused on the chemical states of trace amount of cesium. For this purpose, we applied total reflection X-ray photoelectron spectroscopy (TR-XPS).

## 2 Experiment

The micaceous oxide (mica) was a single crystal of artificially synthesized phlogopite. The chemical composition of the mica was  $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$ . Alkali metals (M: Na, Rb, and Cs) were sorbed by immersing mica in 20 mM MCl solution. XPS measurements were performed at the BL-27A station. The typical photon energy was 3000 eV. For normal XPS, the X-rays were irradiated at 35° from the surface. In the TR-XPS mode, the incident X-rays were irradiated at 0.2° that is fairly lower than the critical angle of the total reflection.

## 3 Results and Discussion

Fig. 1 shows the XPS wide-scan spectra of Cs-adsorbed mica for two incident X-ray angles. The spectra around Cs 3d region are displayed in small inset. For TR-XPS, the background around 730 eV, where Cs 3d peaks are located, was less than 1/10 of that for normal XPS. Owing to the background reduction, the detection limit of cesium by TR-XPS was about 100 pg·cm<sup>-2</sup>. If all of the cesium is composed of <sup>137</sup>Cs ( $t_{1/2}=30.2$  y), this weight corresponds to about 200 Bq of <sup>137</sup>Cs. So it was

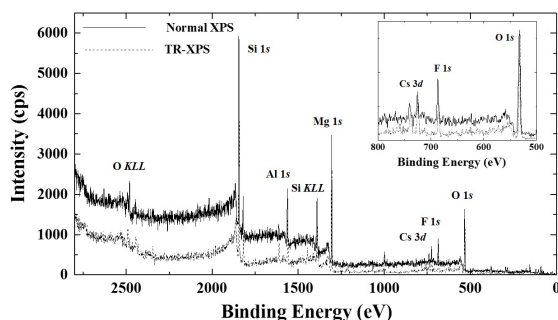


Fig. 1: XPS wide scan spectra for cesium-adsorbed mica for two different incident angles.

demonstrated that the ultra-trace amount of cesium

comparable to the radioactive cesium level can be measured by TR-XPS.

In Fig. 2, the core-level energy for three alkali metals is plotted as a function of the layer thickness. For Cs and Rb, the core-level energy shifts to lower binding-energy side with the decrease in the thickness. On the other hand, the

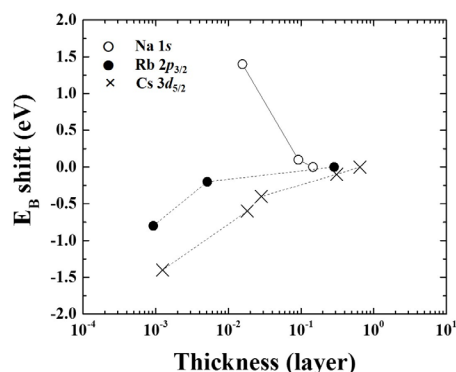


Fig. 2: Core-level binding energy shifts ( $E_B$  shift) for Na, Rb and Cs adsorbed on mica as a function of the thickness.

core-level energy of Na 1s for sodium shifts to higher binding-energy side with the decrease in the thickness.

Generally, when we consider a compound M-X (M: metal, X: counter anion), the higher the polarization of an M-X bond is, the higher the core-level energy of M becomes. Namely, when the  $\delta$  value in  $\text{M}^{\delta+}\text{-X}^{\delta-}$  bond becomes large, the XPS core-level binding energy of M shifts to higher energy side. Actually, the Na 1s binding energy for sodium shifts to higher energy sides with the increase in the electronegativity of the counter anion [1]. However, this general tendency does not hold for cesium. In the case of cesium, the core-level energy shifts to lower energy side with the increase of the polarization of the chemical bond [2]. Thus in all three alkali metals, the chemical bond between alkali metals and micaceous oxides for thin layer is more polarized than that for thick layer. This means that the ultra-trace amount of alkali metals sorbed in micaceous oxides is more ionically bonded with the substrate compared with thick layer.

## References

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