

# X-ray Microprobe Analysis of Cs-Containing Micas from Hanford, Washington

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## Introduction

Cesium-137 is an abundant waste contaminant in Hanford sediments, so the retention of Cs<sup>+</sup> has significant implications for waste remediation. The micas, including biotite and muscovite, in Hanford sediments have a crystallographic structure that strongly binds poorly hydrated monovalent cations such as Cs<sup>+</sup>. This structure consists of metal ions, principally aluminum and silicon but including isomorphous substitutions of iron and other metals, in sheets where they are octahedrally and tetrahedrally coordinated with oxygen. These sheets are bound together by potassium to form a book structure. Typically, a fraction of Cs<sup>+</sup> is intransigent to desorption after an extended residence on the mica surface. Chemically frayed sites at flake edges (“frayed edges sites” or FES) and interlayer sites, where Cs<sup>+</sup> could displace and substitute for K<sup>+</sup>, are hypothetically responsible for this retention.<sup>1-4</sup> The significance of the latter binding reaction (diffusion of Cs<sup>+</sup> into interlayer space by displacement of K<sup>+</sup>) has been questioned, since solid phase diffusion measurements yield infinitesimally slow rates of less than 1 nm per year.<sup>5</sup> We carefully examined the spatial residence of Cs<sup>+</sup> on the surfaces and the interiors of Hanford mica flakes to establish whether Cs was preferentially sorbed to FES and whether it could access the flake interiors by diffusion.

## Materials and Methods

Micas were hand picked from uncontaminated Hanford formation fine sands (35 to 55 ft below ground surface). Three phases were differentiated on the basis of color and x-ray diffraction pattern: clear muscovite, rust vermiculite, and black biotite. Small numbers of flakes were exposed to varying concentrations of CsNO<sub>3</sub> (0.001, 0.01, and 0.08 M) for 28 days, then washed in deionized water and air dried. Some of the flakes were then mounted to glass slides (plan view), while others were imbedded in epoxy and fixed to glass slides as polished thin sections about 50 μm-thick, cut normal to the basal plane.

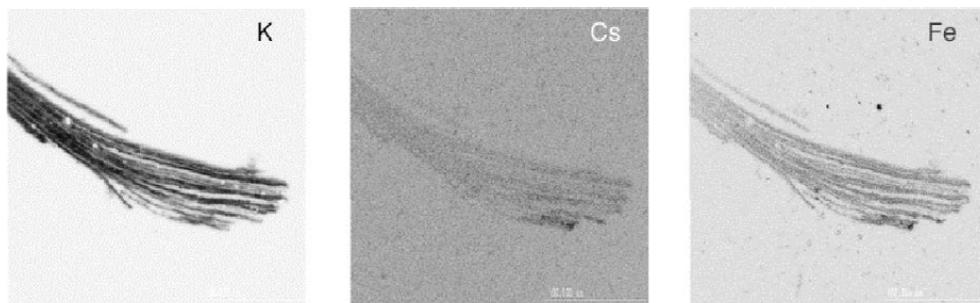


FIG. 1. Muscovite section imaged as K, Cs, and Fe abundance by electron microprobe. The mica flake is weathered and its component plates are splayed where it has been most severely altered. Cesium is distributed at the edges of mica plates. Iron and Cesium are correspondingly enriched near the platelet ends.

Cesium distribution in muscovite was imaged using the GSE-CARS beamline. The beam was focused using Kirkpatrick-Baez mirrors.<sup>6</sup> The entrance slits were set at 0.3 × 0.3 mm and the beam focused to ~4 × 4 μm. The sample was rotated 45° from normal incidence, giving an effective horizontal spot of about 4 × 6 mm. The beam energy was selected with a Si(111) double crystal monochromator. The fluorescence from the sample was detected with a wavelength dispersive spectrometer (WDS) with 10 eV resolution, tuned to the Cs L<sub>α</sub> fluorescence line. The incident energy was set to 7.0 keV.

## Results

Preliminary investigations using an electron microprobe (Fig. 1) clearly showed structural splaying of the mica edge by weathering. Cesium was concentrated at the ends of weathered plates but was also present above background on the flake interior or in the relatively unweathered core. (The possible presence of natural Cs in micas was investigated at the PNC-CAT — data not shown — and no detectable Cs was present in natural biotites or muscovites.) A correlation of Cs adsorption density with elevated Fe concentrations was observed. Fe has low abundance in muscovite, and the brightness levels in the image were manipulated to enhance contrast. Although the optical resolution of the images was high, the detection limit, defined by the ability to perceive Cs above background, was near the level at which Cs<sup>+</sup> was adsorbed. Investigations of the internal distribution of Cs in micas required a much lower detection limit, supplied by x-ray microprobe (XMP).

On muscovite in plan view (Fig. 2), Cs was concentrated at flake edges and along fractures or cracks on the muscovite surface. In cross section (Fig. 3), Cs was detected at an estimated operational detection limit of 1 ppm. This image showed several important details of Cs distribution, highlighted or in the figure by detail insets. At the flake’s edge, there are many zones of Cs localization; this is a confirmation of the observed concentration of Cs near the flake edge in Fig. 1. The sensitivity of XMP showed that these zones were discrete and spatially compressed. Also identified were laterally continuous zones of high Cs adsorption density in the flake interior, which indicated that dissolved Cs was able to access sorption sites in portions of the flake interior. This result was not expected, since solid-state diffusion limitations would prevent Cs from significantly accessing the interior. As seen dimly in the optical image, the flake has some

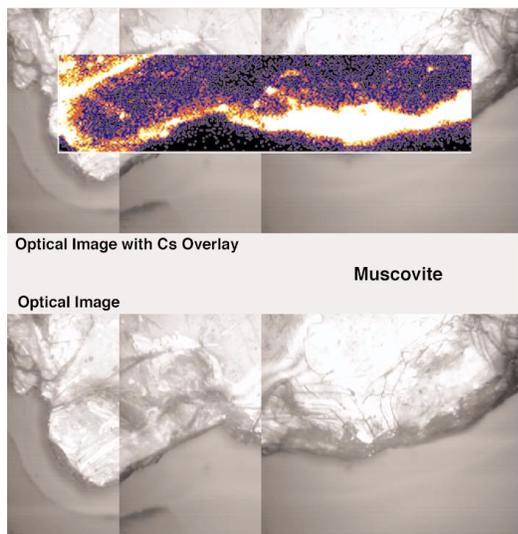


FIG. 2. Optical image of muscovite flake with Cs abundance overlay by XMP. Cesium is most abundant at edges and along cracks on the flake surface. Blue is an indication of Cs below detection; white is maximum abundance. XMP image is 1.3 mm across.

internal open areas, and Cs was apparently channeled to the flake interior along cracks and delamination features.

## Conclusions

Our experiments demonstrated that  $\text{Cs}^+$  was rapidly sorbed by micas extracted from sediments. After short contact in our experiments,  $\text{Cs}^+$  was concentrated at edge sites on mica particles and penetrated the mica flakes along planes of delamination and fractures to bind to sites in the flake interiors. This work confirms the existence on micas of high-energy sites capable of sorbing and immobilizing contaminant  $\text{Cs}^+$  from tank waste leakage. The ability of  $\text{Cs}^+$  to access high-energy sites internal to mica flakes markedly enhances the sorption capacity of micas, provides a transport limitation to desorption, and increases the overall immobilization of  $\text{Cs}^+$  in these sediments.

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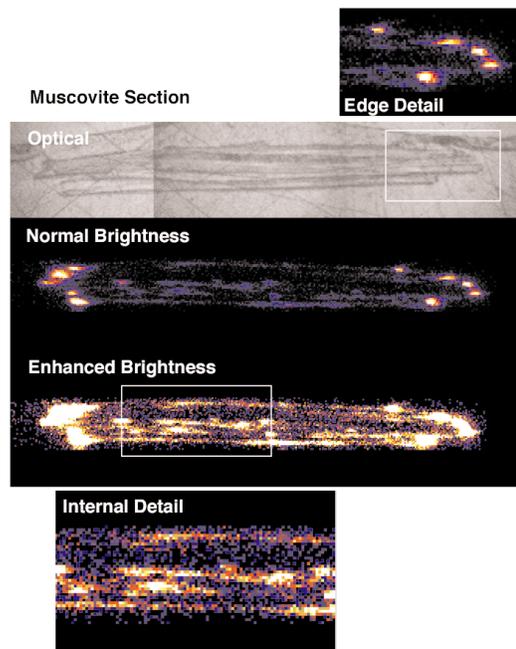


FIG. 3. The abundance of Cs within a muscovite flake. The sectioned flake is about cesium. 1.2 mm long. Cesium is concentrated at platelet edges on the ends of the flake and within restricted zones in the flake interior.

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