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# TOF-SIMS study of Cs<sup>+</sup> sorption on natural kaolinite

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## Abstract

The sorption of Cs<sup>+</sup> on natural kaolinite has been studied using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Depth profiling up to 70 Å was performed to study the change in the amount of sorbed Cs<sup>+</sup> as a function of depth in the kaolinite matrix. Quantitative determination of the amounts of primary cations in the kaolinite structure before and after sorption of Cs<sup>+</sup> ions was carried out to identify which cations are possibly taking part in the sorption process. The experimental results showed that large amounts of Cs<sup>+</sup> are sorbed onto the surface of kaolinite and that sorption decreases sharply over the first 10-Å depth. The fact that kaolinite surface was negatively charged under the operating pH indicates that physisorption has an important contribution to the sorption process. The results also showed that Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Fe<sup>3+</sup> were involved in the sorption process with Cs<sup>+</sup> and that the total decrease in the amounts of these cations is close to the amount of sorbed Cs<sup>+</sup>, suggesting that ion exchange is the dominant sorption mechanism. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Sorption; Kaolinite; Migration; Radionuclides; TOF-SIMS; Depth-profiling

## 1. Introduction

The retardation of radionuclide migration in the biosphere by sorption on clay minerals and soil fractions is widely proposed as a suitable means through which their dispersion in the environment can be controlled.

The radioisotope <sup>137</sup>Cs ( $t_{1/2} = 30.17$  years) being a fission product with a long half life, and also

one of the most mobile radionuclides in the geosphere, is very important in radioactive waste management considerations. A number of studies to determine various aspects of the sorption behavior of Cs<sup>+</sup> on different clay minerals was carried out at our laboratories (Erten et al., 1988a,b; Shahwan et al., 1998). It is important to note that soil fractions and glaciofluvial sediments could replace the solid clay matrix in such studies. However, it is known that among the constituents; sand, silt and clay, the clay minerals are by far the highest contributors to the cation exchange capacity of soil or sediments (Erten et al.,

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1988b, Grutter et al., 1990). The organic components of soil and sediments are known to be effective only in the sorption of certain anions (Bors et al., 1991).

Kaolinite is a member of the two layered clay family which contains tetrahedral and octahedral sheets (silica and gibbsite sheets) that are stacked on each other and held mainly by van der Waals forces. Kaolinite is a non-expanding clay that rarely contains isomorphous substitutions. It, therefore, has a relatively low cation exchange capacity (CEC), typically of the order of 4–8 meq/100 g.

In this work, our main concern was to study the extent of  $\text{Cs}^+$  diffusion inside the layers of kaolinite (i.e. within the top 70 Å of the surface) and the mechanism of  $\text{Cs}^+$  sorption. In general, sorption of cations on solids is due to various kinds of interactions (Lieser, 1995): fixation by; ion exchange; chemisorption; physisorption; precipitation or coprecipitation. In all cases the surface and exchange properties of the solid are important, as well as a knowledge of the cationic species in the aqueous system.

TOF-SIMS, a powerful tool of ion spectrometry, was used in our studies. This is a rapidly evolving technique that can be applied to surface analysis of different kinds of materials as well as for sorption studies (Groenewold et al., 1998). Our work represents the first thorough study of sorption by TOF-SIMS. The technique is well suited for the analysis of sorption and exchange processes involving  $\text{Cs}^+$  since many of the elements involved in these processes readily form gas-phase secondary ions. By applying a pulsed, microfocused  $\text{Ga}^{2+}$  primary ion beam, analysis may be performed without excessive sputtering of the sample, enabling the generation of a number of alkali metal, alkaline-earth, and transition metal ions from the kaolinite samples as secondary ions. Etching of the samples was performed at 10-Å intervals up to a depth of 70 Å.

For quantitative analysis, the experimental data was first corrected using the relative sensitivity factor of each element, and then corrected for variations in the intensity of the secondary beam and the concentration of that element relative to a reference element. Since Al and Si, contained

in the skeleton of the clay, are assumed not to be involved in the ion-exchange process, they were used in the normalization of experimental data of each element. Further calculations were performed using these normalized results.

## 2. Experimental

The samples of natural kaolinite were obtained from the Turkish Mining Institute (MTA). The samples were sieved and those with a particle size  $< 38 \mu\text{m}$  were used in our experiments. The XRD characterization of kaolinite was carried out using a Phillips DY 687 model diffractometer. The spectra showed that the mineral samples contained together with kaolinite, other geological fractions such as smectite, quartz and feldspars. The composition of natural kaolinite used in our sorption studies is given in Table 1.

### 2.1. The sorption experiments

Samples of kaolinite weighing 4 g each were exposed to 400-ml aliquots of a solution of 0.01 M CsCl and stirred on a magnetic stirrer for 48 h. The exchanged samples were then filtered and dried overnight at 90°C. The starting pH was 6.8, and this value increased up to 7.6 at the end of the exposure interval.

### 2.2. Analyzing kaolinite samples before and after sorption of $\text{Cs}^+$

TOF-SIMS analysis was performed for kaolinite samples before and after sorption, using a Vacuum Generator TOF-SIMS instrument located at the University of Bristol Interface Surface Analysis Centre. Powder samples were pressed lightly onto a sample stub using a carbon dag and then left to dry prior to analysis. During analysis, the vacuum in the analysis chamber was

Table 1  
The percentage compositions of geological fractions in kaolinite

Fraction	Kaolinite	Smectite	Quartz	Feldspars
Percentage	65	20	10	5

kept at approximately  $10^{-9}$  mbar. Spectra were recorded over 50 accumulations, at  $\times 5000$  magnification, i.e. an area of  $64 \times 48 \mu\text{m}$ . The ion beam pulse length was 30 ns with a repetition rate of 10 kHz. The  $\text{Ga}^{2+}$  ion gun used to produce the ions was operated at 1 nA current and 20 keV energy. The electron flood gun was used as required for neutralization. The above conditions resulted in an etch rate of approximately  $10 \text{ \AA}/50\text{-s}$  etch. The samples were etched and analysis performed at successive depths of 10, 20, 30, 40, 50 and 70  $\text{\AA}$ .

### 3. Discussion of results

Analysis of the experimental data showed that kaolinite contained a variety of cations together with Al and Si (which are in the network structure) as shown in Fig. 1, in which a TOF-SIMS spectrum of kaolinite before sorption is given. The inset in the same figure shows the change in the amount of sorbed  $\text{Cs}^+$  as a function of depth in the kaolinite matrix.

Table 2 gives the amount of each cation contained within the lattice of kaolinite normalized to the amount of Al + Si (after being corrected for relative sensitivities) before and after  $\text{Cs}^+$  sorption. The amounts of different cations decrease after  $\text{Cs}^+$  sorption, suggesting that all of these cations are taking part in the sorption process.

The ratio of these cations after  $\text{Cs}^+$  sorption to those before sorption as a function of depth gives significant information on the sorption process, such a plot is shown in Fig. 2. The ratios are plotted as a function of depth in the kaolinite structure. The reference line in the figure represents no change between samples before and after sorption. Data below this line indicate a decrease in the particular ion concentration upon  $\text{Cs}^+$  sorption. The extent of deviation is a measure of the affinity of exchange of the particular cation with the sorbed cation. Based on Fig. 2, the affinity of exchange of the monovalent and diva-

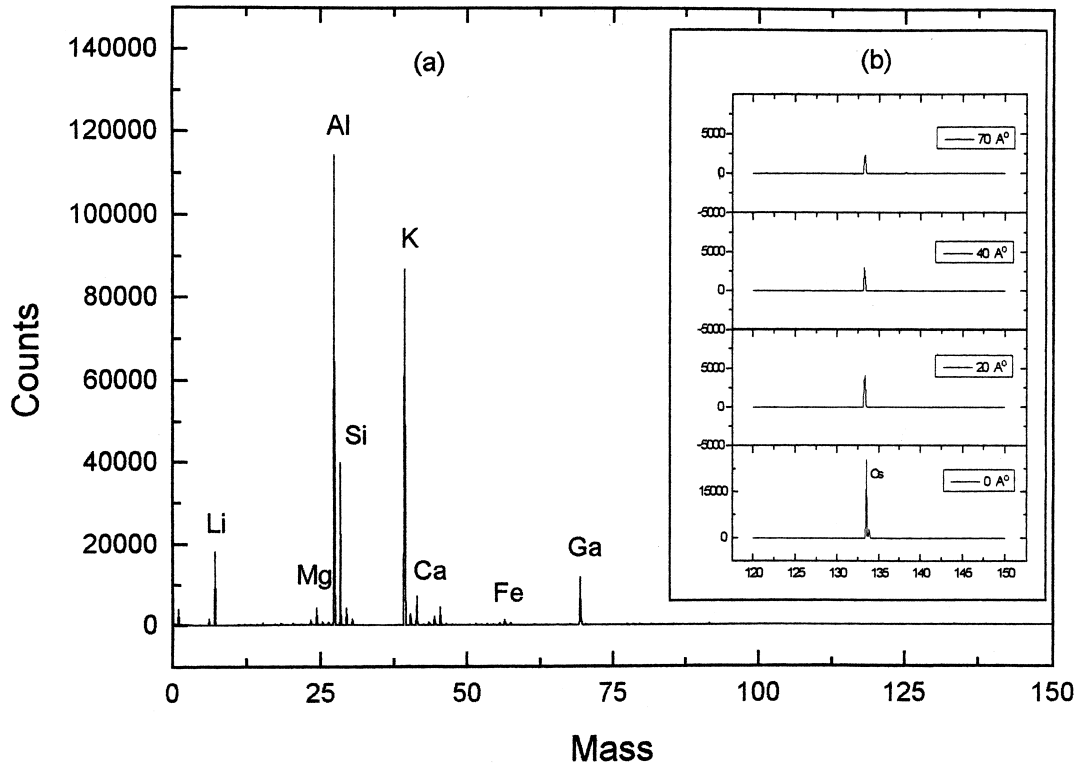


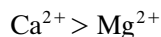
Fig. 1. (a) A TOF-SIMS spectrum of kaolinite before sorption; and (b) the  $\text{Cs}^+$  depth profile after sorption.

Table 2

The amounts of different cations in kaolinite before and after Cs<sup>+</sup> sorption normalized to (Al + Si), at various matrix depths

Ion	R (Å)	Sample	0 Å	10 Å	20 Å	30 Å	40 Å	50 Å	70 Å	Total
Li <sup>+</sup>	0.68	Kaolinite	0.0055	0.0047	0.0041	0.0038	0.0035	0.0033	0.0021	0.0269
		Cs <sup>+</sup> -kaol.	0.0047	0.0038	0.0029	0.0025	0.0023	0.0028	0.0016	0.0206
Na <sup>+</sup>	0.97	Kaolinite	0.0020	0.0006	0.0005	0.0005	0.0005	0.0006	0.0006	0.0053
		Cs <sup>+</sup> -kaol.	0.0005	0.0003	0.0002	0.0002	0.0002	0.0004	0.0002	0.0020
Mg <sup>2+</sup>	0.66	Kaolinite	0.0683	0.0342	0.0283	0.0286	0.0271	0.0291	0.0280	0.2436
		Cs <sup>+</sup> -kaol.	0.0456	0.0235	0.0206	0.0186	0.0187	0.0221	0.0183	0.1674
K <sup>+</sup>	1.33	Kaolinite	0.0376	0.0658	0.0715	0.0714	0.0706	0.0663	0.0621	0.4453
		Cs <sup>+</sup> -kaol.	0.0415	0.0568	0.0470	0.0406	0.0358	0.0563	0.0350	0.3130
Ca <sup>2+</sup>	0.99	Kaolinite	0.0690	0.0183	0.0160	0.0153	0.0144	0.0137	0.0105	0.1572
		Cs <sup>+</sup> -kaol.	0.0436	0.0086	0.0080	0.0075	0.0070	0.0074	0.0070	0.0891
Fe <sup>3+</sup>	0.74	Kaolinite	0.3228	0.0856	0.0719	0.0685	0.0634	0.0623	0.0464	0.7209
		Cs <sup>+</sup> -kaol.	0.2360	0.0887	0.0744	0.0613	0.0499	0.0519	0.0509	0.6131
Cs <sup>+</sup>	1.67	Cs <sup>+</sup> -kaol.	0.2876	0.0559	0.0447	0.0372	0.0306	0.0465	0.0295	0.5320

lent cations in the sorption of Cs<sup>+</sup> on kaolinite may be expressed as:



$$\text{Na}^+ > \text{K}^+ > \text{Li}^+$$

It must be noted here that the affinity of exchange refers to the tendency to be replaced by

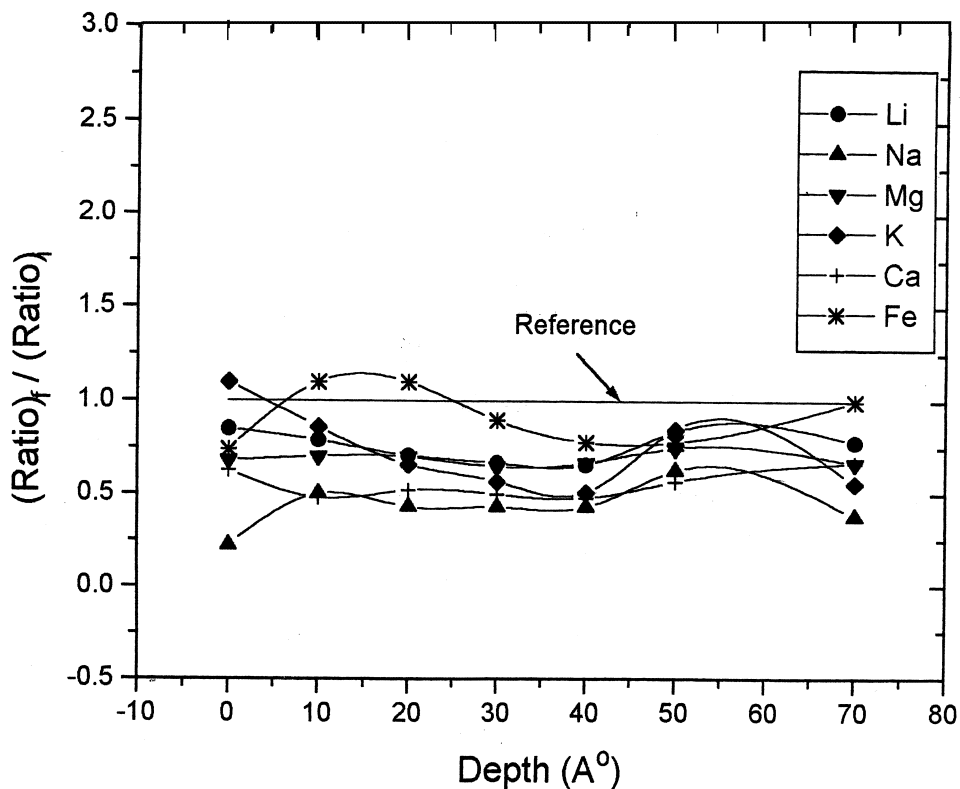


Fig. 2. The ratio of normalized amounts of different cations of Cs<sup>+</sup>-kaolinite to their amounts in kaolinite.

Table 3

The percentage contribution of each cation to the exchange process in the sorption of  $\text{Cs}^+$  on kaolinite

Cation	$\text{Li}^+$	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Fe}^{3+}$
% Contribution	1.62	0.81	19.46	33.37	17.19	27.55

$\text{Cs}^+$ . This is not a function of the amount of the particular cation present in the kaolinite structure. Utilizing the values given in Table 2, the percentage contribution of each cation to the total amount exchanged can be calculated. Table 3 gives the percentage contributions of different cations to the sorption of  $\text{Cs}^+$  on kaolinite. It can be seen that the largest contribution comes from  $\text{K}^+$  which exists in large amounts in the kaolinite lattice.

Fig. 3 shows the variation of the amount of  $\text{Cs}^+$  cation as a function of kaolinite matrix depth; 50% of the total amount of  $\text{Cs}^+$  is adsorbed at

the kaolinite surface. The intensity of the  $\text{Cs}^+$  signal was observed to fall sharply within the first 10 Å of the surface layer, reaching a steady level over the depths of 10–70 Å.

Kaolinite has been shown to possess a negative surface charge at its crystalline edge sites at pH 7, indicating that the exchanged  $\text{Cs}^+$  is bound electrostatically to the outer surface of the kaolinite (Graveling, 1997). The remaining  $\text{Cs}^+$  appeared to have diffused through the surface layer to the internal sites, replacing the constituent cations within the clay lattice. Given that all of exchangeable cations have a smaller radius than  $\text{Cs}^+$  (see Table 2) and that kaolinite is a non-expanding clay with a low CEC, only a limited number of sites are available for substitution in the internal pores or layers. This, together with the negative charge present on the surface of the clay lead to the accumulation of half of the total amount of  $\text{Cs}^+$  ions on the outer surface and edges of the

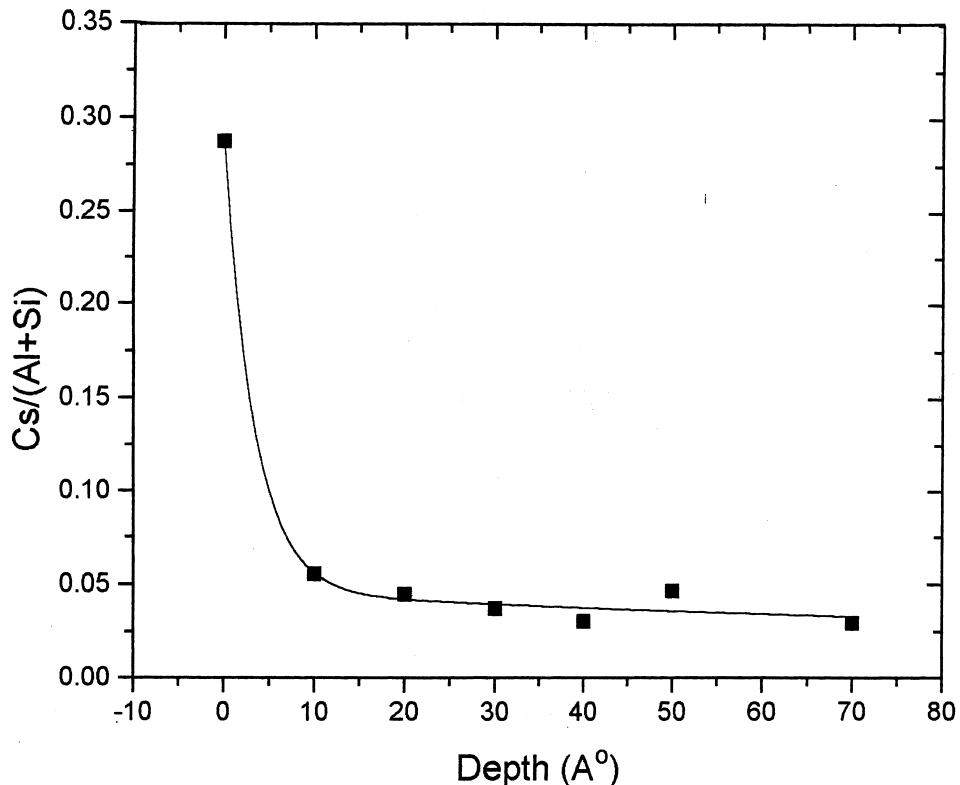


Fig. 3. The change in the normalized amounts of Cs,  $\text{Cs}/(\text{Al} + \text{Si})$ , as a function of depth in kaolinite.

kaolinite structure. Moreover, since natural kaolinite samples contain a significant amount of smectite, which is an expanding clay with a high CEC, the extent of ion exchange is enhanced and an increased amount of  $\text{Cs}^+$  ions is enabled to diffuse to the internal sites.

Quantitatively, if the total amount of sorbed  $\text{Cs}^+$  is compared with the total decrease in the other constituent cations, the values obtained are 0.53 vs. 0.40, respectively. These suggest that ion exchange is the prevailing process in the sorption of  $\text{Cs}^+$  on kaolinite, although there is additional  $\text{Cs}^+$  uptake, due to physisorption onto the surface of the clay particles.

In conclusion, it may be stated that TOF-SIMS is a powerful tool in the detailed study of the sorption process. It may aid in identifying and quantifying the cations that exchange with  $\text{Cs}^+$ , the sorption sites preferred by  $\text{Cs}^+$  ions, and the extent of sorption taking place.

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