Surface spectroscopic studies of Cs^+, and Ba^{2+} sorption on chlorite-illite mixed clay

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Summary. The sorption behavior of Cs^+, and Ba^{2+} on natural clay was investigated using ToF-SIMS, XPS, and XRD. The natural clay was composed mainly of chlorite and illite in addition to quartz and calcite. Depth profiling up to 70 Å was performed at 10 Å steps utilizing ToF-SIMS to study the amount of sorbed Cs^+ and Ba^{2+} as a function of depth in the clay matrix. The results suggest that Cs^+ and Ba^{2+} ions were sorbed primarily by ion exchange coupled with hydrolytic sorption. According to ToF-SIMS and XPS results, the total sorbed amount of Ba^{2+} was larger than that of Cs^+. Quantitative determination of the primary cations within the analyzed clay before and after sorption indicated that for Ba^{2+} sorption, Ca^{2+}, Mg^{2+} and for Cs^+ sorption Ca^{2+}, K^+ were the major exchanging ions. The XRD spectra of Ba-sorbed clay contained new peaks that were identified as $BaCO_3$.

Introduction

Radioactive wastes resulting from the world wide increase in various nuclear activities are a great threat to the biosphere. Geological formations that contain clay minerals as natural barriers against their leakage, are considered as suitable repository sites for the disposal of radioactive wastes. The use of clay minerals is particularly attractive because of their low permeability, good sorption characteristics, and wide availability. Illites are the most common clay minerals in nature, making up the bulk of ancient shales. They belong to the mica group where each structural unit is composed of one octahedral layer placed in-between two tetrahedral layers. A permanent negative charge on the illite layers is usually generated as a result of the substitution of an Al^{3+} ion for one of the four Si^{4+} ions in the tetrahedral layer. This charge is usually neutralized by introducing one K^+ ion into the interlayer position. Thus layers in illites are held together by relatively strong electrostatic forces between the negatively charged silicate layers and the K^+ ions. Illites may frequently contain Mg and Fe and exist as a mixed layer type [1]. The mineral chlorite belongs to a group of hydrous silicates of aluminum which may contain appreciable amounts of magnesium and iron. Each structural unit of chlorite is composed of two tetrahedral silica sheets and two octahedral sheets. Chlorites are abundant in sedimentary rocks and are present in many clay formations and shales. Like most aluminosilicates, the chemical composition of chlorite exhibit considerable variations due to isomorphous substitution in both tetrahedral and octahedral sheets by ions of lower valence [2].

The radioactive isotopes ^{137}Cs ($t_{1/2} = 30.2$ y) and ^{140}Ba ($t_{1/2} = 12.8$ d) are produced during nuclear fission with high yields, i.e. 6.18% and 6.21% respectively [3]. Cs radioisotopes are considered as hazardous nuclides due to their relatively long half lifes and the high water solubility of its compounds. ^{140}Ba is a serious radiocontaminant during the first 100 days of its discharge to the environment. Ba, being a congener of Ra which has isotopes important in radioactive waste considerations, is a suitable representative of the alkali-earth homologs.

Up to now, a number of studies investigating the sorption behavior of Cs^+ and Ba^{2+} on different clay minerals and soil fractions were carried out in our laboratories using radiochemical techniques [4–8]. In this study, the sorption behaviors of Cs^+ and Ba^{2+} ions on a chlorite-illite natural clay mixture were studied using Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS), X-Ray Photoelectron Spectroscopy (XPS), and X-Ray Diffraction (XRD). Depth profiling measurements using ToF-SIMS were done in order to determine the cationic composition of the near surface region of natural-, Cs-, and Ba-sorbed clay samples. It was thus possible to determine the extent of sorption of Cs^+ and Ba^{2+} and to find out the affinity of exchange of various cations. Flame Atomic Absorption Spectroscopy (FAAS) was used as a complementary method to measure the concentrations of the exchanged cations in the aqueous phase. The XRD analysis was used to determine the mineralogical composition of the natural clay and to detect any structural changes that might have occured upon the sorption of Cs^+ and Ba^{2+} ions.

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Experimental

Preparation of the samples

The natural clay used was obtained from the Turkish Mining Institute (MTA). It originated from Afyon, a city located in the western part of Anatolia. The samples were dry and wet sieved and fractions with a particle size $< 38\,\mu m$ were used in the experiments. The particle size distribution was obtained by using Andreasen pipette. The percent by weight were 16, 24, 35, and 25 for the size fractions (μm); 2–4, 4–10, 10–20, and 20–38, respectively.

The batch method was used, clay samples weighing 4.0 g each were exposed to 400.0 mL aliquots of solutions of 0.010 M CsCl or 0.010 M $BaCl_2$ and mixed for 48 hours using a magnetic stirrer. The samples were then filtered and dried overnight at 90 °C and finally ground. The pH of Cs^+ and Ba^{2+} solutions prior to contact with the solid phase were 7.8 and 8.2, and they were 7.6 and 7.5, respectively following sorption. Samples were then filtrated. The aqueous phase concentrations were measured using a Perkin Elmer 1100B Model atomic absorption spectrometer. The elements Na, K, Ca, Mg, Fe, and Al at the corresponding wavelengths (nm) 589.1, 766.5, 422.7, 285.2, 248.2, and 309.2, were determined.

ToF-SIMS Analysis of clay samples before and after sorption

ToF-SIMS analysis of the solid phase before and after Cs^+ and Ba^{2+} sorption were performed using a Vacuum Generator ToF-SIMS instrument located at the University of Bristol Interface 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 kept at approximately 10^{-9} mbar. Spectra were recorded over fifty accumulations, at $\times5000$ magnification, i.e. an area of $64 \times 48\,\mu m$. The ion beam pulse length was 30 ns with a repetition rate of 10 kHz. The 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 Å per 50 second etch. The samples were etched and analysis performed at successive depths of 10, 20, 30, 40, 50, and 70 Å.

XPS Analysis of clay samples before and after sorption

X-ray photoelectron spectra were recorded using a VG Scientific Escascope instrument with Mg K_α X-rays ($h\nu = 1253.6$ eV). Wide and regional spectra were recorded with step scans of 40 eV, 30 eV and step sizes of 1.0 and 0.1 eV, respectively. Samples were mounted as freshly ground powders pressed onto adhesive copper tape. Pressure was kept below 1×10^{-8} mbar during analysis. C 1*s* line (B.E = 284.8 eV) originating from the adventitious hydrocarbons at the surface of the samples was used as the reference line. Sensitivity corrections were done using Wagner sensitivity factors and quantification was performed *via* a VG Scientific VGS5250 software.

XRD Analysis of clay samples before and after sorption

Samples of natural-, Cs-, and Ba-sorbed clays were ground prior to mounting on single crystal silicon wafers for X-ray diffraction analysis. Methanol was used to disperse the powder samples evenly over the holder. A Bruker AXS D500 X-ray diffractometer was used. The source consisted of unfiltered Cu K_α radiation, generated in a tube operating at 40 kV and 30 mA. Spectra were recorded with 2 theta values ranging from 3 to 35 degrees in steps of 0.02 degree and dwell times of 10 s per step. The samples were rotated during analysis, which was performed at ambient temperature. Bruker AXS DIFFRAC-AT software was used to process the results and compare them with the Joint Committee on Powder Diffraction Standards (JCPDS) database.

Results and discussions

The XRD analysis indicated that the natural clay used in our studies contained primarily chlorite and illite, some quartz
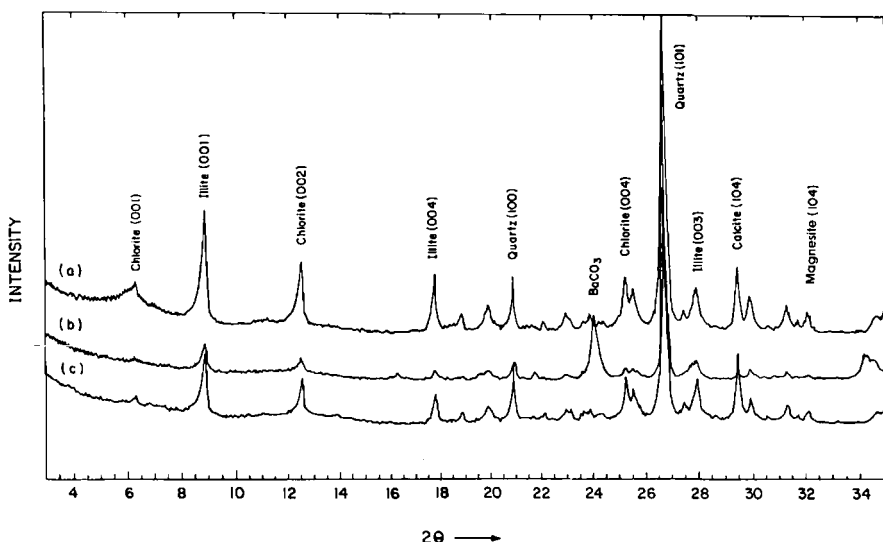

Fig. 1. XRD spectra of (**a**) natural clay used in this work, (**b**) Ba-clay, and (**c**) Cs-clay.

and calcite and minor quantity of magnesite as shown in Fig. 1a. The XRD spectra of Ba²⁺-, and Cs⁺- sorbed clay are also given in Figs. 1b,c. The ToF-SIMS data revealed that, within a matrix depth of 70 Å, the main cations in the clay samples were Si, Al, Fe, Ca, Mg, and K. The relative amounts (expressed as atom percentages) of these cations before and after Cs⁺ and Ba²⁺ sorption are given in Table 1 together with the corresponding XPS results. It should be noted here that a direct comparison between ToF-SIMS and XPS results show some differences, resulting mainly from the differences in the escape depth.

Fig. 2 shows a typical ToF-SIMS spectrum of our clay. The two insets in the figure show the change in intensity of sorbed Ba²⁺ and Cs⁺ at different matrix depths. In Fig. 3, the XPS spectra of the clay before and after Cs⁺ and Ba²⁺ sorption are shown.

The ToF-SIMS analysis of clay samples before and after Cs⁺ and Ba²⁺ sorption showed a decrease in the contents of Ca²⁺, Mg²⁺, and K⁺ following sorption, while the Si and Al contents remained unchanged. Utilizing this fact, all the elements were expressed relative to the (Al + Si) content. This allowed meaningful comparisons in examining the elemental changes that the clay undergoes following sorption. The amounts of Mg²⁺, K⁺, Ca²⁺, Cs⁺, and Ba²⁺ (cation/Al + Si) as a function of depth before and after sorption are given in Figs. 4a,b. In order to compare the affinity

of exchange of the cations in the clay surface upon sorption of Cs⁺ and Ba²⁺, a 'Depletion Factor', DF, for a particular cation x in the solid matrix is defined as:

$$(DF)_x = \frac{(R_i)_x - (R_f)_x}{(R_i)_x} \tag{1}$$

Here, $(R_i)_x$ is the cation/(Al + Si) ratio of cation x in the original sample, $(R_f)_x$ is the cation/(Al + Si) ratio of cation x in the sample after Cs⁺ or Ba²⁺ sorption. In this sense, DF is some sort of affinity of the cation x to migrate from the solid phase to the aqueous phase. Its highest possible value of unity indicates complete transfer to aqueous phase, and its lowest value of zero indicates no transfer. The depletion factors of different cations as a function of depth are given in Table 2. In the case of Cs⁺ sorption the depletion factors decrease with depth except those of K⁺ ion. This suggests that sorption primarily take place on the outermost surface and edges. The ToF-SIMS results showed that K⁺ content in the upper 10 Å region of the clay surface was much less than those in the deeper regions. This is inline with its observed exchange behavior (Fig. 4a). For Ba²⁺ sorption the depletion factors do not change appreciably with depth. The higher the value of DF of a particular cation, the higher its affinity to leave the clay surface upon sorption. In this sense it is seen that Ca²⁺ shows the highest exchange affinity in Ba²⁺ sorp-
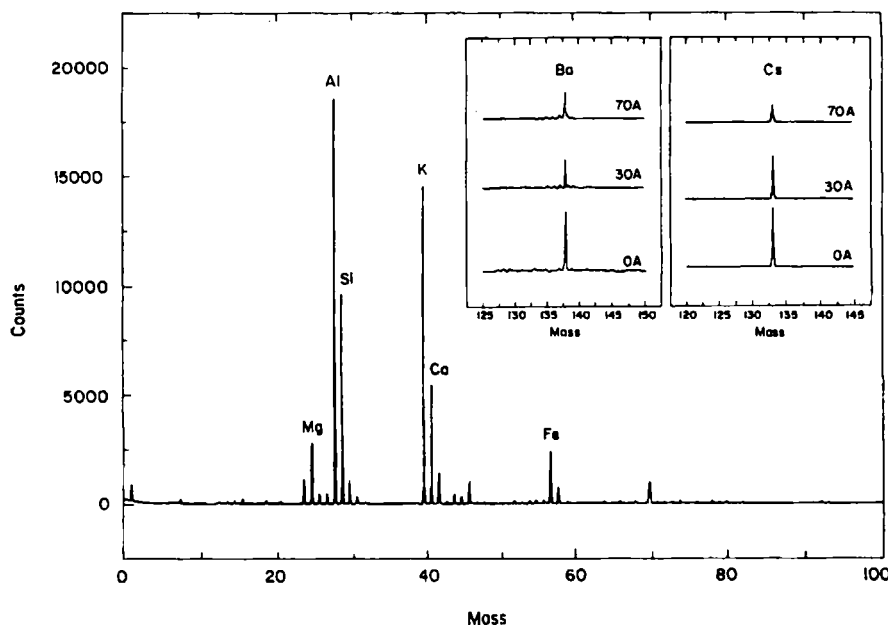

Fig. 2. ToF-SIMS spectrum of natural clay and the change of Cs and Ba signals as a function of matrix depth following Cs⁺ and Ba²⁺ sorption.

Table 1. Distribution of primary elements in the clay matrix prior to and following sorption of Cs⁺ and Ba²⁺ ions obtained from ToF-SIMS (within a depth of 70 Å) and XPS measurements.

| | Percentage of element (atom %) | | | | | |
| | Natural clay | | Cs-clay | | Ba-clay | |
Element	ToF-SIMS	XPS	ToF-SIMS	XPS	ToF-SIMS	XPS
Mg	2.9	–	2.7	–	2.7	–
Al	21.1	27.8	20.5	16.6	22.5	23.3
Si	51.9	60.3	54.9	70.2	52.3	64.1
K	1.5	1.4	0.8	2.3	1.2	2.8
Ca	3.0	8.9	2.1	7.8	1.5	–
Fe	19.4	1.6	15.4	–	15.7	–
Others	< 1.0	–	< 1.0	–	< 1.0	–
Cs, Ba	–	–	3.5	3.1	3.9	9.8
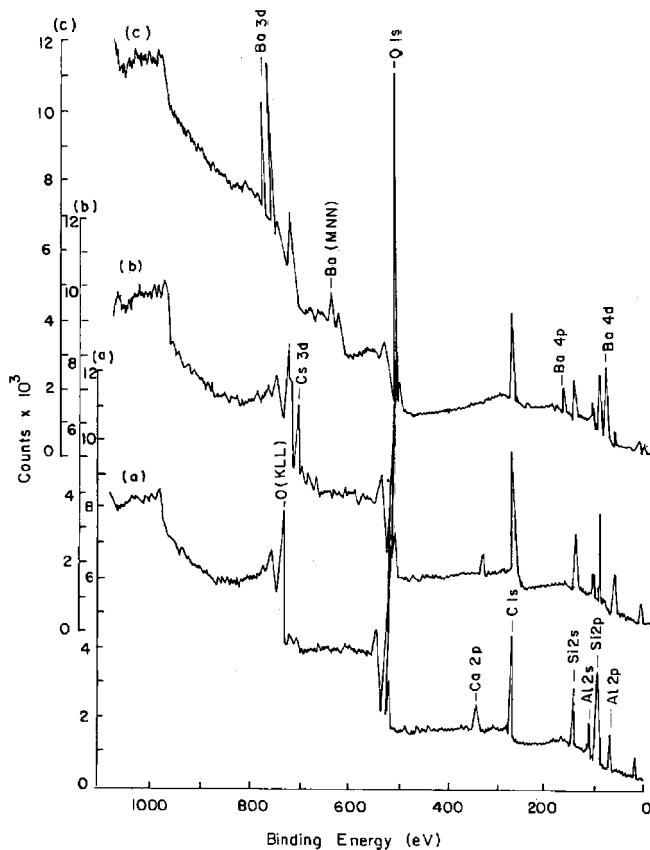
Fig. 3. XPS spectra of: (**a**) natural clay used in this work, (**b**) Cs-clay, and (**c**) Ba-clay.
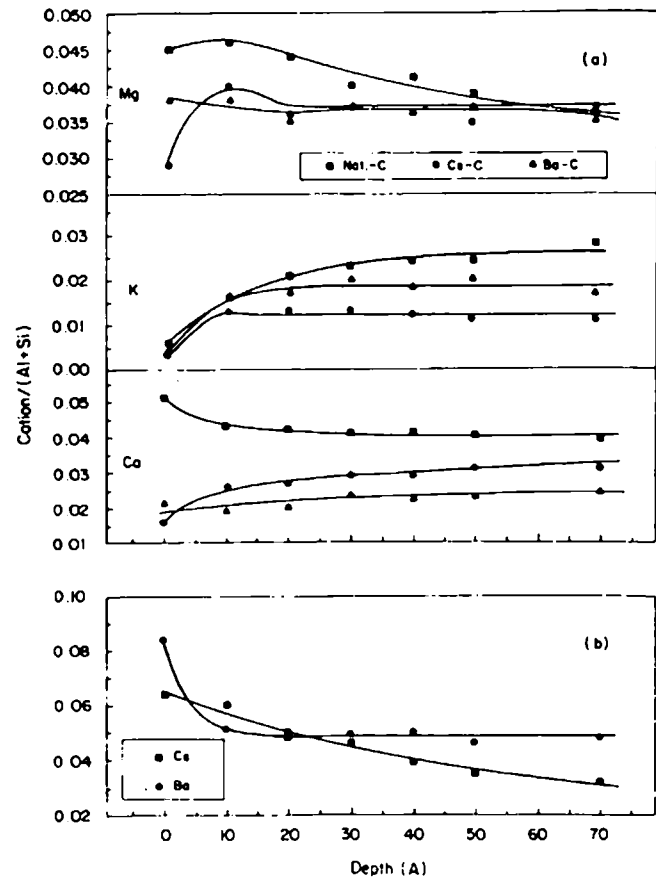

Fig. 4. (**a**) Cation/(Al + Si) ratios of Mg^{2+}, K^+, and Ca^{2+} in natural and Cs-, Ba-sorbed clay as a function of matrix depth, obtained from ToF-SIMS measurements. (**b**) Cation/(Al + Si) ratios of sorbed Cs^+ and Ba^{2+} as a function of clay matrix depth, obtained from ToF-SIMS measurements.

tion, whereas in Cs^+ sorption, both Ca^{2+} and K^+ show high exchange affinities.

The depleted amount of cation x in equivalents is calculated by multiplying the difference $\left[(R_i)_x - (R_f)_x \right]$ by z_x, the charge of cation x. This may be defined as the Equivalent Depleted Amount (EDA). The percentage contribution of cation x to the total depletion of all cations at a given depth is then given as:

$$D_x = \frac{\left[(R_i)_x - (R_f)_x \right] \cdot z_x}{\sum_1^n \left\{ \left[(R_i)_x - (R_f)_x \right] \cdot z_x \right\}_n} \times 100 \,. \qquad (2)$$

Based on ToF-SIMS data, the EDA and D_x values of principal cations in the clay matrix as a function of depth, following the sorption of Cs^+ and Ba^{2+} are given in Table 3. In both cases, Ca^{2+} is the cation with the highest contribution, i.e. it is the primary cation which exchanges most with the sorbed Cs^+ and Ba^{2+} ions. The total EDA values show that

the amount of Ca^{2+} exchanged with Ba^{2+} is somewhat larger than that of Cs^+. Since Mg^{2+} is usually a part of the skeletal structure of chlorite fractions [9], it is believed that the exchanged Mg^{2+} ions originate from another source, probably magnesite $(MgCO)_3$ which exist in minor quantities in the analyzed clay. This is supported by the fact that although the total original content of Mg^{2+} in the clay was comparable to that of Ca^{2+}, its contribution to the total exchange is much less than Ca^{2+} in both Cs^+ and Ba^{2+} sorption.

The XPS measurements showed that while the Ca^{2+} ions exchange almost totally with Ba^{2+} ions, they show only a partial exchange with Cs^+ ions, inline with ToF-SIMS findings. On the other hand, in the XPS results iron content of clay appears to be extremely small and is completely depleted upon sorption of Cs^+ or Ba^{2+} ions. This

Table 2. The Depletion Factors 'DF' of various cations in the clay matrix after sorption of Cs^+ and Ba^{2+} ions calculated from ToF-SIMS measurements.

Depth (Å)	Cs-Clay			Ba-Clay		
	Mg^{2+}	K^+	Ca^{2+}	Mg^{2+}	K^+	Ca^{2+}
0	0.35	0.49	0.69	0.15	0.24	0.59
10	0.14	0.12	0.40	0.18	0.02	0.55
20	0.18	0.41	0.36	0.20	0.22	0.53
30	0.09	0.41	0.29	0.07	0.11	0.43
40	0.11	0.50	0.29	0.11	0.22	0.45
50	0.11	0.54	0.23	0.06	0.16	0.42
70	0.0	0.62	0.20	0.01	0.39	0.39

Table 3. The initial and final ratios of cation/(Al + Si), R_i and R_f, the Equivalent Depleted Amounts (EDA), and the percentage contribution to total depletion, D_x, for different cations as a function of depth in the clay matrix. The equivalent sorbed amounts of Cs⁺ and Ba²⁺ within the 70 Å matrix depth are also shown. All calculations are based on ToF-SIMS measurements.

Cation	Depth (Å)	Cs-clay				Ba-clay			
		R_i	R_f	EDA	D_x(%)	R_i	R_f	EDA	D_x(%)
Mg²⁺	0	0.045	0.029	0.032	30.5	0.045	0.038	0.014	18.7
	10	0.046	0.040	0.012	25.0	0.046	0.038	0.016	24.7
	20	0.044	0.036	0.016	29.6	0.044	0.035	0.018	27.3
	30	0.040	0.036	0.008	19.0	0.040	0.037	0.006	13.3
	40	0.041	0.036	0.010	21.7	0.041	0.036	0.010	18.5
	50	0.039	0.035	0.008	20.5	0.039	0.037	0.004	9.5
	70	0.036	0.031	0.010	23.3	0.036	0.035	0.002	4.7
	Total			0.096				0.070	
K⁺	0	0.006	0.003	0.003	2.9	0.006	0.005	0.001	1.3
	10	0.016	0.014	0.002	4.2	0.016	0.015	0.001	1.5
	20	0.021	0.013	0.008	14.8	0.021	0.017	0.004	6.1
	30	0.023	0.013	0.010	23.8	0.023	0.020	0.003	6.7
	40	0.024	0.012	0.012	26.1	0.024	0.018	0.006	11.1
	50	0.024	0.011	0.013	33.3	0.024	0.020	0.004	9.5
	70	0.028	0.011	0.017	39.5	0.028	0.017	0.011	25.6
	Total			0.065				0.030	
Ca²⁺	0	0.051	0.016	0.070	66.6	0.051	0.021	0.060	80.0
	10	0.043	0.026	0.034	70.8	0.043	0.019	0.048	73.8
	20	0.042	0.027	0.030	55.6	0.042	0.020	0.044	66.6
	30	0.041	0.029	0.024	57.2	0.041	0.023	0.036	80.0
	40	0.041	0.029	0.024	52.2	0.041	0.022	0.038	70.4
	50	0.040	0.031	0.018	46.2	0.040	0.023	0.034	81.0
	70	0.039	0.031	0.016	37.2	0.039	0.024	0.030	69.7
	Total			0.216				0.290	
Cs⁺	Total			0.324					
Ba²⁺	Total							0.754	

Table 4. The intensities (normalized to quartz (101) peak) of different peaks corresponding to the main mineralogical fractions in natural, Cs-sorbed, and Ba-sorbed clay determined using XRD measurements.

Mineral. fraction	Natural clay		Cs-clay		Ba-clay	
	d_{hkl} (Å)	Intensity	d_{hkl} (Å)	Intensity	d_{hkl} (Å)	Intensity
Quartz (101)	3.335	100	3.335	100	3.334	100
Illite (001)	9.947	36	9.950	21	10.10	21
Chlorite (002)	7.052	20	7.043	13	7.070	13
Calcite (104)	3.029	16	3.028	17	3.028	2
Illite (004)	4.977	13	4.978	8	4.985	8
Quartz (100)	4.243	11	4.244	13	4.245	12
Chlorite (004)	3.523	14	3.529	10	3.523	7
Chlorite (001)	14.08	14	14.08	2	14.12	2
BaCO₃ (104)	–	–	–	–	3.700	96

is not confirmed by ToF-SIMS data which showed much larger iron quantities. This is further verified by the XRD features of chlorite fractions where the (001/002) peak ratio appears to be small as in the case of iron-rich chlorite. Moreover, Fe is a matrix element that is not readily exchangeable.

Flame Atomic Absorption Spectroscopy (FAAS) measurements of the elements Al, Fe, Ca, K, and Mg were carried out after separating the solid phase from solutions of Cs-, Ba-, and distilled water-treated clay. The results indicate that Ca is the primary exchanging cation with concentration (in ppm) of 51, 62, and 15 in filtrates of Cs-, Ba-, and distilled water-treated clay, respectively. The aqueous phase concentrations of K and Mg were relatively smaller and ranged between 1–4 ppm. On the other hand, the concentrations of Al and Fe were below the detection limits of the instrument which are 0.11 and 200 ppb, respectively.

Depth profiles and XRD analysis of Cs^+- and Ba^{2+}-sorbed clay

Fig. 4b shows the sorbed amounts of Cs^+ and Ba^{2+} as a function of depth from the clay surface obtained using ToF-SIMS. The amount of Ba^{2+} sorbed is seen to be more than that of Cs^+ (Table 3). The amount of Cs^+ sorbed decreased linearly through the 70 Å depth, whereas a large fraction of Ba^{2+} (22.3% of the total amount sorbed) accumulates on the outer-most clay surface.

The XRD spectra of Cs- and Ba-chlorite were given in Figs. 1b,c. The peak intensities of the various components in the spectra were normalized to the quartz (101) peak which showed no reduction in different samples. The results are given in Table 4. The sorption of both Cs^+ and Ba^{2+} lead to intensity reductions of chlorite and illite peaks. Moreover, following Ba^{2+} sorption severe reduction in calcite peak intensity occured and new features identified as $BaCO_3$ appeared in the spectrum (Fig. 1b). The formation of $BaCO_3$ might have resulted from exchange of Ca^{2+} in calcite with Ba^{2+} and/or dissolution of calcite followed by formation of $BaCO_3$ as a precipitate. The Cs^+ sorption did not affect the intensity of the calcite peaks (Fig. 4c). This is inline with the low sorption capacity of calcite for Cs^+ ions [10].

The extent of depletion of Mg^{2+}, K^+, Ca^{2+} ions upon sorption of Cs^+ and Ba^{2+} indicate that ion exchange is the primary sorption mechanism. In fact in the case of Cs^+ sorption the total depleted amount of the above cations is about equal to the amount of sorbed Cs^+ (Table 3). The fact that the operating $pH \geq 7$ is above the Zero Point of Charge (ZPC), which is usually below $pH = 4$ for aluminosilicates [1], suggests the possibility of hydrolytic sorption as a complementary sorption mechanism. Hydrolytic sorption refers to the fixation of sorbing cations by the hydroxyl groups located on the oxide surfaces and clay edges [3]. Together with ion exchange, this type of sorption – which is pH dependent – is expected to be effective in the case of Ba^{2+} sorption where the total depleted amount of cations is about half the sorbed amount of Ba^{2+} ions (Table 3).

Conclusions

ToF-SIMS depth profiling coupled with XPS and XRD seems to be a good tool that can be applied for studying various aspects of the sorption process. Comparing ToF-SIMS data of different cations in the clay matrix before and after sorption showed that, Ca^{2+} is the major exchanging cation with both sorbed Cs^+ and Ba^{2+} ions. This finding is also supported by XPS, and FAAS measurements. ToF-SIMS and XPS results showed that the amount of Ba^{2+} sorbed was larger than that of Cs^+ and that the sorption mechanism is primarily ion exchange coupled with hydrolytic sorption. The XRD measurements showed that the illite and chlorite fractions in our clay samples are responsible for the sorption of Cs^+ and Ba^{2+} ions. In addition to illite and chlorite fractions, minor constituents of calcite and magnesite, also take part in Ba^{2+} sorption.

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