

# Photoelectron Spectroscopy: A Tool in Sorption Studies

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Photoelectron spectroscopy using AlK $\alpha$  ( $h\nu=1486.3$  eV) has been applied to study the sorption of Cs $^+$ , Sr $^{2+}$ , Ba $^{2+}$ , Zn $^{2+}$  and Co $^{2+}$  on magnesite kaolinite, smectite and chlorite. From the observed intensities of photoelectron peaks it was determined that in magnesite the sorption affinity of the above ions follow the order: Ba $^{2+}$  > Co $^{2+}$   $\cong$  Sr $^{2+}$   $\cong$  Zn $^{2+}$  > Cs $^+$ . The order for the sorption of Ba $^{2+}$  and Cs $^+$  are also determined as chlorite > magnesite > smectite > kaolinite and smectite > chlorite  $\cong$  kaolinite > magnesite, respectively.

## Introduction

All types of radioactive waste are planned to be disposed of either in shallow or in deep geological repositories. Clay minerals are envisaged as buffer materials in these repositories for their ability to sorb radionuclides, thus retarding their migration. Many investigations on radionuclide sorption and migration behavior have been carried out with the aim of examining the effects of different parameters such as composition of ground water, its pH, concentration of the sorbed species and the structure of the solid matrix (1-7). Since adsorption primarily takes place at the ground water/clay mineral interface, involving surface functional sites, use of surface sensitive analysis techniques like X-ray photoelectron spectroscopy (XPS) becomes particularly valuable in assessment of sensitivity and, more importantly, selectivity of the sorption process. Application of the XPS and the related Auger Electron Spectroscopic (AES) techniques to various geological samples has been reviewed by Hochella (8) and more recently by Paterson and Swaffield (9). Besides the early studies (10-16), applications of these powerful techniques to sorption studies especially on clays or clay minerals have not been very extensive.

Identification of the exchanged species and/or sites or exchange affinity of certain clay minerals towards the various cations has been one of the main focus for XPS investigations. Kappelman and Dillard (12) studied the uptake of Cu(II) and Ni(II) by illite, kaolinite and chlorite. Later the same group reported a similar study of Cr(III) on the same minerals (14). In a more recent study, Davidson et. al. (16) reported an XPS study for probing the sorption sites for Co $^{2+}$  and Ni $^{2+}$  on hectorite and montmorillonite. They concluded that Co $^{2+}$  had a greater affinity for exchange on hectorite than did Ni $^{2+}$ : but Ni $^{2+}$  had a greater affinity for the surface of montmorillonite than for hectorite. In the present study we report a similar investigation of sorption of certain cations with magnesite, kaolinite, smectite and chlorite minerals. The

cations used in this study were  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$ . The first three have radioisotopes  $^{137}\text{Cs}$  ( $t_{1/2}=30.1\text{y}$ ),  $^{90}\text{Sr}$  ( $t_{1/2}=29.1\text{y}$ ),  $^{140}\text{Ba}$  ( $t_{1/2}=12.8\text{d}$ ), which are produced in high yields in fission, whereas  $^{65}\text{Zn}$  ( $t_{1/2}=243.9\text{d}$ ), and  $^{60}\text{Co}$  ( $t_{1/2}=5.3\text{y}$ ), are activation products. All of them are important in radioactive waste considerations.

In the first part of the experiments, selective adsorption of these cations on magnesite was studied, since magnesite had only  $\text{Mg}^{2+}$  as the exchange cation. In the second part of the experiments, monovalent  $\text{Cs}^+$  and divalent  $\text{Ba}^{2+}$  cations were used in the study of the sorption affinity of different clay minerals.

## Materials and Methods

Magnesite, kaolinite, smectite and chlorite minerals from various mineral deposits in Turkey were obtained from the Mineral Research and Exploration Institute (MTA) of Turkey. The particle size of the minerals used were all  $< 38\ \mu\text{m}$  after dry sieving. Structural characterization of the minerals was carried out by FTIR and XRD measurements. The composition and the cation exchange capacity (CEC) of the mineral samples used in this work determined by the silver-thiourea method (17) are given in Table 1. In the sorption experiments duplicate 100 mL, 0.1 M aqueous solutions of the cations of interest were stirred with 1.0 g of respective solids for 48 hours at room temperature. The samples were then filtered, washed thoroughly several times and dried at  $60^\circ\text{C}$  for 12 hours. The pH of the aqueous phases following sorption ranged from 5.3 to 7.5. No attempt was made to control the pH. For  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , solutions chloride salts and for  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  solutions nitrate salts were used.

**Table 1.** Mineral Compositions and Cation Exchange Capacities (CEC) of the samples used in this study.

Solid Matrix	Major Component	Minor Components	CEC (meq/100g)
Magnesite	Magnesite	Quartz	6
Kaolinite	Kaolinite	Quartz	6
Kaolinite	Kaolinite	Quartz, Mica	6
Smectite	Smectite	Quartz	21
Chlorite	Chlorite	Quartz, Smectite	15

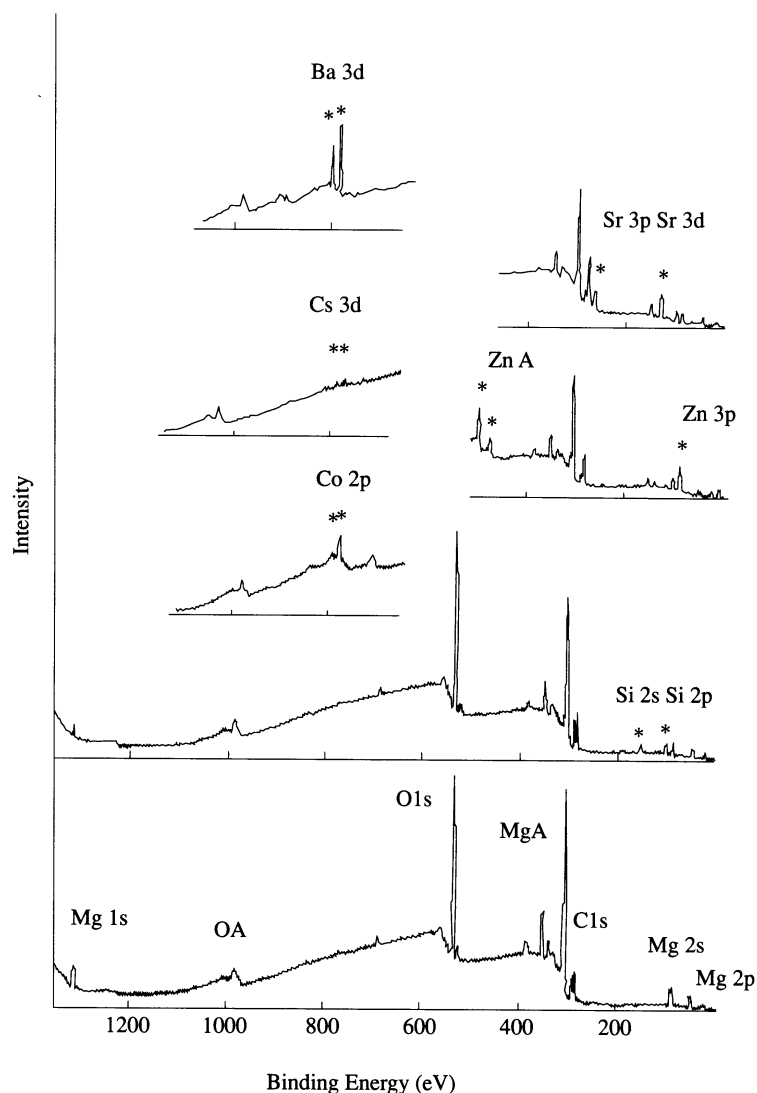
X-ray photoelectron spectra were recorded using a KRATOS ES 300 spectrometer with  $\text{AlK}\alpha$  x-rays ( $h\nu+1486.3\ \text{eV}$ ). Samples were introduced as powders pressed onto adhesive Cu-tape. The pressure in the analyzer chamber was maintained below  $5 \times 10^{-9}$  torr during analyses C1s line (B.E.285.0 eV) from the residual hydrocarbons deposited and/or incorporated previously onto the surface of the samples was used as reference with an overall accuracy of 0.1 eV in binding energies (18,19). Reproducibility of XPS result was ensured by duplicate measurements.

## Results and Discussion

### I-Selective Adsorption on Magnesite

For the selectivity study of the clay minerals under investigation towards the various cations, we had chosen magnesite assuming that only the  $\text{Mg}^{2+}$  ions would be exchanged. Figure 1 shows the photoelectron spectral of magnesite before, and relevant parts of the spectra after sorption involving different cations. In addition

to the features stemming from magnesium carbonate (Mg 1s, 2s and 2p and KLL Auger lines, O 1s and KLL Auger lines, C 1s from  $\text{CO}_3^{2-}$  and hydrocarbons) the spectrum of magnesite contains additional features, Si 2s and 2p, representing the quartz component. After sorption, the spectra contained additional features due to the cation under investigation. Only the most intense features are reproduced in the figure but each spectrum is normalized with respect to the O1s line which is the strongest feature.



**Figure 1.** Photoelectron spectra of  $\text{MgCO}_3$  (bottom) and magnesite excited by  $\text{AlK}\alpha$  x-rays ( $h\nu=1486.3$  eV). OA and MgA refers to KLL Auger peaks of O and Mg, respectively. Spectra are normalized with respect to O 1s lines in each case. Spectrum of magnesite contains additional Si 2s and 2p peaks from the minor component of the mineral, quartz. C 1s region consist of two peaks corresponding to the C 1s of  $\text{CO}_3^{2-}$  and that of hydrocarbons. Regions displaying the sorbed ions, Co 2p, Zn 3p and Zn Auger (ZnA), Cs 3d, Sr 3p and 3d and Ba 3d are also shown.

Quantitative information, in the form of atomic ratios, can be obtained from the observed intensities using the formula (18,19):

$$\frac{[A]}{[B]} + \left( \frac{I_A}{I_B} \right) \cdot \left( \frac{\sigma_B}{\sigma_A} \right) \cdot \left( \frac{E_k(B)}{(AE_K(A))^{3/2}} \right),$$

where I represents the observed intensity as calculated from the area of the peak,  $\sigma$  is the tabulated photoionization cross section (20),  $E_k$  is the kinetic energy ( $1486.3 - \text{B.E.}$ ) and  $[A]/[B]$  is the computed

atomic ratio of the elements A and B. Although any spectral line corresponding to an element can be used for this calculation large uncertainties may result if the lines are very far apart (large kinetic energy difference) and/or if their cross-sections are widely different. Assuming the total Si content to be constant before and after sorption and that cations are largely exchanged with  $Mg^{2+}$  in magnesite, the intensity of the Mg 1s (K.E.+181 eV), 2s (K.E.+1396) or 2p (K.E.+1435 eV) lines normalized against Si 2p (K.E.+1384 eV) line can be used as an indication of their sorption order. The KRATOS spectrometer has notoriously poor transmission at low kinetic energies hence use of the Mg 1s line can introduce large systematic errors. Therefore, we have used the Mg 2p and Si 2p peak areas to compute atomic ratios since both are close in energy and cross-section. The relevant data are given in Table 2. According to these results the sorption affinity of the cations follow the order:

$$Ba^{2+} > Co^{2+} \cong Sr^{2+} \cong Zn^{2+} > Cs^{+}$$

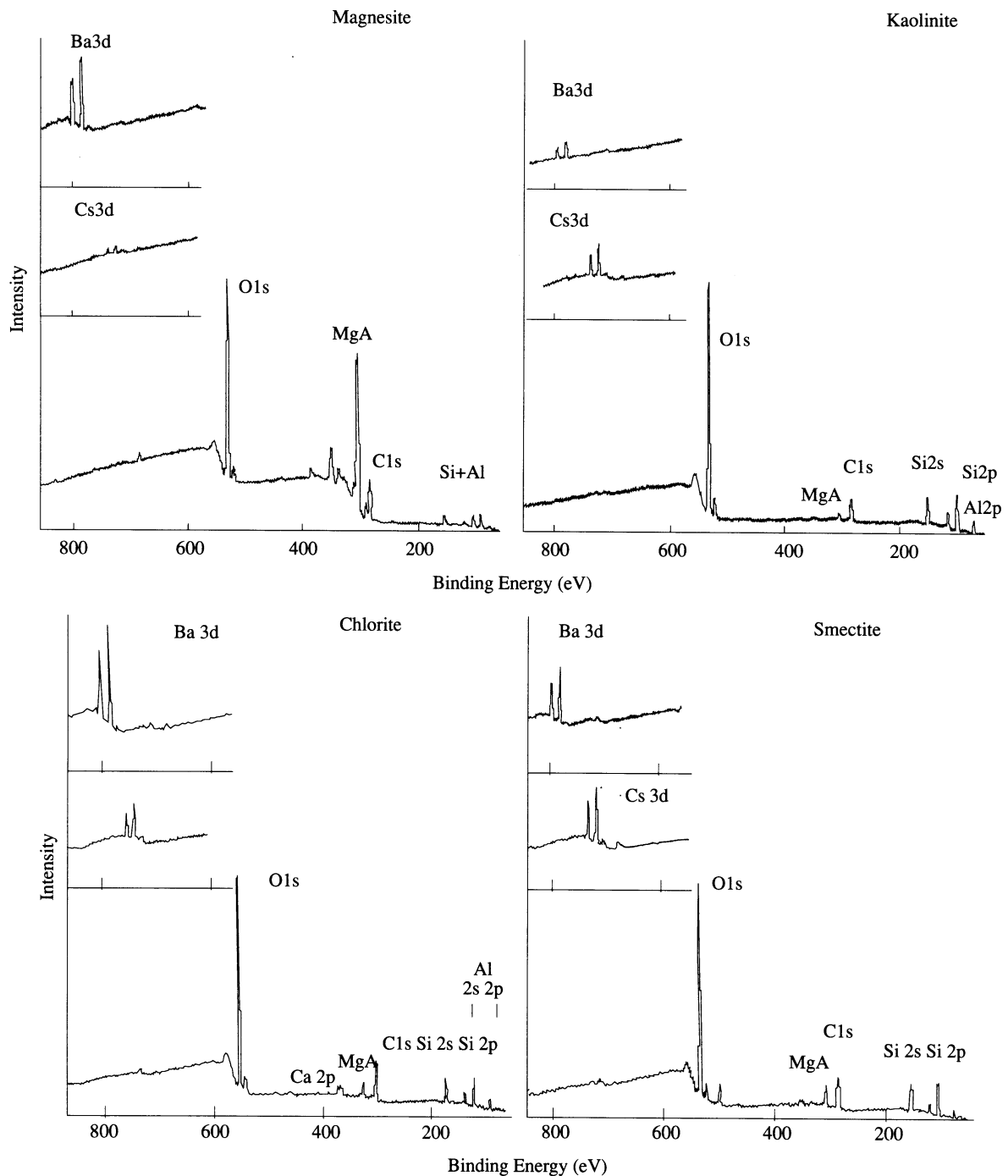
**Table 2.** Binding Energies (in eV), observed intensities (given in parenthesis as areas of the peaks) and atomic ratios.

Material	Binding Energy (eV)						Mg/Si Ratio
	01s	C1s CO <sub>3</sub> <sup>2-</sup>	Mg1s	MgKLL	Mg2p	Si2p	
MgCO <sub>3</sub>	533.7	290.9	1305.6	307.2	51.0	-	-
Magnesite	533.0	291.0	1305.6	307.0	51.0 (1179)	102.5 (1254)	0.940
Sr <sup>2+</sup> Exch.	533.1	290.9	1305.7	307.0	51.0 (950)	103.0 (1726)	0.550
Zn <sup>2+</sup> Exch.	533.0	291.1	1305.2	307.2	51.2 (1663)	102.8 (2927)	0.568
Co <sup>2+</sup> Exch.	533.0	291.0	1306.0	306.5	51.0 (583)	103.5 (1142)	0.511
Cs <sup>1+</sup> Exch.	533.5	291.0	1305.5	307.0	51.0 (770)	103.0 (1256)	0.613
Ba <sup>2+</sup> Exch.	533.0	290.5	1305.5	306.5	50.5 (485)	102.5 (1076)	0.451

## II-Sorption Affinity of Clays towards Cs<sup>+</sup> and Ba<sup>2+</sup>

Monovalent Cs<sup>+</sup> and divalent Ba<sup>2+</sup> had been chosen since they are next to each other in the periodic table and their strongest features in the photoelectron spectra, the 3d lines, were both close in energy and have comparable photoionization cross-sections (20). Figure 2A and 2B display the XPS of magnesite, kaolinite, chlorite and smectite in 800-0 eV binding energy range. Spectra are normalized with respect to O 1s intensity which is the strongest feature in all of them. The regions between 600-0eV binding energy are similar after sorption, hence only parts of the spectra are reproduced in the figure where there is a large change due to 3d lines of Cs and Ba. Spectra after sorption are similarly normalized and have the same intensity axes as the original ones. Due to the above-mentioned proximity of the energies and photoionization cross-sections of the 3d lines of Cs and Ba, a direct visual comparison can also be made from the figure since all the experimental conditions are exactly the same. From further analysis of the data, It is determined that Ba<sup>2+</sup>

is most adsorbed on chlorite and least on kaolinite, whereas  $\text{Cs}^+$  is highly adsorbed on smectite and very little on magnesite. Accordingly, the relative order for  $\text{Ba}^{2+}$  and  $\text{Cs}^+$  sorption can be given as follows:



**Figure 2.** Photoelectron spectra of magnesite and kaolinite (2A) and chlorite and smectite (2B) before sorption and Cs and Ba 3d regions after sorption. The same format as in Figure 1 is used. The spectra are normalized to the strongest peak of O 1s. The same intensity scale applies to all the spectra.

$\text{Ba}^{2+}$  sorption: chlorite > magnesite > smectite > kaolinite

$\text{Cs}^+$  sorption: smectite > chlorite  $\cong$  kaolinite > magnesite

The order of sorption obtained previously using radichemical measurements on three clay minerals are as follows (2, 4);

Ba<sup>2+</sup> sorption: chlorite > smectite > kaolinite

Cs<sup>+</sup> sorption: smectite > chlorite  $\cong$  kaolinite

and agrees quite well with those from XPS. No radiochemical measurements on magnesite sorption are available. Although we have only reported changes in some major components, there are also changes in the minor components since any element except hydrogen and He can be detected by XPS.

Closer examination of the experimental results suggest that in the case of kaolinite and smectite, the principle exchange cation is possibly H<sup>+</sup>, whereas in chlorite they are H<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> and in magnesite it is mostly Mg<sup>2+</sup>. The data presented show that XPS provides valuable information in the study of the sorption process. Further work is being carried out to identify and quantify all of the exchanging ions and sites in different clay minerals.

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