

## EXCHANGE AND SELECTIVE SURFACE UPTAKE OF CATIONS BY LAYERED SILICATES USING X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

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**Abstract**—The cation-exchange capacities (CEC) of a previously well-characterized beidellite have been estimated nondestructively from X-ray photoelectron spectroscopy (XPS) data following exchange by various cations. The CEC obtained as an atomic ratio to silicon from Na- and Ca-clays are close to that derived chemically, i.e., 0.10(2), and 0.10(1), respectively, compared with 0.12(1). However, the apparent CEC obtained following K-, Pb-, and Ba-exchange are all about 50% greater. These measurements are complemented by XPS studies of clay exchanged in a solution containing both Ca and Ba ions where XPS gave a total apparent exchange capacity relative to Si of 0.16, with 0.10 from Ca and 0.06 from Ba. Bulk chemical analysis has, however, shown that the true Ba value is only 0.01. It is concluded that the cation excess detected by XPS—a technique with a total sampling depth of only about 100 Å—is concentrated at the surfaces of the clay particles.

**Key Words**—Beidellite, Cation Exchange, Surface Exchange, X-ray Photoelectron Spectroscopy.

### INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been widely used as a qualitative analytical tool in recent years. Mineralogical examples include iron-containing silicate minerals (Adams *et al.*, 1972; Huntress and Wilson, 1972; Stucki *et al.*, 1976) and lead sorbed on montmorillonite (Counts *et al.*, 1973). However, little attempt could be made in these studies to use XPS in any generally quantitative fashion. Although Wyatt *et al.* (1975) identified some of the factors affecting the use of the technique for the quantitative analysis of solids, generally applicable procedures of predictable reliability have only recently become available (Adams *et al.*, 1977; Evans *et al.*, 1977, 1979a, 1979b). The work described in this paper is thus one of the first applications of quantitative XPS specifically to clay minerals.

In X-ray photoelectron spectroscopy, bombardment of a solid in high vacuum by soft X-rays (in this study, MgK $\alpha$ , 1254 eV) results in the production of photoelectrons from some core levels of all the elements present. A scan of the total electron energy spectrum accessible to the radiation used, taking less than 15 min to record, can give qualitative identification of all elements above He in the periodic table at concentrations exceeding about 2 atom % (see, e.g., Briggs, 1977). Such a procedure is useful by virtue of its speed and its comprehensive and nondestructive nature; and qualitative analysis of 0.1–0.2 atom % is often possible with slower scans. Moreover, XPS can now be used to give a quantitative analysis for all elements present at the 0.5 atom % level and above in about 1 day. Although it is possible to analyze a mineral sample fully by traditional means, such analyses are commonly not carried out because of the time and quantity of material required; thus, the presence of minor elements can remain completely unsuspected.

The region of the X-ray photoelectron spectrum within 100 eV of the valence band is often of particular value in studies of aluminosilicates since at least one peak from most elements likely to be present occurs in this range. Quantitative estimation of the various elements is achieved from a consideration of the relevant peak intensity ratios. Several sources of error are inherent in such procedures, arising principally in the separation of the peaks from the scattered electron background, in the determination of the relative 'sensitivity factors' (Wagner, 1977) or, more precisely, in the determination of the partial subshell photoionization cross sections (Adams *et al.*, 1977; Evans *et al.*, 1977, 1979b), and in the neglect of multi-electron excitations (Evans *et al.*, 1977). Nevertheless, Evans *et al.* (1979b) reported a mean accuracy of  $\leq 12\%$  in determining relative atomic abundances over a wide range of elements. This level of reliability is useful, even though absolute elemental determination cannot easily be performed; it is necessary to refer the number of atoms to a standard, and Si has been set equal to 1.0.

In this work, the maximum uptake of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, and Ba<sup>2+</sup> by a well-characterized beidellite was determined by XPS to assess the utility of the technique in determining the CEC of small quantities of layered silicate minerals and to investigate the extent of surface (as opposed to interlamellar) uptake of a wide variety of cations by a typical clay mineral. The latter objective is difficult to achieve using conventional exchange techniques because strongly adsorbed ions are liable to become 'fixed' in the clay and thus are not accessible to normal cation-exchange procedures. XPS can, however, be used to differentiate between surface and interlamellar uptake since although the total sampling depth of the technique is about 100 Å, the probability of a photoelectron escaping from the surface without

Table 1. Chemical analyses of beidellite.

	Natural beidellite				Ca-clay Ca	Ba-clay Ba	Mixed Ca/Ba clay	
	Si	Al	Mg	Fe			Ca	Ba
% oxide <sup>1</sup>	53.3	27.3	1.4	0.03 <sup>2</sup>	3.02	8.44	— <sup>3</sup>	1.49
Atom ratio (A.R.)	1.00	0.604	0.039	0.0004	0.061 (5)	0.060 (4)	— <sup>3</sup>	0.011 (2)
A.R. from formula of Weiss <i>et al.</i> , 1955	1.00	0.618	0.075	0.003	—	—	—	—
Mean A.R. by XPS (cf. Table 2) (estimated standard deviations in parentheses)	1.00 (2p)	0.59 (3) (2s, 2p)	—	—	0.050 (4) (2s, 2p)	0.079 (8) (3d, 4d)	0.053 (4) (2p)	0.030 (3) (3d, 4d)

<sup>1</sup> Air-dried clay containing 8% loosely bound water removable at 70–100°C (estimated by thermogravimetric analysis).

<sup>2</sup> Fe<sub>2</sub>O<sub>3</sub>.

<sup>3</sup> There was insufficient material for the adequate determination of both Ca and Ba in this sample.

energy loss—and so contributing to the measured peak intensity—decreases exponentially with its depth of origin beneath the surface. As long as the particle sizes are >100 Å in diameter, such a distinction can be validly made even with randomly oriented particles.

#### EXPERIMENTAL AND RESULTS

The beidellite used was similar to that described by Weiss *et al.* (1955) and has a quoted layer composition of (Mg<sub>0.27</sub>Al<sub>1.76</sub>Fe<sub>0.01</sub><sup>3+</sup>)(Si<sub>3.56</sub>Al<sub>0.44</sub>)O<sub>9.92</sub>(OH)<sub>2</sub>. The layer charge of the mineral was determined by the alkyl ammonium method of Lagaly and Weiss (1969) as 0.43 charges per (Si, Al)<sub>4</sub> unit. Two 0.5-g samples of the <2-μm fraction were chemically analyzed by standard procedures for major elements, initial dissolution being by fusion with sodium hydroxide (see Bennett and Reed, 1971). The results are given in Table 1. In addition there was no XPS evidence for the presence of potassium in the original beidellite indicating that this beidellite is not a mixture of smectite and illite as has sometimes been found.

Small samples of the <2-μm fraction of the beidellite were exchanged with Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Ba<sup>2+</sup>, and a Ca<sup>2+</sup>/Ba<sup>2+</sup> mixture at room temperature using solutions of the appropriate chlorides or nitrates at 1 M concentration, except for barium nitrate which saturates at 0.3 M. Exchange was followed in each case by a constant number of alternate centrifugation and washing steps to remove excess salt from the clay. Any loss of material during this washing process should have been the same for each cation-exchanged sample. It is unlikely that there was selective loss of small particle size material by some samples and not by others. After drying at 70–100°C, the samples were powdered and pressed at 10 tons/in.<sup>2</sup> into pellets up to approximately 1 mm in thickness. When the quantity available was limited (~30 mg) thinner pellets were used, but were more difficult to handle. Even smaller quantities of material (≥10 mg) can be pressed into a suitable backing but are then more difficult to reclaim. The surfaces

of the pellets were abraded with a stainless steel razor blade immediately before insertion into an AEI ES 200A electron spectrometer for XPS measurements.

After analogue XPS scans were made to confirm the integrity of the sample (see Figure 1), the principal peaks were recorded digitally in 0.5 eV steps with counting times ≤20 sec. Background was subtracted, and the peak areas were determined using a computer program, assuming the net background at each point to be proportional to the total integrated peak intensity to higher kinetic energy (KE), i.e., lower binding energy. Analogue scans only were used in the study of the Ba-beidellite and peak areas were here obtained by square counting. Although the air-dry clays contained varying amounts of water, the O 2s peak remained constant in intensity with respect to Si within a few percent for all the samples, suggesting that very roughly the same proportion of water molecules is retained under high vacuum in each cation-exchanged species. As XPS is a nondestructive technique, the samples used could be reclaimed for further study. A 30-mg sample of the Ca/Ba-exchanged beidellite and similar samples of the Ba- and Ca-exchanged clays were each fused with NaOH and their Ca (Ca-clay only) and Ba contents determined nephelometrically, as recently described by Adams and Evans (1979). The results are included in Table 1.

The relative atomic abundances of the principal elements were obtained from the XPS peak-intensity ratios by application of the relation

$$\frac{I_A}{I_B} = \frac{n_A \cdot \sigma_A}{n_B \cdot \sigma_B} \cdot \frac{E_A^{0.5}}{E_B^{0.5}} \cdot \frac{\exp(-D/\lambda_A)}{\exp(-D/\lambda_B)}$$

(Adams *et al.*, 1977)

where for elements A and B the peak intensity from the relevant subshells, after correction for the linear increase with electron energy ( $E_A$ ,  $E_B$ ) of the AEI ES 200 analyzer transmission, are  $I_A$  and  $I_B$ ; the numbers of atoms per unit volume are  $n_A$  and  $n_B$ ; the partial subshell cross sections are  $\sigma_A$  and  $\sigma_B$ ; and the variations with

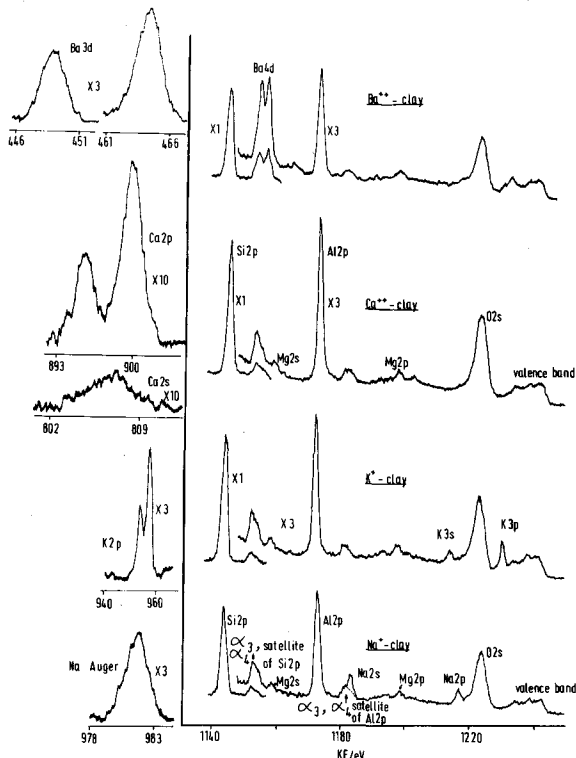


Figure 1. XPS traces of the "fingerprint region" within  $\sim 100$  eV of the valence band for several of the exchanged beidellites. Insets are given of the principal peaks of the exchangeable cation when these are not in this region. The ordinate represents electron count rate, typically  $1-3 \times 10^3$  c/sec for the major peaks shown.

$E$  of the inelastic mean free paths  $\lambda_A$  and  $\lambda_B$  of the photoelectrons are approximated as  $E_A^{0.5}$  and  $E_B^{0.5}$ . In each case a contamination correction is applied to allow for the inevitable presence of adsorbed carbonaceous impurities to a thickness  $D$  on the surfaces of the samples. The exponent of this final term reduces to  $-cE^{-0.5}$  if  $\lambda \propto E^{0.5}$  and the coefficient  $c$  is treated as an empirical constant for a given set of experimental conditions (see Evans *et al.*, 1977). In these studies  $c$  does not exceed 14.3, and thus the correction amounts to only a few percent over the usual KE range. Analytical data obtained by this method for the 6 cation-exchanged beidellite samples are given in Table 2.

## DISCUSSION

Two types of cation uptake by layered silicate minerals are usually considered to be possible. The dominant, and much more extensively investigated, mode of uptake results from penetration of the interlamellar region of the mineral by cations balancing the negative layer charge which accompanies cation substitutions within the aluminosilicate layers. Interlamellar uptake is believed to be responsible for the bulk of the CEC of the 2:1 layer minerals. Exchange of cations at the pe-

riphery of mineral particles, where one might expect to find "unsatisfied valencies," can also occur, and indeed the low CEC of the 1:1 clay minerals is often attributed to such exchange. The extent to which similar effects occur in the 2:1 minerals of the montmorillonite family has, however, remained unclear, although studies of the surface uptake of Co and Zn by some layered silicates have been described by Hodgson and Tiller (1962) and Tiller and Hodgson (1962). Specific surface exchange is not, however, restricted to clay minerals, and Bancroft *et al.* (1977) recently demonstrated that  $Ba^{2+}$  is strongly retained on the surface of calcite crystals.

The CEC of a clay mineral is generally estimated via some exchange process involving two cations which are not strongly retained by the mineral, sodium or calcium being common examples. Consideration of the XPS data in Tables 1 and 2 suggests that exchange by these cations does indeed occur in beidellite to an extent consistent with the independently determined layer charge for the mineral. Uptake of  $K^+$ ,  $Pb^{2+}$ , and  $Ba^{2+}$ , however, apparently occurs to a substantially greater extent. These ions are not normally used in CEC determination because of the risk of their becoming "fixed" in the clay. Since the anions of the salts used for exchange did not give rise to detectable XPS peaks, the washing procedure used in this study to remove excess salt appears to be adequate. For such excess salt on the surface the principal XPS peak would be roughly comparable in intensity with the major cation peak. Only very small quantities of salts could thus have remained undetected on the surfaces of the clay particles; certainly not enough to cause the effects observed. The excess uptake shown in Table 2 is greater than the probable experimental error, and while this might conceivably reflect a greater interlamellar uptake, such an uptake is improbable from a structural point of view. It seems more probable in view of the results for Ba chemical microanalysis that these ions, unlike  $Na^+$  and  $Ca^{2+}$ , are strongly held on the edges or surfaces of clay particles.

The results for the Ca/Ba-exchanged clay provide strong support for this hypothesis. The  $Ca^{2+}$  uptake is essentially identical with that of a purely  $Ca^{2+}$ -exchanged sample, while the  $Ba^{2+}$  uptake, assumed to be exchanged on the surface is equal to the excess uptake found when Ba salts alone are used in the exchange process. It is notable that the smaller  $Ca^{2+}$  ion apparently monopolizes the interlamellar sites even though the independent experiment with the larger cation alone indicates that  $Ba^{2+}$  ions can also penetrate the interlamellar regions.

The extent of excess uptake is the same within experimental error for  $K^+$ ,  $Pb^{2+}$ , and  $Ba^{2+}$ , suggesting that the same sites (possibly hydroxyls at the particle edges) may be active in all three cases. It is, however, interesting that the Ba uptake on Ca/Ba exchange is much less as determined by bulk chemical analysis than as

Table 2. Atom ratios for cation-exchanged beidellite by X-ray photoelectron spectroscopy.

Exchange-able cation	Relative atomic abundances <sup>1</sup>			Cation	Mean cation <sup>2</sup>	Apparent layer charge per Si <sup>3</sup>		
	Layer							
	Si 2p	Al 2s	Al 2p					
Na	1.00	0.64	0.55	0.098 (KLL Auger)	0.087(2s) <sup>3</sup>	0.118(2p)	0.10(2)	0.10(2)
Ca	1.00	0.60	0.58	0.046(2s)	0.054(2p)		0.050(4)	0.10(1)
K	1.00	0.61	0.54	0.160(2s)	0.157(2p)	~0.12(3p) <sup>4</sup>	0.15(2)	0.15(2)
Pb	1.00	0.62	0.57	0.079(4d)	0.066(4f)		0.073(6)	0.15(1)
Ba <sup>5</sup>	1.00	0.58	0.57	~0.08(3d) <sup>6</sup>	0.077(4d)		0.079(6)	0.16(1)
Ca } Ba }	1.00	0.60	0.56	0.053(2p) ~0.031(3d) <sup>6</sup>	0.028(4d) <sup>5</sup>		0.05(Ca) 0.03(Ba)	0.16(2)
Mean	1.00	0.59						

<sup>1</sup> Obtained using cross sections from Evans *et al.* (1978) and Adams *et al.* (1977). Ca 2s and Ba 3d were extrapolated as 0.42 and 9.4 (relative to F 1s = 1.00), respectively.

<sup>2</sup> Estimated standard deviations in parentheses.

<sup>3</sup> Correction applied for overlap with MgK $\alpha_{3,4}$  satellite peaks from Al 2p (Na 2s)/Si 2s (Pb 4f).

<sup>4</sup> Weak peak difficult to separate from adjacent signals.

<sup>5</sup> From analogue scans.

<sup>6</sup> The Ba 3d peaks have such low KE (~450 eV) that these values are significantly less reliable than the 4d determinations.

determined by XPS, and that the excess (bulk) Ba uptake in the Ba-exchanged clay was indeed not even detectable by comparison of the approximate CEC for Ca<sup>2+</sup> and Ba<sup>2+</sup> determined by bulk chemical microanalysis (Table 1). It should, perhaps, be noted here that although it might be possible to account for the apparent excess surface exchange by assuming that some or all of the Pb or Ba were in the form of PbOH<sup>+</sup> or BaOH<sup>+</sup>, this would give Pb or Ba values obtained by bulk chemistry of the same magnitude as those derived from XPS, which is not the case.

Where such surface effects are of little importance, e.g., with Na<sup>+</sup>- and Ca<sup>2+</sup>-clays, the exchange capacities of small quantities of a mineral specimen can evidently be estimated nondestructively to within about 12%. The analytical capability is, moreover, not restricted to CEC determination. In the present work, for example, the Si:Al ratio for the beidellite layers was estimated by XPS as 1:0.59 (Table 1), within 3% of the value given by bulk gravimetric analyses (1:0.604, Table 1). XPS is thus valuable in the study of both the bulk and the surface chemistry of clay minerals.

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**Резюме**—По данным рентгеновской фотоэлектронной спектроскопии (КФС) после обмена различными катионами оценивались катионно-обменные способности (КОС) предварительно хорошо охарактеризованного бейделлита без его разрушения. Полученные для Na- и Ca-глин КОС, как атомные отношения к кремнезему близки к отношению, полученному химическим путем, т.е., 0,10(2) и 0,10(1) соответственно по сравнению с 0,12(1). Однако, все кажущиеся КОС, полученные в результате обменов с K-, Pb-, и Ba-выше примерно на 50%. Эти измерения были дополнены исследованиями глины с помощью КФС после реакции обмена в растворе, содержащем ионы Ca и Ba. КФС показала суммарную обменную способность по отношению к Si, равную 0,16, причем вклад Ca—0,10, а Ba—0,06. Объемный химический анализ, однако, показал что истинная величина для Ba является только 0,01. Было сделано заключение, что избыток катионов, отмеченный КФС —способом с суммарной глубиной исследования только примерно 100 Å— сконцентрирован на поверхности глинистых частиц.

**Resümee**—Die Kationenaustauschkapazitäten (CEC) eines Beidelliten, der schon seit einiger Zeit charakterisiert ist, sind ohne Zerstörung durch Röntgen-Photoelektronen-Spektroskopie (XPS) nach Austausch mit verschiedenen Kationen bestimmt worden. Die CEC Werte, welche als atomisches Verhältnis von Na- und Ca-Tonerden zu Silizium erhalten wurden, liegen sehr nahe bei denen, welche chemisch erhalten wurden, d. h., 0,10(2) beziehungsweise 0,10(1) im Vergleich zu 0,12(1). Die scheinbaren CEC Werte, die nach dem K-, Pb-, und Ba-Austausch erhalten werden, sind jedoch alle ungefähr 50% höher. Diese Messungen werden ergänzt durch XPS Untersuchungen von Tonen, die in einer Lösung von Ca- und Ba-Ionen ausgetauscht werden und in denen XPS eine gesamte, scheinbare Austauschkapazität, auf Si bezogen, von 0,16 ergab, von der 0,10 von Ca und 0,06 von Ba stammen. Chemische Massenanalyse hat jedoch gezeigt, daß der wahre Ba-Wert nur 0,01 ist. Es wird beschlossen, daß der Kationenüberschuß, welcher durch XPS Messungen, einer Methode mit einer gesamten Probentiefe von nur etwa 100 Å gefunden wurde, sich auf der Oberfläche der Tonpartikel befindet.

**Résumé**—Les capacités d'échange de cations (CEC) d'une beidellite auparavant bien caractérisée ont été estimées d'une manière non destructive à partir de données de spectroscopie de photoélectrons aux rayons-X (XPS) suivant l'échange de divers cations. Les CEC obtenues en tant que proportion atomique à la silice des argiles de Na et de Ca sont proches de celles dérivées chimiquement, c.à.d., 0,10(2) et 0,10(1), respectivement, comparé à 0,12(1). Cependant, les CEC apparentes obtenues suivant l'échange de K, Pb, et Ba sont toutes environ 50% plus élevées. Ces mesures sont complimentées par des études XPS d'argile échangée dans une solution contenant à la fois des ions Ca et Ba où XPS a donné une capacité d'échange totale apparente relative à Si de 0,16, avec 0,10 venant du Ca et 0,06 venant du Ba. L'analyse chimique de masse a cependant montré que la véritable valeur pour Ba est seulement de 0,01. On a conclu que l'excès de cations détectés par XPS—une technique avec une profondeur d'échantillonnage de seulement environ 100 Å—est concentré sur les surfaces des particules d'argile.