

X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF THE EFFECT OF HEATING ON MONTMORILLONITE CONTAINING SODIUM AND POTASSIUM CATIONS

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Abstract—The effect of heating on montmorillonites containing exchangeable Na and K has been studied by X-ray photoelectron spectroscopy (XPS). The surface composition of the unheated montmorillonite was consistent with the bulk composition, but after the sample recrystallized at 1100°C, the surface abundance of Na increased, whereas that of K decreased. Because Na and K were not present in the high-temperature crystalline products, this behavior suggests that a noncrystalline material separated from the crystalline products. The Na 1s binding energy and $KL_{23}L_{23}$ Auger kinetic energy of montmorillonite were comparable with those of Na in typically ionic compound, such as NaCl. These electron energies became smaller and larger, respectively, on heating and approached those of feldspar (albite). The K $2p_{3/2}$ binding energy of montmorillonite increased slightly on heating. The K $2p_{3/2}$ binding energy of heated sample of montmorillonite was also comparable with that of feldspar (orthoclase). These results suggest that Na and K were incorporated into feldspar-like noncrystalline materials.

Key Words—Montmorillonite, Noncrystalline, Surface composition, Thermal treatment, X-ray photoelectron spectroscopy, X-ray powder diffraction.

要旨—X線光電子分光法(XPS)を用いて、交換性Na及びKを含むモンモリロナイトに対する加熱の影響が研究された。未加熱のモンモリロナイトの表面組成はバルク組成と一致したが、1100°Cで再結晶するとNaの表面における存在量は増大し、Kの表面における存在量は減少した。Na及びKは加熱試料の結晶相中に存在しないので、このような挙動は非晶質の物質が結晶性の生成物から分離したことを示唆している。モンモリロナイトのNa 1s結合エネルギー及び $KL_{23}L_{23}$ オージェ運動エネルギーはNaClのような典型的なイオン結合性物質の値に近く、加熱により各々減少および増大し、長石(曹長石)の値に近づく。モンモリロナイトのK $2p_{3/2}$ 結合エネルギーは加熱により僅かに増大する。加熱試料のK $2p_{3/2}$ 結合エネルギーもまた長石(正長石)の値に近い。これらの結果はNa及びKが長石類似の構造をもつ非晶質の物質中に取り込まれていることを示唆している。

INTRODUCTION

The structural changes of clay minerals on heating have been investigated for many years (see Grim, 1968). Montmorillonite loses interlayer water at 100°–200°C and hydroxyl water at 500°–800°C and undergoes the structural collapse and recrystallization at 800°–1000°C. The thermochemical properties of montmorillonite substantially depend on the nature of its exchangeable cations (Grim, 1968). The major crystalline products formed by the recrystallization of montmorillonite at high temperature have been identified as quartz, cristobalite, spinel, mullite, and cordierite by X-ray powder diffraction (XRD) (Bradley and Grim, 1951; Grim, 1968). These crystalline phases contain Si, Al, Mg, and O, but no cations which occur as exchangeable cations in the montmorillonite. The exchangeable cations may therefore be incorporated into noncrystalline material following the recrystallization step, but little information is available about bonding changes of exchangeable cations in montmorillonite on heating.

X-ray photoelectron spectroscopy (XPS), a surface analytical technique, is applicable to both noncrystalline and crystalline materials. To date, XPS has been applied to the study of the cations adsorbed on clay minerals (Koppelman and Dillard, 1975, 1977, 1978, 1980; Koppelman *et al.*, 1980), the oxidation and reduction reactions of nontronite and biotite (Stucki *et al.*, 1976; Stucki and Roth, 1977), the X-ray photoelectron diffraction (XPD) of single-crystal clay minerals (Adams *et al.*, 1978a, 1978b; Evans and Raftery, 1979, 1980a, 1980b, 1982a, 1982b; Evans *et al.*, 1979), the oxidation states of Ti and of Mn in clay minerals (Evans and Raftery, 1980b, 1982c), calcined Co-kalinite materials (Dillard *et al.*, 1983), and the bonding state of the exchangeable divalent cations in montmorillonite (Seyama and Soma, 1984). In the present study, the effect of heating on the surface elemental composition and on the bonding state of the exchangeable cations in montmorillonite are reported on the basis of the XPS and XRD data.

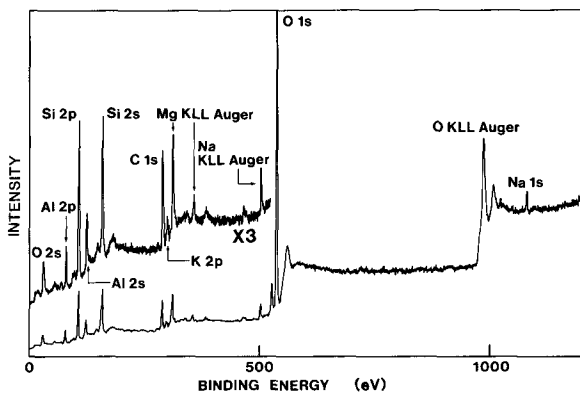


Figure 1. Wide-scan X-ray photoelectron spectrum of Na-K-montmorillonite excited by $AlK\alpha$ X-ray radiation. The ordinate scale of the lower part of spectrum (0–500 eV) in the inset is expanded three times.

EXPERIMENTAL

Materials

The montmorillonite sample was Kunipia F obtained from Kunimine Industries. It was purified from bentonite from the Tsukinuno mine, Yamagata, Japan. The nominal composition of Kunipia F is as follows: SiO_2 , 57.96; Al_2O_3 , 21.87; Fe_2O_3 , 1.92; MgO , 3.44; CaO , 0.54; Na_2O , 2.98; K_2O , 0.14. It was transformed to Na-montmorillonite containing only Na as an exchangeable cation by the method described by Seyama and Soma (1984). XRD analysis of the Na-montmorillonite showed it to contain a very small but detectable amount of quartz as an impurity.

Samples containing exchangeable Na and K were prepared by the cation exchange of Na-montmorillonite as follows. Na-montmorillonite was suspended in KNO_3 aqueous solution for 40–50 hr. The concentration of the KNO_3 solution was 0.0025 M for the preparation of Na-K-montmorillonite (K:Na atomic ratio = 0.73, see Table 1) and 0.1 M for the preparation of K-montmorillonite (the exchange to K was not complete, see Table 1). After the cation exchange, the montmorillonite was separated from the solution by centrifuging, washed by resuspending it in distilled water, separated again by centrifuging, and freeze-dried. The montmorillonite was then heated in a platinum crucible in an electric furnace for 1 hr at 1100°C. Orthoclase from Gifu, Japan, was obtained from Bon Earth Sciences Inc. The sources of other mineral samples were listed in Seyama and Soma (1984). Metal salts were commercial materials.

Methods

Photoelectron and Auger electron spectra were recorded on a Vacuum Generators ESCA LAB 5 instrument using $MgK\alpha$ and $AlK\alpha$ X-ray sources and a Nicolet 1070 signal averager. The measuring conditions

were described by Seyama and Soma (1984). All mineral samples except phlogopite were ground to powders with an agate mortar and pestle. The heated samples of montmorillonites obtained as sintered masses were pulverized as gently as possible in order to minimize the destruction of each grain. A flake of phlogopite was cleaved from a single crystal. These samples were fixed onto stainless-steel sample holders of 10-mm diameter using double-sided sticky tape. Powders of other Na and K compounds were fixed in the same manner or directly deposited onto the sample holders from acetone suspensions.

The relative atomic abundances in the samples were calculated from the area intensities of spectra, divided by the relative atomic sensitivity factors for the electron emission lines. The factors, which depend principally on the photoionization cross sections and also on spectrometer parameters (Seah, 1980), were experimentally determined and reported by Soma *et al.* (1985). The lines used for the calculation of relative atomic abundances are listed in the footnote of Table 1. The uncertainty in the quantification of XPS arises mainly from the application of the atomic sensitivity factor to samples with different matrixes (Seah, 1980). In our measurement, the error estimated empirically was as large as 20%, but rarely exceeded this value. The relative abundances of cations in two heated samples of Na-K-montmorillonite prepared independently were determined by XPS to check the reproducibility of the preparation method. The deviations of Si, Al, and Mg values between two samples were within 10%. The Na and K values of two samples differed by 24% and 14%, respectively. The error caused by the sample preparation was therefore no more than 30%.

Photoelectron binding energies and Auger electron kinetic energies were determined relative to the $Au\ 4f_{7/2}$ binding energy (83.8 eV) of a gold film evaporated onto the sample. For the unheated montmorillonite, the Si 2s binding energy (153.4 eV) determined by this method was used as an internal standard for calibration. The reproducibilities in the determination of electron energies were usually ± 0.2 eV, but those for sodium and potassium fluoride and chloride were ± 0.5 eV.

XRD measurements were carried out by using a Rigaku RAD-IIA powder diffractometer with a $CuK\alpha$ X-ray source, operated at 40 kV and 25 mA. Powdered samples were placed on glass sample holders. The XRD patterns were recorded over a 2θ range of 2° to 90° and compared with the JCPDS mineral powder diffraction file.

RESULTS AND DISCUSSION

Surface compositions

The wide-scan X-ray photoelectron spectrum of unheated Na-K-montmorillonite is shown in Figure 1.

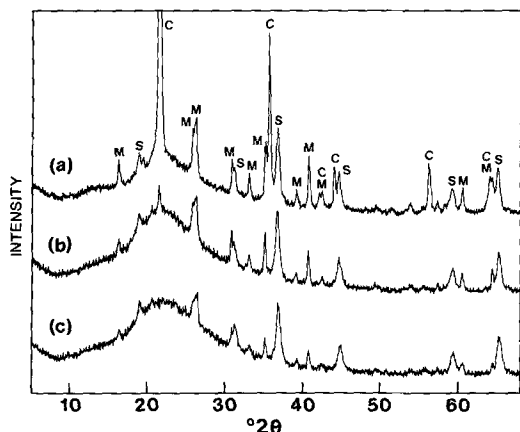


Figure 2. X-Ray powder diffraction patterns of heated samples of montmorillonites: (a) Na-montmorillonite, (b) Na-K-montmorillonite, (c) K-montmorillonite; C = cristobalite line, M = mullite line, S = spinel line.

The electron emission lines due to the constituent elements of the montmorillonite and the carbon of surface contaminant were observed in the spectrum. Although the same lines were observed in the spectrum of the heated sample, the relative intensities of lines of the unheated and heated samples were different.

The XRD patterns (Figure 2) showed that the heated sample of Na-montmorillonite contained more cristobalite than that of Na-K-montmorillonite. No XRD line of cristobalite was observed in the pattern of the heated K-montmorillonite. Thus, the crystalline phase formed in the heated samples was apparently influenced by the exchangeable cation. The XRD lines of spinel and mullite were observed for all the heated samples with comparable intensities. Cristobalite, spinel, and mullite detected by XRD contained essentially no Na and K; consequently, Na and K were probably contained in the noncrystalline material, the presence of which was evidenced by the broad hump in the XRD pattern between 10° and $40^\circ 2\theta$.

Table 1 shows the elemental compositions of samples determined by XPS. The total amount of Si, Al, Mg, Na, and K in each sample is taken as 100%; the atomic percentage of each cation is given in Table 1. Because the probing depth of XPS is very shallow ($< 100 \text{ \AA}$), the composition in Table 1 is regarded as an average composition of the outer surface of particles.¹ The surface abundance of Si, Al, and Mg in three unheated montmorillonites was identical, within experimental error. The bulk atomic abundances of Si, Al, and Mg

¹ What is actually probed by the X-rays is the outermost layers of the sample. Because the probing depth is much smaller than the average particle size and the arrangement of the particle on the sample holder is assumed to be random, the average surface composition of particles is determined by XPS.

Table 1. Surface compositions of unheated and heated samples of montmorillonites determined by X-ray photoelectron spectroscopy.

Sample	Si	Al	Mg	Na	K
Unheated sample					
Na-montmorillonite	59.6	27.5	5.8	7.1	—
Na-K-montmorillonite	59.5	27.5	5.8	4.1	3.0
K-montmorillonite	59.3	27.7	5.8	0.3	6.9
Heated sample (1100°C)					
Na-montmorillonite	49.3	32.9	7.9	9.9	—
Na-K-montmorillonite	39.9	41.2	11.1	5.8	2.1
K-montmorillonite	40.0	43.5	10.9	0.9	4.8

Values are relative abundances (atomic %) of cations. Lines used for calculation are Si, 2s; Al, 2p; Mg, $KL_{23}L_{23}$ Auger; Na, $KL_{23}L_{23}$ Auger; and K, 2p.

calculated from the cation-exchange capacity (99 meq/100 g; Seyama and Soma, 1984) and the nominal composition of Kunipia F are 61.1, 27.2, and 5.4%, respectively. The surface and bulk values differed by no more than 10%. The total abundances of exchangeable cations (Na and K) obtained by XPS was about 7.1% for each unheated sample. The calculated bulk value is 6.3%. The difference between the two values was also within the uncertainty of the XPS method. Accordingly, the preferential adsorption of Na and K on the outer surface of montmorillonite did not seem to be significant, and these cations appeared to be held mostly between the montmorillonite layers. This result is consistent with that reported by Seyama and Soma (1984).

On the other hand, the surface composition of each heated sample was not the same as that of the corresponding unheated sample, nor did the surface compositions of three heated samples agree. A common

Table 2. Na 1s binding energies and $KL_{23}L_{23}$ Auger kinetic energies of unheated and heated samples of montmorillonites and other compounds.

Compound	Na 1s (eV)	Na $KL_{23}L_{23}$ Auger (eV)
Unheated sample		
Na-montmorillonite ¹	1072.5	988.7
Na-K-montmorillonite	1072.4	988.7
K-montmorillonite	1072.3	988.9
Heated sample (1100°C)		
Na-montmorillonite	1072.1	988.9
Na-K-montmorillonite	1071.9	989.2
K-montmorillonite	1071.9	989.4
NaF ¹	1072.5	987.6
NaCl ¹	1072.6	989.0
NaBr ¹	1072.3	989.9
Analcime ¹	1072.7	988.3
Albite ¹	1072.0	989.2

¹ Reported previously by Seyama and Soma (1985).

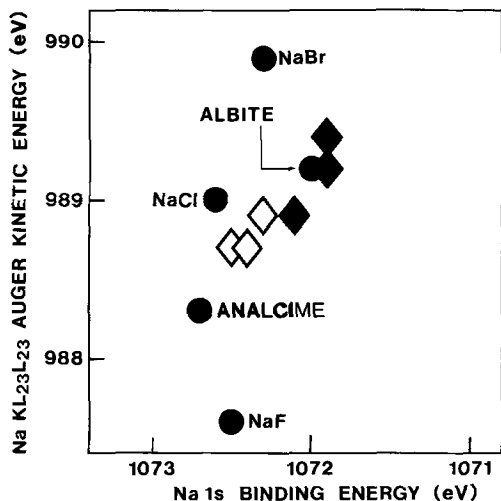


Figure 3. Chemical state plot for Na: \diamond , unheated montmorillonite; \blacklozenge , heated sample of montmorillonite; \bullet , other compound.

trend, however, was noted in the change of the surface composition with heating (see Table 1). The surface abundance of Si decreased, whereas those of Al and Mg increased on heating. Although the Na and K in montmorillonite were both exchangeable, the surface abundance of Na increased, but that of K decreased on heating. These results suggest that the elemental distribution with depth of the montmorillonite grain becomes heterogeneous as the montmorillonite is destroyed and recrystallizes at 1100°C.

Photoelectron binding energies and Auger electron kinetic energies

The Na 1s binding energies and $KL_{23}L_{23}$ Auger kinetic energies of montmorillonite samples and other compounds are shown in Table 2. All the electron energies of the three unheated montmorillonites are identical within experimental error. The differences in both electron energies between the unheated and heated samples of montmorillonite are small. The Na 1s binding energies and $KL_{23}L_{23}$ Auger kinetic energies of the heated samples, however, are slightly smaller and larger, respectively, compared with the electron energies of the unheated samples. A comparison of these electron energies with those of other compounds is shown in Figure 3 as a two-dimensional plot (chemical state plot, Wagner *et al.*, 1979), which is useful in characterizing the bonding state of the element in question. As pointed out by Seyama and Soma (1985), the chemical state of the exchangeable Na of montmorillonite and analcime fall between those of typically ionic NaCl and NaF. The position of Na in the heated sample of montmorillonite shifted close to that of Na in albite. Accordingly, by the destruction of montmorillonite layer structure, Na was probably incorporated into a

Table 3. K $2p_{3/2}$ binding energies of unheated and heated samples of montmorillonites and other compounds.

Compound	K $2p_{3/2}$ (eV)
Unheated sample	
Na-K-montmorillonite	293.1
K-montmorillonite	293.2
Heated sample (1100°C)	
Na-K-montmorillonite	293.6
K-montmorillonite	293.6
KF	294.4
KCl	293.5
KBr	293.1
Orthoclase	293.4
Phlogopite	292.7

noncrystalline material having a network structure similar to that of albite.

The K $2p_{3/2}$ binding energies are shown in Table 3. The K $2p_{3/2}$ binding energies of two unheated montmorillonites, which are the same within experimental error, are smaller than those of KF and close to those of KCl, KBr, and orthoclase. K, the ionic radius of which is larger than that of Na, tends to be fixed between the aluminosilicate layers of clay mineral. Thus, the K in montmorillonite appears to be more subject to screening and relaxation in the photoionization process by the negative charge in the aluminosilicate layer than the Na in montmorillonite. This effect lowers the K $2p_{3/2}$ binding energy and is more pronounced in phlogopite, because the K in phlogopite is completely fixed between the aluminosilicate layers. This fixation of K explains why the K $2p_{3/2}$ binding energies of unheated montmorillonite and phlogopite can be less than that of orthoclase, whereas the Na 1s binding energy of unheated montmorillonite is greater than that of albite. Although the K $2p_{3/2}$ binding energy difference between the unheated montmorillonite and orthoclase was small, the increase of the K $2p_{3/2}$ binding energy of montmorillonite on heating suggests that the K was incorporated into the feldspar-like noncrystalline material in the same manner as Na.

Mechanism of recrystallization

Based on the information obtained by XPS and XRD, the following recrystallization scheme of montmorillonite heated at 1100°C is proposed. For Na-montmorillonite, cristobalite, spinel, and mullite form, and Na is excluded to a noncrystalline material. Cristobalite probably occupies the inner part of the grain and Na-rich noncrystalline material is segregated to the outer part. In K-containing montmorillonite, the crystallization of cristobalite is hindered, presumably because of the stronger binding of K to the silicate layer. K-containing noncrystalline material remains in the inner

part of the grain, whereas Na-containing noncrystalline material is segregated to the outer part.

REFERENCES

- Adams, J. M., Evans, S., and Thomas, J. M. (1978a) X-ray photoelectron diffraction: a novel method of structural analysis in complex monocrystalline solids: *J. Chem. Soc. Chem. Commun.*, 210–211.
- Adams, J. M., Evans, S., and Thomas, J. M. (1978b) X-ray photoelectron diffraction: a new technique for structural studies of complex solids: *J. Amer. Chem. Soc.* **100**, 3260–3262.
- Bradley, W. F. and Grim, R. E. (1951) High temperature thermal effects of clay and related materials: *Amer. Mineral.* **36**, 182–201.
- Dillard, J. G., Schenck, C. V., and Koppelman, M. H. (1983) Surface chemistry of cobalt in calcined cobalt-kaolinite materials: *Clays & Clay Minerals* **31**, 69–72.
- Evans, S., Adams, J. M., and Thomas, J. M. (1979) The surface structure and composition of layered silicate minerals: novel insights from X-ray photoelectron diffraction, K-emission spectroscopy and cognate techniques: *Phil. Trans. Roy. Soc. London, Ser. A* **292**, 563–591.
- Evans, S. and Raftery, E. (1979) Angular variations in core-level XPS peak intensity ratios from single-crystal solids: *Surf. Sci.* **89**, 64–75.
- Evans, S. and Raftery, E. (1980a) Quantitative X-ray photoelectron diffraction studies of single-crystal silicates: *Solid State Commun.* **33**, 1213–1215.
- Evans, S. and Raftery, E. (1980b) X-ray photoelectron studies of titanium in biotite and phlogopite: *Clay Miner.* **15**, 209–218.
- Evans, S. and Raftery, E. (1982a) X-ray photoelectron diffraction studies of sodium in biotite: *J. Chem. Research (S)*, 170–171.
- Evans, S. and Raftery, E. (1982b) X-ray photoelectron diffraction studies of lepidolite: *Clay Miner.* **17**, 443–452.
- Evans, S. and Raftery, E. (1982c) Determination of the oxidation state of manganese in lepidolite by X-ray photoelectron spectroscopy: *Clay Miner.* **17**, 477–481.
- Grim, R. E. (1968) *Clay Mineralogy*: 2nd ed., McGraw-Hill, New York, 278–352.
- Koppelman, M. H. and Dillard, J. G. (1975) An ESCA study of sorbed metal ions on clay minerals: *ACS Symp. Ser.* **18**, 186–201.
- Koppelman, M. H. and Dillard, J. G. (1977) A study of the adsorption of Ni(II) and Cu(II) by clay minerals: *Clays & Clay Minerals* **25**, 457–462.
- Koppelman, M. H. and Dillard, J. G. (1978) An X-ray photoelectron spectroscopic (XPS) study of cobalt adsorbed on the clay mineral chlorite: *J. Colloid Interface Sci.* **66**, 345–351.
- Koppelman, M. H. and Dillard, J. G. (1980) Adsorption of $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{en})_3^{3+}$ on clay minerals and the characterization of chromium by X-ray photoelectron spectroscopy: *Clays & Clay Minerals* **28**, 211–216.
- Koppelman, M. H., Emerson, A. B., and Dillard, J. G. (1980) Adsorbed Cr(III) on chlorite, illite, and kaolinite: an X-ray photoelectron spectroscopic study: *Clays & Clay Minerals* **28**, 119–124.
- Seah, M. P. (1980) The quantitative analysis of surfaces by XPS: *Surf. Interface Anal.* **2**, 222–239.
- Seyama, H. and Soma, M. (1984) X-ray photoelectron spectroscopic study of montmorillonite containing exchangeable divalent cations: *J. Chem. Soc., Faraday Trans. 1* **80**, 237–248.
- Seyama, H. and Soma, M. (1985) Bonding-state characterization of the constituent elements of silicate minerals by X-ray photoelectron spectroscopy: *J. Chem. Soc., Faraday Trans. 1* **81**, 485–495.
- Soma, M., Seyama, H., and Okamoto, K. (1985) Characterization of sediment reference materials by X-ray photoelectron spectroscopy: *Talanta* **32**, 177–181.
- Stucki, J. W. and Roth, C. B. (1977) Oxidation-reduction mechanism for structural iron in nontronite: *Soil Sci. Soc. Amer. J.* **41**, 808–814.
- Stucki, J. W., Roth, C. B., and Baitinger, W. E. (1976) Analysis of iron-bearing clay minerals by electron spectroscopy for chemical analysis (ESCA): *Clays & Clay Minerals* **24**, 289–292.
- Wagner, C. D., Gale, L. H., and Raymond, R. H. (1979) Two-dimensional chemical state plots: a standardized data set for use in identifying chemical states by X-ray photoelectron spectroscopy: *Anal. Chem.* **51**, 466–482.

(Received 18 November 1985; accepted 29 March 1986; Ms. 1533)