CHEMISTRY LETTERS, pp. 1009-1012, 1981.

X-RAY PHOTOELECTRON AND AUGER ELECTRON SPECTROSCOPIC STUDY OF Mg-MONTMORILLONITE

Haruhiko SEYAMA* and Mitsuyuki SOMA
National Institute for Environmental Studies,
Yatabe, Tsukuba, Ibaraki 305

Deconvolution of X-ray excited Mg 1s photoelectron and Auger ($KL_{23}L_{23}$) electron spectra of Mg-montmorillonite into the spectra of the exchangeable and non-exchangeable skeletal magnesium of the clay revealed considerable difference in the electronic state for magnesium of the two origins. The chemical state of the exchangeable magnesium in montmorillonite was similar to that of magnesium in magnesium fluoride and chloride.

Cation exchange capability of clay minerals has great significance in their natural behavior as well as in their practical applications.1) From the environmental point of view, specifically, it influences the accumulation, chemical states and reactions of cations in soil and sediment. So many investigations on the cation exchange reactions of clay minerals have been undertaken, but there has been lack of the systematic knowledge concerning the electronic states of the exchanged cations simply because methods applicable to wide range of elements have not been in hand. Electron spectroscopy like X-ray photoelectron or Auger electron spectroscopy (termed as ESCA) is undoubtedly such a versatile spectroscopic method. A few attempts have been reported of the application of X-ray photoelectron spectroscopy in the study of elemental composition of clay minerals2,3) and electronic state of specific ion in clay minerals.4-9)

In this letter, as a preliminary account on the systematic electron spectroscopic studies of the exchangeable cations in clay minerals, we will report on the X-ray excited photoelectron and Auger electron spectra of Mg-montmorillonite, a clay mineral which contains exchangeable magnesium cation as well as non-exchangeable skeletal magnesium cation, and show the capability of the method to distinguish magnesium in the two different states.

Sample of Mg-montmorillonite was prepared from commercial montmorillonite, Kunipia F which is a processed natural bentonite from Tsukinuno mine, Yamagata, Japan and obtained from Kunimine Ind.. The nominal composition in wt% and cation exchange capacity (CEC) of Kunipia F are 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; CEC, 119 meq/100g. This montmorillonite was suspended in magnesium nitrate aqueous solution for about 1 day to replace the exchangeable cations in the montmorillonite with magnesium cation by cation exchange reaction. The Mg-montmorillonite formed was separated from the solution by centrifugation, washed by resuspending in double distilled water, separated again by centrifugation and dried in a vacuum desiccator. MgF_2(>97%), $MgCl_2 \cdot 6H_2O$(>98%), $MgBr_2 \cdot 6H_2O$(99.9%) and MgO(>97%) were commercial materials and used without further purification. All samples were fixed onto stainless steel sample holders using double sided sticky tapes for electron spectroscopic measurement. X-Ray (Al Kα) excited photoelectron and Auger electron spectra were taken on a Vacuum Generator ESCA LAB 5 instrument. The measured photoelectron binding energies and Auger electron kinetic energies were determined relative to C 1s binding energy (284.4 eV) of surface carbon contaminant which was calibrated against Au $4f_{7/2}$ binding energy (83.8 eV) of a vacuum evaporated gold film.

Figure 1 shows the measured Mg 1s and Auger($KL_{23}L_{23}$) spectra of Mg-montmorillonite. They are broad in comparison with those of montmorillonite which does not contain exchangeable magnesium cation but non-exchangeable one. In Mg-montmorillonite, the exchangeable and non-exchangeable magnesium have different location, i.e., the former exists between the aluminosilicate layers of montmorillonite while the latter is one of constituent elements of the aluminosilicate layers of montmorillonite. Therefore the broad character of the spectra of Mg-montmorillonite can be ascribed to the existence of two kinds of magnesium cations in the clay. The observed Mg 1s and Mg Auger($KL_{23}L_{23}$) spectra were deconvoluted into two components as follows. The Mg Auger($KL_{23}L_{23}$) electron kinetic energy for non-exchangeable magnesium and its intensity relative to Al 2p line due to skeletal aluminium were determined on Na-montmorillonite which contains sodium as an exchangeable cation and was prepared by the procedure similar to that in Mg-montmorillonite preparation. Then this component was subtracted from the Mg Auger($KL_{23}L_{23}$) spectrum of Mg-montmorillonite and the residual spectrum was assigned to the exchangeable magnesium. The result of the deconvolution is shown in Fig. 1. The relative intensities of two

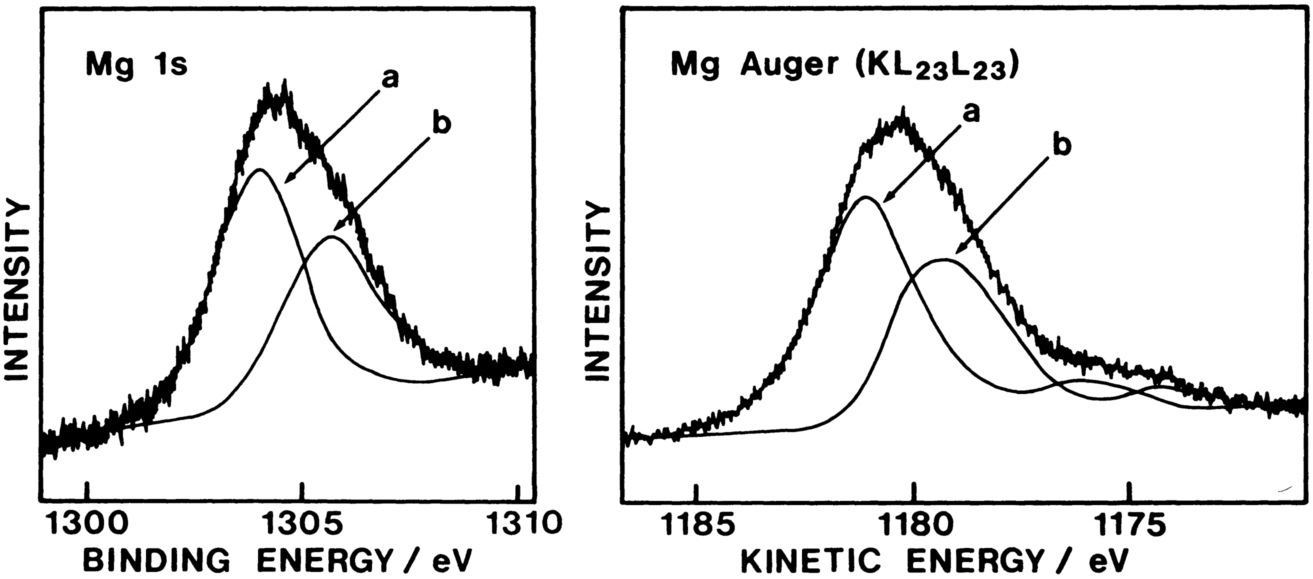

Fig. 1. Mg 1s and Mg Auger($KL_{23}L_{23}$) spectra of Mg-montmorillonite.
(a) non-exchangeable magnesium and (b) exchangeable magnesium.

components were consistent with the relative abundance of the non-exchangeable skeletal magnesium and exchangeable cation as determined with Na-montmorillonite. The Mg 1s line was also deconvoluted similarly but with readjustment of the intensity factor in order to make the relative intensity of the deconvoluted spectra consistent with the Mg Auger($KL_{23}L_{23}$) result, as Mg 1s intensity relative to Al 2p line varied from sample to sample. This variation was attributed to the shallow escaping depth of Mg 1s photoelectron with small kinetic energy (about 180 eV) and thus its intensity is rather sensitive to the amount of surface carbon contaminant. The deconvoluted Mg 1s spectra are also included in Fig. 1.

On the basis of the relative sensitivity of Al 2p, Si 2s and Mg Auger($KL_{23}L_{23}$) lines which were experimentally determined by the photoelectron and Auger electron peak intensities of some compounds containing Al, Si or Mg, the relative atomic abundances of Al, Si and Mg in Mg-montmorillonite were calculated from Al 2p, Si 2s and Mg Auger($KL_{23}L_{23}$) peak intensities of Mg-montmorillonite. The calculated atomic abundances relative to Al (atom ratios) are Al, 1.0; Si, 2.2; Mg (non-exchangeable), 0.23; Mg (exchangeable), 0.14. These values agree with the relative atomic abundances calculated from the nominal composition of Kunipia F within 20%.

The deconvoluted Mg 1s photoelectron binding energy and Mg Auger($KL_{23}L_{23}$) electron kinetic energy for the exchangeable magnesium were 1305.7 eV and 1179.3 eV respectively. On the other hand, the Mg 1s photoelectron binding energy and Mg Auger($KL_{23}L_{23}$) electron kinetic energy for the non-exchangeable magnesium were 1304.0 eV and 1181.1 eV respectively. Thus it became apparent that there were differences more than 1 eV in both electron energies between the exchangeable and

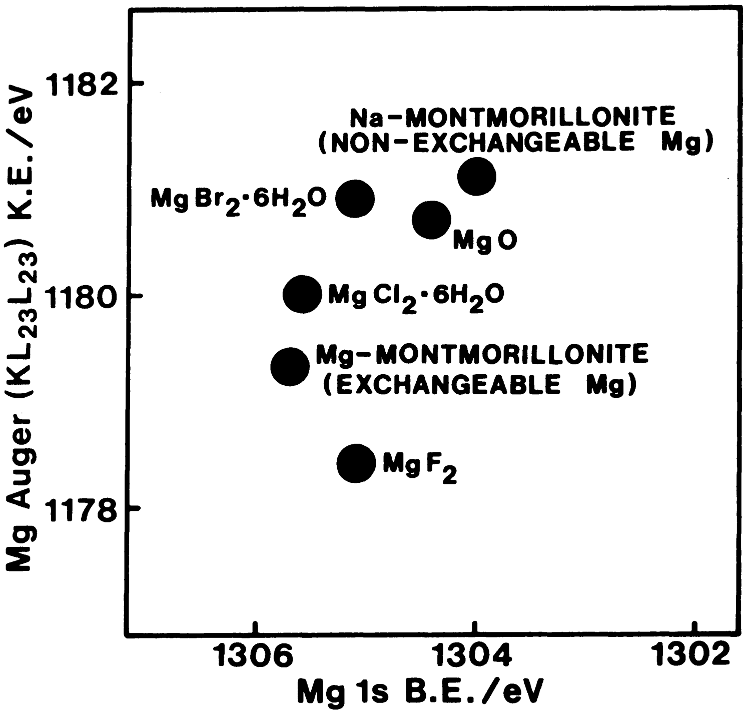

Fig. 2. Chemical state plot for magnesium.

non-exchangeable magnesium in montmorillonite.

A comparison of the chemical state of the exchangeable and non-exchangeable magnesium in montmorillonite with that of magnesium in magnesium halides and oxide is shown in Fig. 2. Such two dimensional chemical state plot of photoelectron binding energy and Auger electron kinetic energy was proposed by Wagner and his coworkers.10) Measured starting materials of magnesium chloride and bromide were hexahydrates. However the observed O 1s peak-heights for the compounds were lower than those expected for hexahydrates, so it was considered that the crystal waters of these samples were partly lost in ultrahigh vacuum of the instrument.

It can be seen from Fig. 2, that the chemical state plot of the exchangeable magnesium in montmorillonite falls between magnesium fluoride and chloride. Thus the chemical state of the exchangeable magnesium which exists between the aluminosilicate layers of montmorillonite is similar to that of magnesium in typical ionic compounds such as magnesium fluoride. On the other hand, the chemical state of the non-exchangeable magnesium atom which is surrounded by six oxygen atoms in the aluminosilicate layers of montmorillonite is close to that of magnesium atom in magnesium oxide.

The same conclusion that the exchangeable cations in montmorillonite have photoelectron binding energies and Auger electron kinetic energies close to the corresponding fluoride or chloride but not to oxide was obtained with Na- and Cd-montmorillonite, although for the former example, the situation was less clear. The above examples clearly demonstrate the power of X-ray photoelectron and Auger electron spectroscopy in specifying chemical state of the exchangeable cations in clay minerals.

References

1) R. E. Grim, "Clay Mineralogy," 2nd ed., McGraw-Hill, New York (1968).
2) J. M. Adams, S. Evans, P. I. Reid, J. M. Thomas, and M. J. Walters, Anal. Chem., 49, 2001 (1977).
3) J. M. Adams and S. Evans, Clays Clay Miner., 27, 248 (1979).
4) M. H. Koppelman and J. G. Dillard, ACS Symp. Ser., 18, 186 (1975).
5) M. H. Koppelman, A. B. Emerson, and J. G. Dillard, Clays Clay Miner., 28, 119 (1980).
6) M. H. Koppelman and J. G. Dillard, Clays Clay Miner., 28, 211 (1980).
7) M. H. Koppelman and J. G. Dillard, J. Colloid Interface Sci., 66, 345 (1978).
8) J. W. Stucki, C. B. Roth, and W. E. Baitinger, Clays Clay Miner., 24, 289 (1976).
9) M. E. Counts, J. S. C. Jen, and J. P. Wightman, J. Phys. Chem., 77, 1924 (1973).
10) C. D. Wagner, L. H. Gale, and R. H. Raymond, Anal. Chem., 51, 466 (1979).

(Received May 14, 1981)