ANALYSIS OF IRON-BEARING CLAY MINERALS BY ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)*

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Abstract—Nontronite and biotite were analyzed by Electron Spectroscopy for Chemical Analysis (ESCA). Both minerals yielded ESCA spectra with well-defined peaks and the elements identified by the ESCA spectra were in good agreement with the molecular formulas. High resolution scans were made of the iron ($2p_{3/2}$) and oxygen ($1s$) electron binding energies for oxidized and reduced forms of nontronite and biotite. Binding energies for Fe^{3+} were observed at 711.8 eV in dithionite-reduced nontronite and in oxidized biotite. Peaks for Fe^{2+} occurred at 710.0 eV for unaltered biotite, at 709 eV for oxidized biotite and at 708.6 eV for hydrazine-reduced and dithionite-reduced nontronite. The oxygen ($1s$) peak for unaltered nontronite was skewed to the high energy side of the 530.6 eV maximum, but became more symmetrical as the Fe^{2+} content increased.

INTRODUCTION

Electron Spectroscopy for Chemical Analysis (ESCA) is a powerful analytical technique that allows the study of *surface* phenomena as well as direct measurement of the energy levels of electrons within elements and compounds. The basic operating principles of an ESCA spectrometer involve irradiation of a sample with X-rays from a particular anode material causing photoelectrons to be ejected. Many of these electrons come from the outermost 5–50 Å of the sample surface and will have suffered no collisions with lattice atoms. The kinetic energy of these photoelectrons is measured and their number plotted as a function of their energy. The resulting energy spectrum has sharp peaks corresponding to the electronic energy states of the sample. The energy relationship involved in this process is given by the equation

$$E_b = hv - E_k - e\phi, \qquad (1)$$

where E_b is the electron binding energy, hv is the X-ray photon energy, E_k is the electron kinetic energy, e is the electronic charge, and ϕ is the spectrometer work function. Information that may be obtained by examining the binding energy of the photoelectrons includes qualitative elemental analysis and the oxidation state and coordination environment of an element.

ESCA has been used to study numerous types of solid systems (Hercules, 1972; Hercules and Carver,

1974; Jolly, 1974; Baitinger and Amy, 1974), but only recently has it been applied to clays, minerals and soils. Core binding energies for Fe, Mg, Al, Si, and O electrons in ten well-characterized silicate minerals (none of them clays) were determined by Adams *et al.* (1972). ESCA spectra of lunar samples reported by Huntress and Wilson (1972) revealed chemical shifts of the Fe ($2p$) line which are characteristic of Fe^{2+}. A difference in core binding energies of bridging and non-bridging oxygen atoms in the silicate tetrahedra of olivines and pyroxenes has been observed (Yin *et al.*, 1971). Anderson and Swartz (1974) reported identical Al ($2p$) binding energies for both tetrahedral and octahedral aluminum in aluminosilicates. Counts *et al.* (1973) determined the binding energies of Pb adsorbed onto a montmorillonite surface. Quantitative determination of Pb in soils is reported by Wyatt *et al.* (1975).

The mechanisms by which oxidation and reduction reactions proceed in nontronite and biotite could be elucidated if changes in oxidation states and elecenvironments of octahedral iron could be monitored. The purpose of this study is to determine the utility of ESCA as an analytical technique to detect changes in electronic structure of lattice atoms as a result of chemical action to change the oxidation state of structural iron.

MATERIALS AND METHODS

Samples studied were nontronite (Garfield, WA, supplied by Ward's Natural Science Establishment), a 2:1, dioctahedral smectite clay mineral with Fe^{3+} as the predominant octahedral cation; and biotite (Bancroft, Ont., supplied by Ward's Natural Science Establishment), a trioctahedral mica which contains Fe^{2+} and Mg^{2+} as the principal octahedral cations. The molecular formulas were determined from ele-

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Table 1. Compositional formulas for nontronite (Garfield, WA) and biotite (Bancroft, Ont.)

Nontronite
$M_{1.09}^{+}(Si_{7.09}Al_{0.91})(Fe_{3.54}^{3+}Fe_{0.27}^{2+}Mg_{0.09}Al_{0.16})O_{20}(OH)_4$
Biotite
$K_{2.04}(Si_{6.38}Al_{1.62})(Fe_{0.54}^{3+}Fe_{1.86}^{2+}Mg_{3.08})O_{20}(OH)_4$

mental analyses for K, Al, Si, Mg, and Fe (Table 1). Samples for Fe, Mg, and K determination were digested using a modified procedure to that described by Shapiro and Brannock (1956) in which 0.5 M $HClO_4$ was substituted for concentrated H_2SO_4. Ferric and ferrous iron were determined colorimetrically at 510 nm by the method of Roth *et al.* (1969). A Varian Model AA–6D atomic absorption spectrometer was used to determine K by atomic emission at 766.5 nm in an air–acetylene flame, and Mg by atomic absorption at 285.2 nm in a nitrous oxide–acetylene flame. Aluminum and Si were determined by the aluminon and molybdosilicic acid methods, (Jackson, 1958) respectively, on solutions obtained by NaOH fusion (Shapiro and Brannock, 1956).

ESCA spectra were obtained using a Hewlett–Packard 5950A ESCA spectrometer equipped with an electron gun to flood non-conducting surfaces with zero energy electrons in order to avoid charge build-up at the surface of the sample. A dry box and prepump chamber were also used to maintain inert atmospheres and to remove excess water from sample surfaces prior to insertion into the high vacuum chamber. The ESCA spectrometer was calibrated against a gold standard at 83.9 eV (Au $4f_{7/2}$ electronic level), and resolution obtained was better than 0.5 eV.

Unaltered nontronite was Mg^{2+}-saturated by washing an aqueous suspension three times with 0.2 N $MgCl_2$ followed by washing with water until free of excess salt. The resulting suspension was allowed to dry onto a gold blank which served as the mounting material for the ESCA spectrometer. Two differ-

ent methods were employed to prepare samples of reduced nontronite: (1) a self-supporting film of Na^{+}-saturated nontronite was exposed to hydrazine vapor in a vacuum chamber, then the film was supported between a solid gold blank and a flanged, slotted cover which allowed access to the clay surface by the X-ray beam; and (2) a Na^{+}-saturated suspension was reduced with sodium dithionite salt, then Mg^{2+} saturated, washed free of excess salt in an oxygen-free environment, and dried onto a gold blank.

The original large sheets of biotite were ground in water with a Sorvall Omni mixer. The 2–5 μm particle size was fractionated by gravity sedimentation.

Unaltered biotite was prepared by drying a portion of the 2–5 μm stock suspension directly onto a gold blank. The unaltered biotite was oxidized by heating to 80°C for six months in saturated bromine water (Gilkes *et al.*, 1972). The excess bromine was removed by warming, then the oxidized biotite was washed with water and dried onto a gold blank.

RESULTS AND DISCUSSION

Nontronite and biotite yield ESCA spectra with well-defined peaks, as shown in Figure 1. The elements and electronic energy levels are assigned to each peak according to binding energies published by Siegbahn *et al.* (1967) and the observed elements correspond well with the respective molecular formulas from Table 1. No attempt was made to obtain a complete quantitative determination of atomic ratios from the ESCA spectra, although semi-quantitative analysis is possible if the appropriate precautions are taken (Swingle, 1975; Wyatt *et al.*, 1975).

Iron ($2p_{3/2}$) electron binding energies were obtained at high resolution for samples of unaltered, hydrazine-reduced, and dithionite-reduced nontronite (Figure 2). The binding energy at 711.8 eV in spectrum (a) for unaltered nontronite is consistent with values for Fe^{3+} in hematite and $K_3Fe(CN)_6$ reported by Kishi
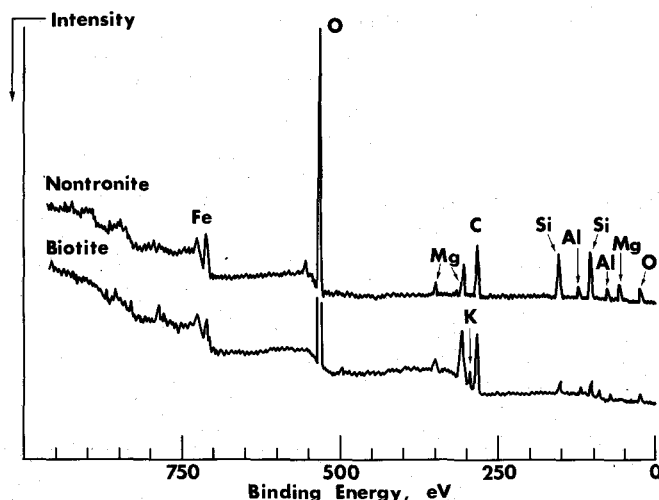

Figure 1. ESCA spectra depicting electron binding energies from 0 to 1000 eV for nontronite and biotite.
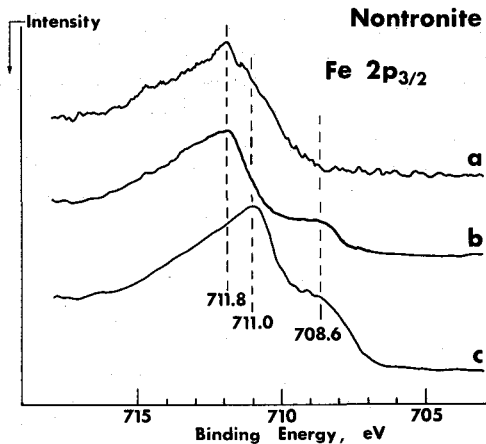
Figure 2. Iron ($2p_{3/2}$) electron binding energies for nontronite (a) unaltered, (b) hydrazine-reduced, and (c) dithionite-reduced.

and Ikeda (1973). It should be pointed out, however, that such comparisons may be somewhat inconclusive since binding energies are sensitive to the particular matrix in which the cation is located. A more convincing comparison is with the molecular formula in Table 1, which indicates that Fe^{3+} is the dominant iron species and only a small amount of Fe^{2+} is present. Since binding energies for Fe^{2+} are characteristically 2–3 eV lower than for Fe^{3+} and only one peak is observed, the peak at 711.8 eV is assigned to Fe^{3+} and the small Fe^{2+} peak is assumed to be masked by the background of the larger Fe^{3+} peak.

Figure 2 also shows that exposure of the nontronite clay to hydrazine vapor has no apparent effect upon the position of the original Fe^{3+} peak, as seen in spectrum (b), but a new peak is observed at 708.6 eV. Spectrum (c) reveals that dithionite-reduced nontronite also contains a peak at 708.6 eV, except with greater intensity than in spectrum (b). Ferric to ferrous ratios were obtained colorimetrically and compared with the relative intensities of the 711.8 eV and 708.6 eV peaks for each sample (Table 2). Close relationship of relative intensities with Fe^{3+}/Fe^{2+} ratios clearly demonstrated that both Fe^{3+} and Fe^{2+} can be determined semi-quantitatively by ESCA in the same mineral. An earlier report indicated that this may be difficult in silicate minerals (Adams et al., 1972).

Many solid systems can exhibit different composition at the surface than in the bulk due to oxidation, layering, or other surface forces. However, the results

Table 2. Ferric–ferrous ratios and relative intensities of iron ($2p_{3/2}$) binding energies for Fe^{3+} and Fe^{2+} in oxidized and reduced nontronites

Mineral Treatment	Fe^{3+}/Fe^{2+}	I_{3+}/I_{2+}
Nontronite Unaltered	13.1	*
Nontronite Hydrazine-Reduced	6.4	6
Nontronite Dithionite-Reduced	2.2	2.5

* Only one peak was observed.

in Table 2 indicate that the surface analysis of clay minerals is indeed representative of the overall composition as determined on the bulk material. This is to be expected since clay mineral layers should be of similar composition whether at the surface of an aggregate or in the center.

A unique feature of the dithionite-reduced nontronite (Figure 2c) is that the position of the Fe^{3+} peak is shifted to a lower binding energy, from 711.8 eV to 711.0 eV. One explanation for the shift is a change in the coordination environment surrounding the Fe^{3+} ion. This may be due to either Fe^{2+} in the structure or to a change in the coordination number of Fe^{3+} as a result of the reduction reaction. Since the presence of Fe^{2+} in spectrum (b) has no influence on the Fe^{3+} peak position, any role of Fe^{2+} in shifting the binding energy of the Fe^{3+} electrons is discounted. On the other hand, if the coordination number of Fe^{3+} is altered within the structure, one would expect a similar change for Fe^{2+}, and a subsequent shift in the peak at 708.6 eV. The actual explanation remains to be clarified. Since the presence of Fe^{2+} as a result of hydrazine treatment has no influence on the Fe^{3+} peak position, the evidence suggests that the reduction process in the clay mineral nontronite follows either two different reactions depending on the reducing agent, or a two stage reaction depending on the degree of reduction.

The peaks for Fe ($2p_{3/2}$) electrons in biotite (Figure 3) are rather broad and somewhat less defined than the nontronite peaks. The binding energy of unaltered biotite is positioned at 710 eV (Figure 3a) and separated into peaks at 711.0 and 709.0 eV upon oxidation (Figure 3b). The binding energies at 711.0 and 709.0 eV are assigned to Fe^{3+} and Fe^{2+}, respectively. Very little is known about the location of iron in biotite following oxidation, although some have suggested that Fe^{3+} moves into the interlayer region during oxidation (Farmer et al., 1971). ESCA evidence dealing with silicate minerals is insufficient to make a judgement as to the position of iron in the lattice. The shift of the Fe^{2+} peak to lower binding energy does indicate that a change in coordination environment has occurred upon oxidation. Whether this is due to

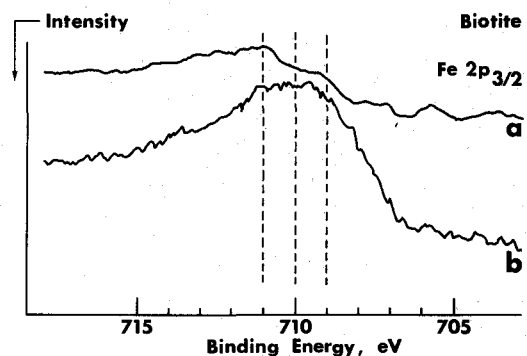
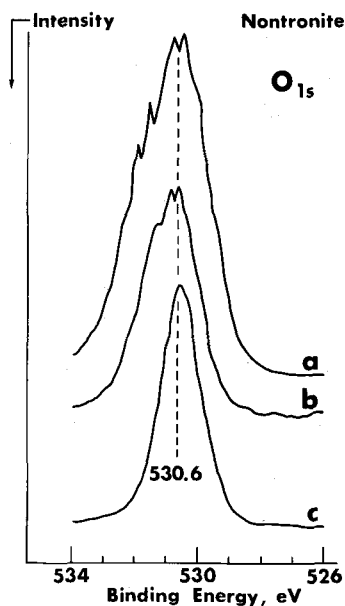Figure 3. Iron ($2p_{3/2}$) electron binding energies for biotite (a) unaltered and (b) oxidized.

Figure 4. Oxygen (1s) electron binding energies for nontronite (a) unaltered, (b) hydrazine-reduced, and (c) dithionite-reduced.

the presence of Fe^{3+} or to some other alteration in the crystal structure is unclear.

Looking back to the spectra of nontronite, the oxygen (1s) binding energies are analyzed in more detail. The spectra depicting these binding energies for unaltered and reduced nontronites are found in Figure 4. Some interesting changes in the peak shapes and positions are observed as the amount of Fe^{2+} increases. Spectrum (a) is for the unaltered specimen and shows the peak to be broadened slightly to the high energy side, which suggests the presence of more than one component to the peak, or oxygen in more than one environment. When the clay is treated with hydrazine vapor (Figure 4b), the peak becomes more symmetrical with the exception of a small shoulder on the high energy side. The position of the primary maximum at 530.6 eV in the hydrazine-reduced sample corresponds to that in the unaltered case. Further reduction of structural Fe^{3+} using sodium dithionite yields a single, symmetrical peak centered at 530.6 eV with no broadening on the high energy side (Figure 4c). These changes indicate that the electronic environments of oxygen atoms in reduced nontronite become progressively more similar as the Fe^{2+} content increases. A possible explanation for this observation is that the reduction process results in a relaxation of the stress forces between the tetrahedral and octahedral layers. Future work may provide additional information from which a more definitive conclusion can be reached.

In summary, the results of this study show that ESCA is a useful analytical technique for qualitative elemental analysis of clay minerals. Semi-quantitative determination of Fe^{3+} and Fe^{2+} is possible in the same mineral, and shifts in binding energies of Fe^{3+}

in nontronite and Fe^{2+} in biotite with oxidation and reduction suggest that changes in coordination environment are also detected. The O (1s) line was examined for nontronite and observed to be sensitive to the oxidation state of the iron.

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