

ION BOMBARDMENT AND ADSORPTION STUDIES
ON ILMENITE (FeTiO₃) BY
X-RAY PHOTOELECTRON SPECTROSCOPY

by

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ABSTRACT

The effects of 5 KeV argon and oxygen ion bombardment on FeTiO₃ (ilmenite) at low temperatures have been studied using X-ray photoelectron spectroscopy (XPS). Also, using this same technique, the adsorption of O₂, NO, N₂O, and CO at 300 K and the adsorption of O₂ and D₂O at 150 K have been studied.

Argon and oxygen ion bombardment of ilmenite have confirmed earlier studies on metal oxides that argon ions generally reduce the anion species while oxygen ions generally oxidize the anion species. The two iron states involved were Fe⁺² and Fe⁰. The reduction of Ti⁺⁴ was not verified although a significant shift in the Ti(2p_{1,3}) binding energies toward the metallic state was observed after oxygen ion bombardment at low temperatures.

At temperatures above 150 K, O₂ adsorbs dissociatively on ilmenite while D₂O adsorbs molecularly below 170 K. Above 300 K NO, N₂O, and CO do not appear to adsorb dissociatively. Low temperature adsorption of D₂O was found to be inhibited by predosing the ilmenite with O₂.

Center Research Advisor: Dave S. McKay

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been used extensively to study solar-wind reduction mechanisms on lunar samples¹⁻⁶ and more recently, to study ion-bombardment damaged metal surfaces.⁷⁻⁹ The earlier experiments showed that under ion bombardment, the surface Fe^{+2} in the iron rich lunar samples could be reduced to metallic Fe or Fe^0 . In general, studies have shown that under ion bombardment the reduction to the metallic state is (1) accompanied by the loss of the anion species, e.g., O^- in the case of FeO , and (2) is nearly independent of the incident ion mass.^{4,7} In contrast to the reduction of the cation species under argon ion bombardment, the dominant process during oxygen ion bombardment has been found to be cation oxidation.⁸

Recently this laboratory has been using the technique of XPS to study the adsorption properties of gases on transition metal surfaces.¹⁰⁻¹¹ In the present work we have begun a sequence of experiments designed to investigate the adsorption of small molecules on FeTeO_3 (ilmenite) as a function of ion-bombardment parameters and temperature. Specifically we have considered thus far the adsorption of D_2O , O_2 , NO , N_2O , and CO on polycrystalline terrestrial samples of ilmenite under varying conditions of radiation damage.

EXPERIMENTAL

The present experiments were performed in an ultra-high vacuum chamber having a base pressure on the order of 10^{-9} torr which was equipped with a quadrupole mass spectrometer, a 0-5 keV ion gun, an electron gun for Auger spectroscopy, a magnesium X-ray source (1253.6 eV), and a high-resolution double-pass cylindrical mirror electron energy analyzer.

The XPS data were obtained by coupling the energy analyzer to a 1024 channel analyzer and microcomputer. The ilmenite sample was cut from a larger rock sample with a slow speed diamond saw. The unpolished sample was attached to tantalum foil by bending tabs over the edges of the ilmenite. The foil was then spotwelded to tantalum posts which were in turn attached to a liquid nitrogen-cooled cold stage. The sample could be heated well above 1000 K by passing a current through the tantalum foil. The temperature was monitored by a thermocouple spotwelded to the tantalum foil. The ilmenite was ion bombarded in situ by raising the chamber background pressure of the desired gas to around 10^{-5} torr with the ion gun in the rastering mode. All adsorbates except D_2O , were admitted to the sample chamber through a leak valve after being passed through an appropriate cold trap in order to remove any water.

ION BOMBARDMENT RESULTS AND DISCUSSION

In order to characterize the ilmenite sample and in order to establish a baseline for the present studies, the effects of 5 KeV argon, hydrogen, and oxygen ion bombardment on the sample at 300 K and 150 K were considered. Typical XPS spectra in the $Fe(2p_{1,3})$ region taken after oxygen and argon ion bombardment at 150 K are shown in figure 1. Also seen is the $O(KVV)$ Auger peak near 742 eV. Ion bombardment was found to have little effect on the position of the $O(KVV)$ or $O(1s)$, not shown, binding energies but does alter the peak intensities (peak areas). The $Fe(2p_{1,3})$ peaks were found to be very sensitive to ion bombardment. Argon and hydrogen ions reduced the Fe^{+2} to Fe^0 with approximately the same efficiency. The Fe binding energies from computer deconvolved spectra are given in table 1. The $Fe^0(2p_{1,3})$ states are clearly seen in figure 1 near 710 eV and 722 eV respectively.

TABLE 1. Fe Binding Energies (B.E.) in Electron Volts.

| State | Fe ⁰ | | Fe ⁺² | |
|-------|-----------------|-----------------|------------------|-----------------|
| | 2p ₁ | 2p ₃ | 2p ₁ | 2p ₃ |
| B.E. | 711.7 | 707.8 | 724.3 | 720.7 |

As was expected, very little difference was found between the spectra after argon and hydrogen ion bombardment. Both ions were found to reduce Fe⁺² to Fe⁰ but neither ion would produce any reduction of the Ti⁺⁴ state of ilmenite. Kim, *et. al.*,¹² using XPS, found that Ti⁺³ in Ti₂O₃ was not reduced during argon ion bombardment. In contrast to argon and hydrogen ion bombardment, oxygen ion bombardment would not reduce Fe⁺² but would oxidize any Fe⁰ present near the surface. The O(KVV) intensity during oxygen ion bombardment increased as expected. Figure 2 shows the XPS spectra in the Ti(2p_{1,3}) region for oxygen ion-bombarded FeTiO₃ at 150 K and 300 K. Somewhat surprising was the nearly 1 eV shift to lower binding energies at 150 K. This shift was observed only after oxygen ion bombardment at low temperatures. Work is continuing to determine the origin of this shift and the states that are involved. Oxygen ion bombardment did produce much sharper spectra at 150 K than at 300 K. The spectra after argon ion bombardment gave no indication of any temperature dependence.

ADSORPTION RESULTS AND DISCUSSION

The adsorption of O₂, NO, N₂O, and CO on ilmenite between 300 K and 800 K, and D₂O and O₂ at 150 K has been studied. One difficulty in studying these molecules on ilmenite is the presence of a strong O(1s) XPS signal from the FeO and TiO₂ complexes. Additional O(1s)

contributions are thus hard to observe unless the adsorbate contributions are either very large or several eV's removed from the substrate O(1s) binding energy.

The present study showed that the oxygen-containing molecules NO, N₂O, and CO do not adsorb dissociatively on ilmenite between 300 K and 800 K. This was indicated by the lack of oxidation of Fe⁰ on an argon ion-bombarded surface. Oxygen was found to adsorb dissociatively above 150 K. The oxygen would oxidize the Fe⁰ but not as well as oxygen ions during ion bombardment. This suggests that the radiation damage extends many atomic layers beneath the surface whereas the oxidation that was observed occurs only at the top few atomic layers. Future studies using angle-resolved XPS would be useful in examining this problem.

Figure 3 shows XPS spectra taken in the O(1s) region for argon ion-bombarded ilmenite followed by exposures of 50 L and 250 L (1 L = 1 Langmuir = 10⁻⁶ torr-sec) D₂O at 150 K. Also shown is the spectrum for 200 L D₂O adsorbed on ilmenite predosed with 10 L O₂. The D₂O adsorbed molecularly at 150 K with an O(1s) binding energy of 534.4 eV as opposed to 530.8 eV for the O(1s) of FeTiO₃. Mass spectrometer data yielded a D₂O desorption temperature of 170 K. At 215 K, XPS spectra verified the absence of D₂O from the O(1s) region and also verified the absence of any Fe⁰ oxidation which would have occurred if the D₂O had dissociated upon warming. Curve (d) in figure 3 indicates that the presence of preadsorbed oxygen atoms tends to inhibit the adsorption of D₂O. Similar results were found after oxygen ion bombardment.

CONCLUSIONS

Hydrogen and argon ion bombardment reduced the surface Fe^{+2} to metallic Fe of FeTiO_3 with approximately the same efficiency. Neither ion reduced Ti^{+4} . Oxygen ion bombardment oxidized a previously reduced surface much more efficiently at 150 K than at 300 K. At 150 K, oxygen ion bombardment produced 1 eV shift in the $\text{Ti}(2p_{1,3})$ spectra that was not observed after argon and oxygen ion bombardment.

At 300 K NO , N_2O , and CO would not adsorb dissociatively on an argon ion-bombarded surface of ilmenite. Oxygen was found to adsorb dissociatively above 150 K while D_2O was found to adsorb molecularly below 170 K. Finally, an argon ion-bombarded surface having a preadsorbed oxygen layer or an oxygen ion-bombarded surface inhibits the formation of D_2O ice layers.

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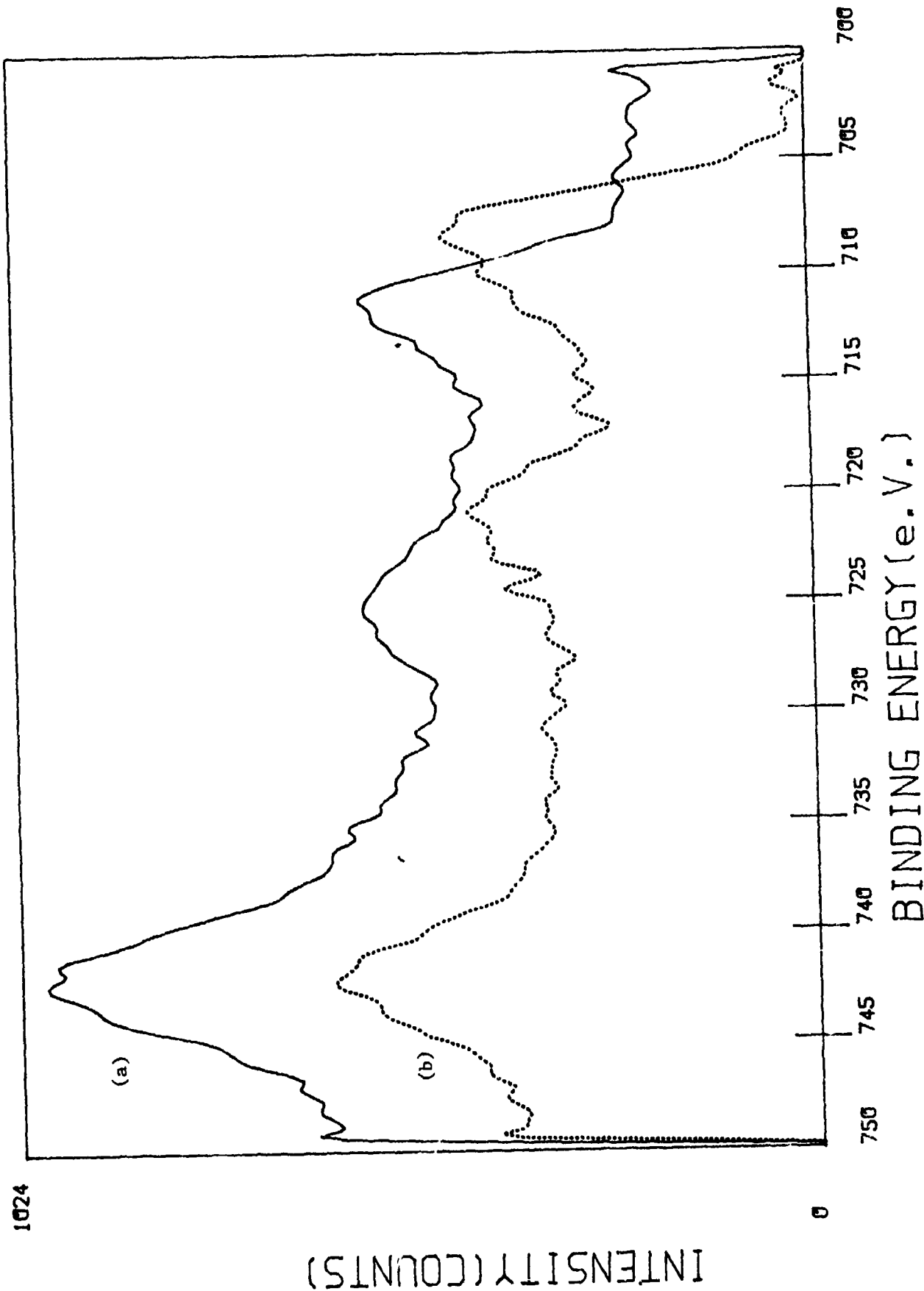


Figure 1. XPS Fe(2p) region at 150 k for (a) oxygen and (b) argon ion-bombarded ilmenite. The curves have been shifted vertically for clarity.

1024

INTENSITY (COUNTS)

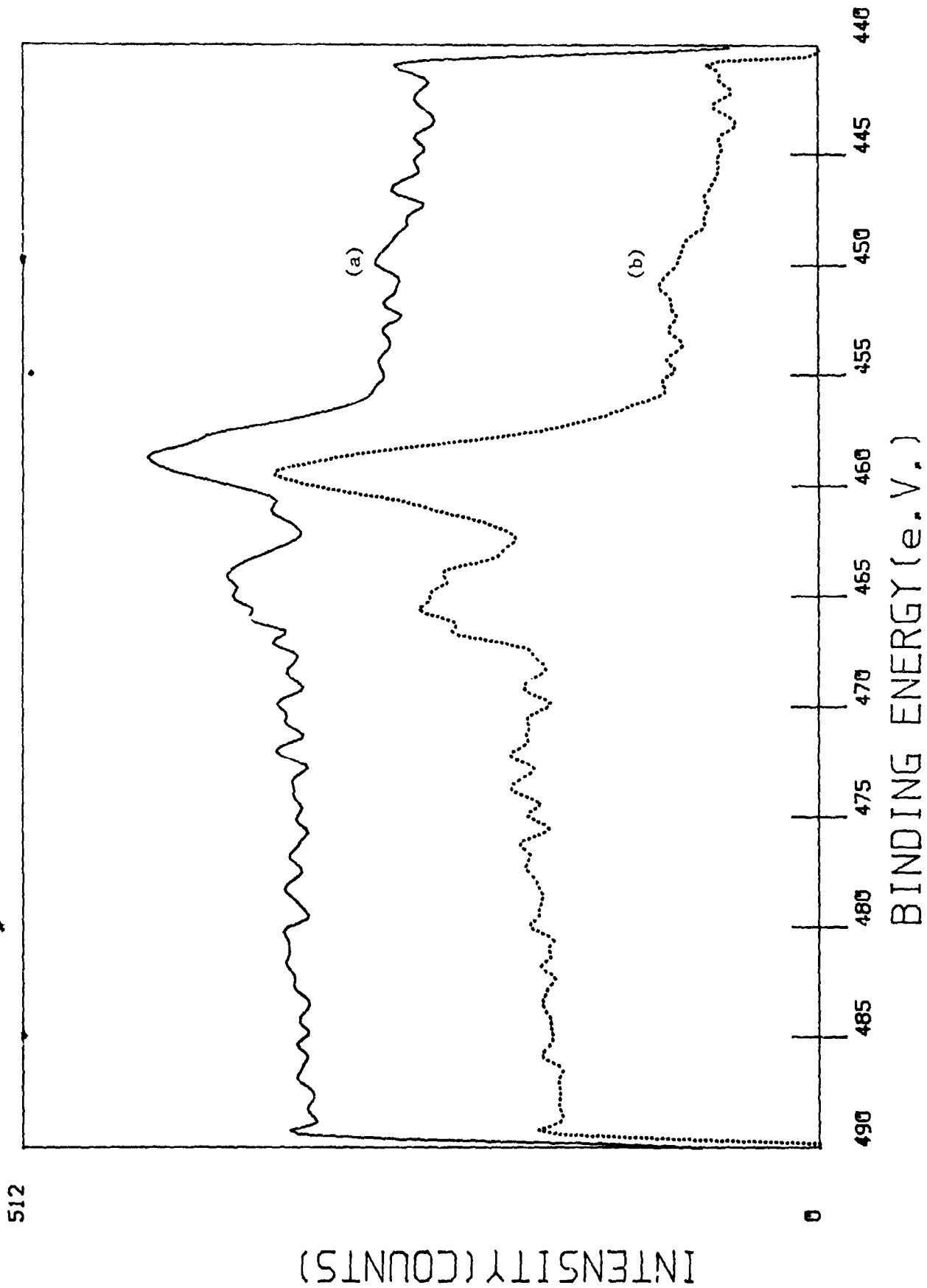


Figure 2. XPS Ti(2p) region for an oxygen ion-bombarded ilmenite surface at (a) 150 K and (b) 300 K. The curves have been shifted vertically for clarity.

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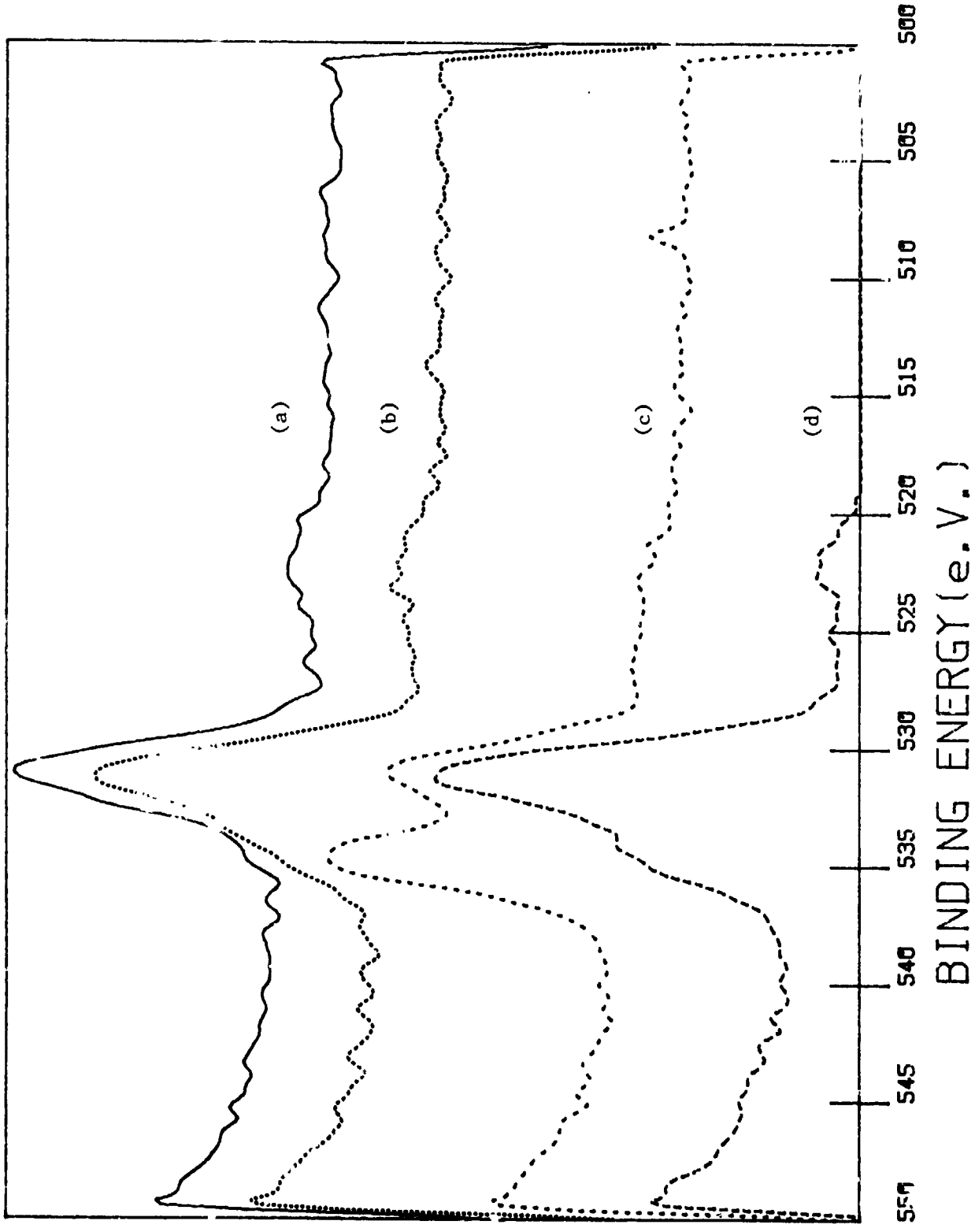


Figure 3. XPS O(1s) region at 150 K for an (a) argon ion-bombarded ilmenite surface and for the same surface exposed to (b) 50 L D₂O; (c) 250 L D₂O; and (d) 10 L O₂ + 200 L D₂O. The curves have been shifted vertically for clarity.