MICROPROBE INVESTIGATIONS OF THE OXIDATION STATE OF Fe AND Ti IN ILMENITE IN APOLLO 11, APOLLO 12, AND APOLLO 14 CRYSTALLINE ROCKS, M. Pavicevic, P. Ramdohr, A. El Goresy, Max-Planck-Institut fur Kernphysik 69 Heidelberg, Germany

The oxidation states of iron and titanium in the Apollo samples has been a subject of concern in several lunar investigations. The presence of metallic iron in the Apollo 11 basalts and Fe Ni alloys in the Apollo 12 and 14 crystalline rocks suggests that iron is present in the divalent state in the Fe-Ti oxide minerals. However, Haggerty and Meyer (1) suggested the presence of Fe$^{3+}$ in some members of the chromite-ulvospinel series present in the Apollo 12 basaltic rocks. The principal aim of the present investigation was to develop a quantitative technique for the direct experimental determination of the oxidation state of iron and titanium in simple binary systems and to apply this technique to determine the oxidation states of these elements in opaque minerals present in the lunar samples.

In an attempt to apply the electron microprobe for semiquantitative determination of the oxidation state of Fe and Mn, Albee and Chodos (2) performed several measurements of the L spectra of these elements present in oxides and silicates at 15 kV. O'Nions and Smith (3) recently presented new results on the L$^\alpha$ and L$^\beta$ spectra of several iron and titanium oxides over a wide range of excitation potentials and have defined several of the experimental and theoretical difficulties involved in this technique.

Our investigations of the L$^\alpha$ and L$^\beta$ spectra were conducted using pure synthetic standards in the solid solution series ilmenite-hematite, ulvospinel-magnetite, and ferropseudobrookite-pseudobrookite. The measurements were expanded to lunar ilmenites and ulvospinels. Our probe investigations of the Fe L$^\alpha$ and L$^\beta$ spectra indicate that any change in the oxidation state of iron among members of a solid solution series influence the spectra in the following manner:

1) As the total amount of Fe increases, the peak position shifts continuously, but nonlinearly toward shorter wavelengths. 2) The L$^\beta$/L$^\alpha$ peak intensity ratio decreases almost linearly with the increase in the oxidation state. 3) There is an

Fig. 1
apparent wave length shift of the spectra to higher wave lengths upon increase of the excitation potential.

The nonlinearity of the wave length shift (point 1) with change in the oxidation state of iron disqualifies this phenomenon from further quantitative evaluation. However, measurements of the LB/La intensity ratios (point 2) of several members of a solid solution series over a wide range of excitation potentials allows the construction of calibration curves for the determination of the oxidation states of Fe in minerals belonging to the same series. Figures 1 and 2 show such calibration curves for compounds along the FeTiO$_3$-Fe$_2$O$_3$ and Fe$_2$TiO$_4$-FeO joins, respectively. These calibration curves, however, can only be used for members of the binary series - i.e. the presence of high concentrations of impurities such as MgO lowers the LB/La intensity ratio and leads to meaningless results. Fig. 1 shows the variation of the LB/La ratio for Ilm$_{100}$-Hem$_0$, Ilm$_{96}$ - Hem$_4$, and Ilm$_{100}$ - Hem$_0$ and Fig. 2 shows these peak ratios for Usp$_{100}$ - Mt$_4$, Usp$_{80}$ - Mt$_{20}$, and Usp$_{100}$ - Mt$_{100}$. The distance between the curves in Fig. 2 is a direct function of the amount of the Fe$_2$O$_3$ molecule present. The Fe LB/La ratios for lunar ilmenites together with the values for the standards used, as measured at 10 kV are compiled in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>LB/La ratio</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ilm$_{100}$</td>
<td>0.857 ± 0.004</td>
<td>0.024</td>
</tr>
<tr>
<td>2. Ilm$_{96}$ - Hem$_4$</td>
<td>0.842 ± 0.004</td>
<td>0.024</td>
</tr>
<tr>
<td>3. Hem$_{100}$</td>
<td>0.413 ± 0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>4. 10047</td>
<td>0.867 ± 0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>5. 12063</td>
<td>0.855 ± 0.026</td>
<td>0.026</td>
</tr>
<tr>
<td>6. 14053</td>
<td>0.857 ± 0.030</td>
<td>0.030</td>
</tr>
</tbody>
</table>

The results presented in Table 1 indicate that the iron in the ilmenites studied in Apollo 11 rock 10047, Apollo 12 rock 12063, and Apollo 14 rock 14053 is present as Fe$^2+$. The LB/La intensity ratio of the lunar ilmenites agree within the experimental error with the values for pure synthetic ilmenite Fe$^2+$(Ti$_2$O$_3$)$_2$. Albee and Chodos give a LB/La value of 0.84 obtained at 15 kV for both pure ilmenite and ulvospinel (Fig. 4 in their paper); however, our values for ilmenite and ulvospinel at 15 kV are 0.89 and 0.675, respectively. Our measurements also indicate that the
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\[ \text{LB/La variation curve for ulvospinel is distinctly lower than the ilmenite curve. The calibration curves for members of the } \text{Fe}_2\text{TiO}_4 - \text{Fe}_3\text{O}_4 \text{ join cannot be applied for the majority of the lunar ulvospinels, since they contain appreciable amounts of the chromite molecule. Only one ulvospinel with low concentrations of Cr, Mg, Mn, V, and Al in Apollo 12 microgabbro 12063 was found to have a LB/Lo value close to that of Usp} \text{100 (El Goresy et al., 4).} \]

We have also measured the TiLa and LB spectra in the lunar and synthetic ilmenites, and several terrestrial ilmenites using a focused clinochlore crystal (2d = 28.6 Å). With one exception we have found no indication of wave length shifts or intensity variations, despite the drastic compositional differences in these ilmenites. We believe that a little to no change in the Ti valence state takes place in compounds along the join FeTiO$_2$ - Fe$_2$O$_3$, i.e. titanium is present as Ti$^{4+}$ in these compounds. Therefore measurements of Ti LB/Lo intensity ratios for these compounds results in an average value for the presence of 100% Ti$^{4+}$.

The Ti LB/Lo intensity ratios in ilmenites of the same approximate composition should be identical if, and only if, Ti is solely present as Ti$^{4+}$. However, as shown in Table 2, measurement of several ilmenites in Apollo 14 sample 14053, 2 resulted in LB/Lo ratios which are significantly higher than values obtained from the synthetic standards or Apollo 11 and 12 ilmenites. These higher values can only be interpreted as due to the presence of Ti$^{3+}$. However, it would be difficult in our present state of development to estimate the amount of Ti$^{3+}$ present. This first determination of the presence of Ti$^{3+}$ in lunar minerals is, perhaps, not so surprising when other mineralogical features of rock 14053 are considered. El Goresy et al. (5) have recently described several observations made on this rock which led them to conclude that rock 14053 crystallized under more reducing conditions than any Apollo 11 or 12 rocks. That is, in an environment conducive to the formation and preservation of Ti in the trivalent state.

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**References:**


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