Introduction—During the slow cooling of iron meteorites in their parent asteroidal bodies, a b.c.c. phase α nucleates on the close packed planes of the parent f.c.c. phase γ and grows by the diffusion of Fe-Ni between the two phases (1,2). As temperature decreases significant Fe-Ni gradients develop in the γ phase, within 5 microns of the α/γ boundary. To develop an understanding of the growth process at low temperatures the compositional gradients close to the α/γ interface must be accurately measured. These measurements can be obtained by focused electron beam and X-ray analysis of thin foil iron meteorite samples. This study reports on the use of calibration standards for the measurement of Fe, Ni and P contents in these samples.

Method—Cliff and Lorimer (3) have shown that if the primary X-rays generated in the specimen are neither absorbed nor cause X-ray fluorescence, then the following expression:

\[ \frac{I_1}{I_2} = k_{12} \left( \frac{C_1}{C_2} \right) \]  

(1)

where \( I_1 \) and \( I_2 \) are the measured characteristic X-ray intensities from elements 1 and 2, \( C_1 \) and \( C_2 \) are the weight fractions of the two elements in question and \( k_{12} \) is a factor which can be determined from thin film standards, can be used to carry out quantitative analysis. The thin foil limit or specimen thickness, where X-ray absorption and fluorescence become significant, is to a first approximation greater than the limit where a specimen is sufficiently thin to carry out conventional 100 kV transmission electron microscopy. If this thin foil criterion is satisfied, the intensity ratio \( I_1/I_2 \) is also independent of specimen thickness.

Measurements were carried out using the EMMA-4 instrument fitted with a Kevex energy dispersive detector. All analyses were obtained at 100 kV with a probe current of 2-5 nA and a beam diameter of 100-150 nm. Characteristic Fe, Ni and P X-ray peaks were integrated using a Kevex series 6000 data processor. Continuum background was subtracted either by measuring an average background above and below the peak or by manually selecting one background level close to the peak and subtracting this value from each channel integrated. Two binary Fe-Ni and one ternary Fe-Ni-P calibration standards were used. The bulk compositions are 35.3 ± 0.54 wt% Ni, remainder Fe and 50.2 ± 0.32 wt% Ni, remainder Fe. The Fe-Ni-P standard was heat treated at 750°C for approximately one month in order to produce a two phase alloy containing a b.c.c. α phase of 1.99 ± 0.04 wt% Ni, 0.90 ± 0.04 wt% P and a phosphide (Ph) phase of 2.97 ± 0.10 wt% Ni and 15.6 ± 0.25 wt% P (4).

Results, FeNi Standard—Measurements of \( I_1 = I_{Ni} \) and \( I_2 = I_{Fe} \) were obtained from ion thinned specimens of the two binary alloys. From the intensity measurements and known compositions, a value of \( k_{12} = k_{NiFe} \) from Eqn. 1 was calculated. The thickness of the specimen was obtained at each analysis point using the method of Lorimer et al. (5). This method consists of measuring the separation between contamination spots from the top and bottom of the thin specimen after the sample is tilted through a known angle. Figure 1 shows the variation of \( k_{NiFe} \) with specimen thickness for the 35 and 50 wt% Ni alloys. Average error limits in the determination of the \( k \) ratio and foil thickness are also given. At a thickness \( \geq 0.7 \) μm the specimen is no longer transmission thin to the conventional 100 kV electron microscope. The value of \( k_{NiFe} \) obtained from the calibration curve of Cliff and Lorimer (6) is 1.157 (Fig. 1).

It can be observed from Figure 1 that \( k_{NiFe} \) increases with increasing foil thick-
ness above 0.45 \mu m. This variation is primarily caused by X-ray absorption. The appropriate mass absorption coefficients are listed in Table I.

TABLE I: Mass Absorption Coefficients \( \mu \rho (\text{cm}^2/\text{g}) \) for K\textsubscript{\alpha} Lines (7)

<table>
<thead>
<tr>
<th>Absorber</th>
<th>P</th>
<th>Fe</th>
<th>Ni</th>
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<tbody>
<tr>
<td>Fe</td>
<td>280</td>
<td>141</td>
<td>91</td>
</tr>
<tr>
<td>Ni</td>
<td>1677</td>
<td>71</td>
<td>380</td>
</tr>
<tr>
<td>P</td>
<td>2113</td>
<td>90</td>
<td>59</td>
</tr>
</tbody>
</table>

For a 50-50 Ni-Fe alloy the maximum loss of Ni K\textsubscript{\alpha} intensity due to absorption is 1.7%, 8.1% and 11.9% for foil thicknesses of 0.1, 0.5 and 0.75 microns. The corresponding Fe values are much smaller, 1%, 3% and 4%. Consideration of absorption effects show that the ratio \( I_{\text{Ni}}/I_{\text{Fe}} \) should decrease with increasing thickness for the same alloy. According to Eqn. 1, the value of \( k_{\text{NiFe}} \) should also increase. Our results for a 0.5\mu m thick specimen show an increase in \( k_{\text{NiFe}} \) of 1.3% for the 35 wt% Ni alloy and 3.9% for the 50 wt% Ni alloy. Using the new \( k_{\text{NiFe}} \) values from the 50-50 Fe-Ni standard leads to an increase of only 1.3 wt% Ni (2.5% relative) at the 50 wt% Ni level. The results of this study indicate that for all practical purposes the effect of thickness below the transmission thin limit can be neglected for the Fe-Ni system.

Application to Iron Meteorites--Figure 2 shows the structure of the Dayton iron meteorite containing \( \alpha \) and \( \gamma \) platelets. A bright field electron microscope image of several of the lamellae platelets showing the contamination spots left from the EMMA analyses is given in Figure 3. The resultant Ni concentration vs distance plot is shown in Figure 4. The Ni concentration was calculated using Eqn. 1 and the \( k_{\text{NiFe}} \) of Cliff and Lorimer (6). As is shown in Figure 3 the \( \alpha/\gamma \) interface is not exactly perpendicular to the film surface. This leads to a degradation in X-ray resolution at the interface. A Ni content of greater than 50 wt% at the \( \alpha/\gamma \) interface indicates equilibration at the interface to below 350\degree C while the meteorite was cooled within its parent body.

Results, Fe-Ni-P Standard--Analyses of Fe, Ni, and P in the 2 phase ternary standard were also made. Using the \( k_{\text{NiFe}} \) value of Cliff and Lorimer (6), the Ni content of the \( \gamma \) measured 1.75 \pm 0.2 wt%. Considering the low counting rates and the subjectivity in choosing the continuum background value, these values compare very favorably with the standard \( \gamma \) (1.99 wt% Ni, Ph-2.97 wt% Ni) values. Calculations of P content in the phosphides of this standard using Eqn. 1 and the \( k_{\text{PFeNi}} \) and \( k_{\text{PFe}} \) from Cliff and Lorimer (6) gave values between 12.5 and 13.0 wt%. These P content are well below the known values of 15.6 wt%. Measurements of P in phosphides from two meteorites Coahuila and Dayton gave values \( \leq 10 \) wt%. The phosphide regions analyzed in the two meteorites were thicker than the surrounding metal matrix and in some cases approached the transmission thin limit. The absorption coefficient of k\textsubscript{\alpha} in the Fe-Ni phosphate is over 4 times that of k\textsubscript{\alpha} in the FeNi phosphate (Table I). For the phosphide the maximum loss of P intensity by absorption is 12%, 47% and 61% for film thicknesses of 0.1, 0.5 and 0.75 microns. Since the ratio \( I_{\text{p}}/I_{\text{Fe}} \) or \( I_{\text{p}}/I_{\text{Ni}} \) decreases with increasing thickness for the same alloy, the appropriate value of \( k_{\text{PFeNi}} \) and \( k_{\text{PFe}} \) in the standard and meteorite samples is significantly higher than the Cliff and Lorimer \( k \) values obtained from very thin films.

In summary it appears that for characteristic X-ray lines where the mass absorption coefficient for the material of interest is generally less than 200 cm\(^2\)/g and the specimen is transmission thin, the Cliff and Lorimer (6) method is applicable. For X-ray lines where the mass absorption coefficient is greater than 200 cm\(^2\)/g, e.g. P\textsubscript{\alpha} in Fe-Ni, the \( k \) values must be known as a function of thickness or a separate absorption calculation must be made after the specimen thickness is measured.

Fig. 1: Variation of $k_{NiFe}$ with foil thickness for two Fe-Ni alloys.

Fig. 2: Microstructure of the Dayton Iron Meteorite. Field of view 3.7 x 3.0 mm.

Fig. 3: Bright field electron microscope image of lamellar platelets of the Dayton Iron Meteorite. Magnification marker, 1.25 $\mu$m.

Fig. 4: Ni concentration vs. distance plot obtained from EMMA measurements of $\alpha/\gamma/\alpha$ trace in Figure 3.