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ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY IN MINERALS PROCESSING

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A review of the possibilities of performing microchemical analysis in thin sections using a combination of scanning transmission electron microscopy and energy dispersive spectroscopy of x-rays is given. Particular attention is paid to the factors that limit accurate analysis at the highest spatial resolution. As an example of the use of these techniques applied to a potential problem in minerals processing, the identification of pyrite and pyrrhotite particles in Illinois, Herrin #6 coal is presented. (29 references)

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Introduction

A common problem associated with the utilization of materials such as low grade ores (for subsequent element extraction) and coals (for energy purposes) is the identification of mineral content, particularly when such mineral compounds are distributed on an extremely fine scale (e.g. submicron). Thus, it is often important to know whether a given element is present in a sample in the form of a crystalline phase, and also to know the elemental/chemical composition of such phases. During the recent past, there has been considerable effort directed at the possibility of performing microchemical analysis in thin samples (1, 2). This development has generally involved the use of transmission electron microscopy with its well known capability of providing high resolution images together with diffraction information. Elemental analysis may be achieved either through a study of energy dispersive spectroscopy of the emitted characteristic x-rays (EDS) or by electron energy loss spectroscopy of the transmitted electron beam (ELS). Two factors tend to limit the spatial resolution of these analytical techniques, the first being the incident electron probe diameter, the second involving the spreading of the electron probe within the sample by elastic and inelastic scattering processes. The first of these factors has led to the development of the scanning transmission electron microscope (STEM), an instrument capable of focussing an electron probe down to $\sim 3 \text{ \AA}$ while still providing imaging and diffraction information. The second of these factors is obviated to a certain extent by the use of an electron transmission technique, which requires the production and use of very thin sections; beam spreading may then be minimized and the spatial resolution optimized.

The combined techniques of STEM with either EDS or ELS provide very exciting possibilities concerning the analysis of mineral phases present in samples. Since the area involving ELS is still relatively recent in terms of application, this paper concentrates on the factors limiting accurate analysis at the limit of spatial resolution for the combination of STEM and EDS.

Quantitative Analysis

There have been numerous reports on quantitative procedures for elemental analysis using STEM and EDS (3 - 6). Most of these techniques are based on Castaing's original formulation for the electron microprobe (7), and the description given below is similar in nature.

Typically, the determination of microchemistry using EDS involves

recording spectra of x-ray emission from areas of a given specimen. These spectra contain characteristic peaks and it is necessary to establish a relation between the intensity of these peaks and the concentration of element A, C_A , is in fact given by:

$$C_A = \frac{I_A}{I_A^0} \quad (1)$$

where I_A is the measured intensity of the particular emission from element A in the specimen and I_A^0 is the intensity of the same emission assuming the sample was composed of pure A. The term I_A^0 may be either deduced from the use of standards or calculated (the so-called standardless method). Both types of approach are described below.

Measurement of I_A . A typical x-ray peak is shown in Fig. 1. To

Fig. 1 - Schematic diagram of a characteristic x-ray peak showing the continuum background and integral FWHM value.

determine an appropriate value for I_A , it is necessary to subtract the continuum of background upon which the characteristic peak is superimposed. The continuum spectrum generated from thin foils may be simulated by fitting a polynomial expression to the measured background. A given x-ray peak in an EDS spectrum is essentially the convolution of the x-ray line with the response of the detector, and is represented as a gaussian function. Since the width of this gaussian varies with energy, it is important when deducing I_A that an integral value be determined, usually that defined by the full width at half maximum intensity (FWHM). It is customary to fit gaussian profiles to the x-ray peaks of interest (using an appropriate minimization routine), and from these fitted profiles deduce FWHM values. However, the authors consider that it is often more appropriate to avoid such profile fitting. Thus, frequently it is

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the presence of a relatively low intensity peak that is of interest; because of the small number of counts in the peak, there may be sufficient noise (statistical) to cause the measured peak to be non-gaussian in appearance. In these cases, a computer-based fitting routine may only serve to compound the errors associated with the relatively low number of counts. It is preferable to set windows that correspond to FWHM values about each peak of the elements of interest; such windows are, of course, established when the given peak has sufficient intensity - for example when a pure standard of the element is used. By following this procedure, the data reduction maintains a simpler relationship with the originally measured numbers.

Determination of I_A^o . There are two methods that may be used to determine the value of I_A^o , one making use of standards, the other involving calculation (the "standardless" approach).

In the case of analysis, the procedure is as follows. Suppose the concentration of element A, C_A , in an alloy AB is required. The procedure for determining I_A^o consists of the production of a thin film of A of known thickness, t_A . The term I_A^o is then given by:

$$I_A^o = (I_A^o)_m \cdot \frac{n_{AB}}{n_A} \cdot \frac{\rho_{AB}}{\rho_A} \cdot \frac{t_o}{t_A} \quad (2)$$

where $(I_A^o)_m$ is the measured intensity from the standard; n_{AB} , n_A are the number of electrons incident on the specimen and standard, respectively; ρ_{AB} , ρ_A are the densities of the specimen and standard, respectively and t_o is the thickness of the specimen (i.e. at the point of analysis). The term n_{AB}/n_A will be unity if the various spectra are generated with equal numbers of incident electrons; this can be achieved using an electrically isolated aperture which monitors gun emission (8), this signal being used to generate the time base in the multichannel analyzer (MCA). The terms involving density (ρ_{AB}/ρ_A) and thickness (t_o/t_A) take into account the differences in mass thicknesses of the films. The term ρ_{AB} is not usually known (since this depends on the composition of AB, a parameter usually being determined by this analysis). For this reason the ratio of concentration of two elements is often determined, such that

$$\frac{C_A}{C_B} = \frac{I_A}{I_B} \cdot \frac{(I_B^o)_m}{(I_A^o)_m} \cdot \frac{n_A}{n_B} \cdot \frac{\rho_A}{\rho_B} \cdot \frac{t_A}{t_B} \quad (3)$$

where the terms have been defined above, and A and B refer to elements A and B, respectively. Providing precautions concerning variations in gun

emission are taken (as described above) the main error in determining concentration by use of standards arises from uncertainties in determining t_A and t_B . A most useful and accurate method of determining thickness, for crystalline materials, involves convergent beam electron (9). Using this technique, it is possible to determine thickness to ~ 2%, and thus must represent the limit to the accuracy of this type of analysis. This type of analysis (viz. involving the use of pure thin foil elemental standards) has been attempted by Fraser, et al (10) for the case of Ni-Al and Ni-Mo compounds, it was found that while the technique yielded reliable results in the case of the Ni-Mo compound, it was not successful in the analysis of the Ni-Al sample. The reason for this apparently concerns the nature of the Al thin foil standard. Thus, it appears that electropolishing results in a surface film containing Al; the intensity of x-rays from Al in this film is not accounted for by the thickness measurement using convergent beam electron diffraction techniques. This source of error that appears to be associated with the preparation of standards is being studied further.

For standardless analysis in thin foils, the calculation of the intensity I_A^0 is relatively straightforward. The reasons for this are twofold. Firstly, because the foil is thin, it is possible to make an assumption that the ionization cross-section is constant in the foil. Secondly, the number of electrons that are backscattered from a thin foil is extremely small, and this phenomenon may be neglected (11). The term I_A^0 is that intensity of the given peak of element A from a standard of pure A, recorded under identical conditions under which I_A is measured in a sample AB, consisting of elements A and B of thickness t_0 . This intensity for the case of the K_α peak of element A is given, following Castaing (7), by:

$$I_A^0 = n_{AB} \cdot Q_A^k \cdot \omega_A \cdot f_A \cdot \frac{N_0}{A_A} \cdot \rho_{AB} \cdot t_0 \quad (4)$$

where n_{AB} is the number of electrons responsible for generating the sample spectrum Q_A^k is the ionization cross-section for the k shell of element A, ω_A the fluorescent yield of A, N_0 Avogadro's number, f_A the fraction of K_α in the K shell emission, A_A the atomic weight of element A, and ρ_{AB} the sample density.

As in the case of analysis using standards, it is more convenient to determine a ratio of compositions (C_A/C_B), so that

$$\frac{C_A}{C_B} = \frac{I_A}{I_B} \cdot \frac{Q_B^k}{Q_A^k} \cdot \frac{\omega_B}{\omega_A} \cdot \frac{f_B}{f_A} \cdot \frac{A_A}{A_B} \quad (5)$$

The ionization cross-section Q_A^k represents one of the main uncertainties in the standardless analysis procedure. Thus, the appropriate value for a given element and accelerating voltage differs with the source of information; Powell (12) has recently produced a comprehensive review, from which reasonable values for the cross-section may be deduced. It should be emphasized that uncertainties in the values of ionization cross-sections limit the accuracy of standardless analysis to $\approx 5\%$; clearly, more work is required in this area.

The other terms in Equation (5), namely ω_x , f_x and A_x , are known to sufficient accuracy in the literature (for sources, see Refs. 3-7), and consequently do not introduce errors into the analysis. One further factor that should be included in Equation (5) involves the absorption of x-rays from the various materials in the detector itself. Thus the Bi window, Au and Si dead layers all reduce the intensities of x-rays being detected, and this absorption must be accounted for in the analysis procedure. Since the thicknesses and mass absorption coefficients of these materials are known, this factor should not lead to significant errors.

Absorption and Fluorescence Corrections. The effects of x-ray absorption and fluorescence cause the measured value of I_A in an experiment to differ from that generated by electron excitation in the specimen. It is, therefore, necessary to estimate these effects on the intensity of I_A , and adjust the values of I_A^0 deduced either from Equation (2) or (4) correspondingly.

X-ray Absorption. As x-rays, generated at points throughout the irradiated volume, propagate through the specimen towards the detector, their intensity is attenuated by the atoms of the sample. Since the extent of x-ray attenuation depends on photon energy, it is important to correct for this effect. The absorption correction, δ_A , ($= I_{t_0}/I_0$ where I_{t_0} is the detected x-ray intensity and I_0 that generated), is given by

$$\delta_A = \frac{1}{t_0} \left[\frac{1 - \exp - \left\{ \left(\frac{\mu}{\rho} \right)_{AB}^{A_K} \cdot \rho_{AB} \cdot \frac{\sin \alpha}{\cos(\alpha-\theta)} \cdot t_0 \right\}}{\left(\frac{\mu}{\rho} \right)_{AB}^{A_K} \cdot \rho_{AB} \cdot \frac{\sin \alpha}{\cos(\alpha-\theta)}} \right] \quad (6)$$

where t_0 is the specimen thickness, $\left(\frac{\mu}{\rho} \right)_{AB}^{A_K}$ is the mass absorption coefficient

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Fig. 3 - Coordinate system and definition of θ and ϕ for the absorption correction.

X-ray Fluorescence. It is possible for both continuum and characteristic x-rays generated in a thin foil, given sufficient energy, to cause inner shell ionizations. Thus, it is necessary to estimate the intensity of characteristic x-rays produced in this manner, since this intensity is simply added to that caused by primary electron excitation. The intensity of x-rays produced by continuum fluorescence may be neglected, since the intensity of the continuum itself in a thin foil is small, and it has been shown (11) that fluorescence by characteristic x-rays may also be neglected if $\left(\frac{\mu}{\rho}\right)_{B_K}^{B_K} \cdot \rho_{AB} \cdot t_o < 0.1$, where $\left(\frac{\mu}{\rho}\right)_{AB}^{B_K}$ is the mass absorption coefficient for K_α x-rays from B in the sample AB, and the other terms are as defined above. When this product exceeds the value of 0.1, then it is necessary to invoke a correction for the intensity of x-rays caused by characteristic fluorescence, I_f^A , given by (11)

$$\frac{I_f^A}{I_A} = \xi_A = 2 \omega_B \cdot C_B \left(\frac{\Gamma_A - 1}{\Gamma_A} \right) \cdot \frac{A_A}{A_B} \cdot \left(\frac{\mu}{\rho}\right)_A^{B_K} \cdot \left(\frac{\mu}{\rho}\right)_{AB}^{B_K} \cdot \frac{E_A}{E_B} \cdot (\rho_{AB} \cdot t_o)^2 \quad (7)$$

where I_A is the primary electron excited intensity, Γ_A is the absorption jump ratio for A, A_A and A_B are the atomic weights of A and B, respectively, $\left(\frac{\mu}{\rho}\right)_A^{B_K}$ is the mass absorption coefficient of K_α x-rays of B in pure A, and E_A/E_B is the ratio of the critical excitation energies for the characteristic emissions of elements A and B.

The corrections involving absorption (δ) and fluorescence (ξ) may be included in Equations (3) and (5) as follows. Thus,

$$\frac{C_A}{C_B} = \frac{C_A'}{C_B'} \cdot \frac{\delta_B}{\delta_A} \cdot \frac{(1 + \xi_B)}{(1 + \xi_A)} \quad (8)$$

here the primes refer to uncorrected values.

Instrumental Factors

This section deals with those factors affecting the accuracy of elemental analysis when using a combination of STEM and EDS that find their origin in instrumentation. This topic has been heavily researched and so it is only necessary to make comments of a cursory nature in this paper.

"System" Peaks. "System" peaks are those characteristic peaks in the x-ray spectrum generated in atoms, not contained in the sample, but from material surrounding the specimens. The solution to this problem

is to machine the cup from material which does not give rise to characteristic peaks in an EDS spectrum such as graphite (13) or Be (14). For supported films, the grids should be of Be or C-coated plastic (nylon).

Sources of Unfocussed Radiation. For the purposes of elemental analysis, the focussed electron probe excites a spectrum of x-rays. However, this electron beam is not the only source of radiation incident on the specimen. Thus, it is possible for hard x-rays, both continuous and characteristic, to be created at the condense aperture (15) and this radiation together with possible stray electrons which are scattered around the various apertures above the specimen (16) to interact with the specimen and generate a contribution to the measured x-ray spectrum. This unfocussed radiation presents a significant problem in attempting elemental analysis, and its intensity has to be minimized. There are a number of ways in which this can be achieved, the manner in which it is done being dependent on the particular source of radiation (15, 16).

Specimen Contamination. Contamination of specimens arises in STEM instruments because of the use of finely focussed electron probes with relatively high current densities. The source of contamination is either from the vacuum system or specimen borne. The extremely detrimental aspects of contamination in elemental analysis have been recently discussed (17), and it is necessary to reduce the extent of contamination as much as possible. Thus, there are basically two serious factors that result from contamination. First, the contamination layer can cause the given area of analysis to become essentially opaque, and therefore positioning of the beam on a particular feature is more or less impossible. This results in a certain loss of spatial resolution which can cause extreme inaccuracies in elemental analysis (18). Second, the contamination layer can cause absorption of x-rays, resulting in a relative change of intensity (and therefore apparent composition) with time (17). It is clearly desirable to reduce its extent as much as possible.

Surface Films. One inherent problem in performing elemental analysis using thin foils is that involving the effect of thin surface layers, e.g., oxides. If such a thin film exists on the surface of a foil, and its elemental composition is rich in one component of the specimen, then inaccuracies in deducing the sample composition may result, particularly in thin areas (19).

Spatial Resolution

When attempting to perform high spatial resolution studies using the STEM/EDS technique, it is usual to reduce the probe size to the point where

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it is less than the dimensions of the region to be analyzed. The actual spatial resolution achieved is generally degraded by broadening of the electron probe within the specimen through high angle elastic scattering, see Fig. 4. There have been several attempts to determine theoretically (19 - 21) this beam spreading and these are described below.

Fig. 4 - Schematic diagram of beam spreading in a thin foil.

With regard to calculation, two models have been developed, one involving a single scattering event (20), the other making use of the Monte Carlo technique where plural scattering is simulated. The Monte Carlo calculations offer a more satisfactory method of deducing not only the diameter of the beam at the exit surface of the foil, but also the electron profile within the sample. Several calculations of elastic scattering have been performed using Monte Carlo techniques. Newbury (21) provides a description of Monte Carlo calculations using William's (22) simple screened Rutherford cross section, whereas Hutchings et al. (23) favored a Monte Carlo Model employing Doyle and Turner's (24) relativistic Hartree-Fock cross sections. Following the lead of Hutchings et al., we have employed Doyle-Turner cross sections in calculating the diameter of a cylinder containing 90% of the integrated electron paths simulated in our Monte Carlo calculations. This diameter is given for various elements and sample thicknesses in Table I. As we recall from Equation (2), x-ray generation is proportional to the electron path in a solid; therefore this diameter also defines a cylinder containing 90% of the x-rays generated by the incident electrons.

	Foil Thickness, Å					e ⁻ mean free path,
	100	500	1000	3000	5000	Å
C	-	3.7	19	150	340	1104
Al	-	8.6	31	230	560	642
Cu	1.9	43	140	860	2600	188
Al	7.4	120	610	7000	18000	52

Table 1. For four elements, we have calculated the diameters of cylinders containing 90% of the integrated pathlengths of 100 kV electrons exciting foils of various thicknesses. The incident electron beam enters a planar foil as a point source perpendicular to the sample. Each imaginary cylinder is perpendicular to the foil, has a height equal to the sample thickness, and is centered about the point electron source. For 100 Å foils of C and Al no cylinder could be small enough to contain only 90% of the electron pathlengths.

While fairly sophisticated techniques may be used to calculate beam spreading, it is of course necessary to validate the theoretical approach by means of suitable experiments. There have been numerous attempts to determine x-ray spatial resolution, including the use of specimens containing small precipitates (25), grain boundaries (26) and phase interfaces (27). Most of these experiments have suffered from the fact that the elements being detected are contained to a certain extent on both sides of the given discontinuity (e.g., phase interface), and also from the occurrence of contamination, which limits the step length between successive points of analysis to ~ 500 Å. A set of experiments which avoided both of these potential difficulties consisted of the measurement of beam spreading in Si films, whose thicknesses were accurately determined using stacking faults induced within the films (23). The Si films were prepared with thin (~ 300 Å) narrow strips of Au on one surface, and the intensity of Au x-rays was measured as a function of position across an edge of an Au layer in ~ 100 Å steps. From these measurements, x-ray resolution, and therefore electron beam spreading, was determined with a large degree of confidence. Monte Carlo calculations were also performed and good agreement has been found between theory and experiment especially for thin specimens. It can be concluded, then, that Monte Carlo calculations do indeed give a fairly accurate assessment of beam spreading in thin foils.

The fairly close agreement between calculation and measurement of beam spreading indicates that elastic scattering of electrons in thin

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foils limits the spatial resolution of the x-ray technique. The occurrence of such scattering has important implications regarding elemental analysis at the 10 nm scale. Thus, it is evident that relatively thin foils should be used so that beam spreading be minimized.

Often, it is not possible to prepare foils that not only contain the feature to be analyzed but are also sufficiently thin to minimize spatial resolution. In this case, a measured x-ray spectrum contains contributions from both the feature of interest and the surrounding matrix, and it is necessary to separate out that part of the spectrum generated in the matrix from the detected spectrum. A method of performing such deconvolution has been described, where the profile of the beam within the specimen (calculated using Monte Carlo techniques) is used to determine the relative fractions of the electron probe that excite the feature and matrices (28).

Minerals in Coal

The techniques described above represent an advanced state of technique application. However, in experiment, several difficulties are encountered that limit successful analysis and these have been described above briefly. For example, the development of thin surface layers during electropolishing sets a severe limit to the case of microchemical analysis of thin metal foils. The problems that exist for samples involving coal or carbonaceous materials are often more complex than those pertaining to simple metals and alloys. The first and most serious problem involves specimen preparation, and it is this difficulty that is responsible for the paucity of work in this area. A method for preparing thin foils of coal suitable for transmission electron microscopy has been described (29), and this will be outlined below. Following that, the identification of the minerals pyrite and pyrrhotite using a combination of electron diffraction and EDS analysis of thinned samples will be shown.

Sample Preparation. Pieces of coal are first sliced into thin sections using a diamond saw. These chips are then polished by hand until approximately 100 μm in thickness. A razor blade is then used to cut approximately 3 mm diameter disks suitable for loading in a standard electron microscope specimen holder. These disks are then introduced into a cold stage of an ion milling machine, where a thinner perforation is achieved by ion sputtering. In this way, it is possible to produce sections sufficiently thin for observation in an electron microscope. An example is shown in Fig. 5. Here a general view of some minerals in an Illinois Herrin #6 coal is given.

Fig. 5 - Typical microstructure of mineral phases in coal. Illinois, Herrin #6 coal sample used. Transmission electron micrograph.

Mineral Identification. As an example of the use of analytical electron microscopy for identifying minerals in coal, we use the example of pyrite and pyrrhotite inclusions in this same Herrin #6 coal (29). This coal is found to contain a relatively large volume fraction of pyrite particles. An example is shown in Fig. 6. The phase is a single crystal, this conclusion being based on the dark field image and the diffraction pattern. The EDS spectrum from the particle, after data reduction, yields a particle chemistry corresponding to FeS_2 . On the other hand, occasionally a pyrrhotite particle is observed, one such being shown in Fig. 7.

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Fig. 6 - Analytical electron microscopy study of pyrite single crystal in Illinois, Herrin #6 coal. Clockwise from top left: selected area diffraction pattern, bright-field transmission electron micrograph, dark-field image, and x-ray spectrum.

Again, a combination of dark field imaging and diffraction indicates that the phase is single crystal, and the EDS spectrum implies a phase chemistry corresponding to $\text{Fe}_{0.9}\text{S}$. A range of homogeneity is well known for the case of pyrrhotite. These examples represent the state-of-the-art for this type of analysis in these specimens, and a report on this work is well documented in literature (29).

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References

1. Analytical Electron Microscopy, Proceedings of a Workshop, Cornell University, Ithaca, NY (1976).
2. Analytical Electron Microscopy, Proceedings of a Specialist Workshop, Cornell University, Ithaca, NY (1978).

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Fig. 7 - Analytical electron microscopy study of pyrrhotite single crystal in Illinois, Herrin #6 coal. X-ray spectrum indicates that the crystal corresponds to $\text{Fe}_{0.9}\text{S}$.

3. J. Philibert and R. Tixier, Brit. J. Appl. Phys., 1, (1968) 685.
4. G. Cliff and G. W. Lorimer, J. Microsc., 103, (1975) 203.
5. N. J. Zaluzec, Ph.D Thesis, University of Illinois (1978); Introd. to AEM, Plenum Press, NY ed. J. J. Hren, J.I. Goldstein and D.C. Joy, (1979) 121.
6. J. I. Goldstein, *ibid.*, (1979) 83.
7. R. Castaing, Ph.D. Thesis, University of Paris, ONERA Pub. #55 (1951).
8. H. L. Fraser and J. B. Woodhouse, p. 191 of Ref. 2 (1978).
9. P. M. Kelly, A. Jostsons, R. G. Blake, and J. G. Napier, Phys. Stat. Sol., 31, (1975) 771.

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FEBRUARY 1979

Fraser 15 16

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10. H. L. Fraser, M. H. Loretto and J. M. Brown, unpublished research (1981).
11. J. Philibert and R. Tixier, Phys. Asp. of Elec. Microsc. and Microbeam Anal., ed. B. M. Siegel and D. R. Beaman, J. Wiley, NY (1975) 333.
12. C. J. Powell, Rev. Mod. Phys., 48 (1976) 33.
13. N. J. Zaluzec and H. L. Fraser, J. Phys. E., 9, (1976) 1051.
14. E. A. Kenik and J. Bentley, 35th Ann. Proc. EMSA, ed. G. W. Bailey, Claitors Publ., Baton Rouge, (1977) 328.
15. N. J. Zaluzec and H. L. Fraser, 34th Ann. Proc. EMSA, ed. G. W. Bailey, Claitors Publ., Baton Rouge, (1976) 420.
16. H. Shuman, A. V. Somlyo and A. P. Somlyo, Untramicroscopy, 1, (1976) 317.
17. N. J. Zaluzec and H. L. Fraser, p. 122 of Ref. 2 (1978).
18. H. L. Fraser, Proc. 11th Ann. SEM Symposium, Los Angeles (SEM Inc.), 1, (1978) 627.
19. P. L. Morris, N. C. Davis and J. A. Treverton, Proc. of EMAS, ed. D. L. Misell, Publ. Inst. of Phys., Bristol, (1977) 237.
20. J. I. Goldstein, J. L. Costley, G. W. Lorimer and S.J.B. Reed, SEM/1977, IITRI, ed. O. Johari, (1977) 315.
21. D. E. Newbury and R. L. Myklebust, Ultramicroscopy, 3, (1979) 391.
22. E. S. Williams, Proc. Roy. Soc. 169, (1939) 531.
23. R. Hutchings, M. N. Loretto, I. P. Jones and R. E. Smallman, Ultramicroscopy, 3 (197) 401.
24. P. A. Doyle and P. S. Turner, Acta Cryst. A24, (1968) 390.
25. S. Mehta, J. I. Goldstein and J. J. Friel, Lunar and Planetary Science, in press (1979).
26. P. Doig and P.E.J. Flewitt, J. Microscopy, 110, (1977) 107.
27. A. Romig, Ph.D. Thesis, Lehigh University (1979).
28. M. E. Twigg and H. L. Fraser, Spring Meeting of AIME, Las Vegas, NV (1980).
29. K. C. Hsieh and C. A. Wert, Matt. Sci. and Eng., in press (1981).

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