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ELECTRON-MICROPROBE ANALYSIS OF MINERALS FOR RARE-EARTH ELEMENTS: USE OF CALCULATED PEAK-OVERLAP CORRECTIONS

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ABSTRACT

The relative intensities of the $L\alpha_1$, $L\beta_1$, $L\beta_2$, $L\beta_3$, and $L\gamma_1$ lines were measured using ten *REE* phosphates. These data were used to calculate peak-overlap corrections for the $L\alpha_1$ and $L\beta_1$ lines of *REE*. Wavelength-dispersion and energy-dispersion spectra of the *L* lines of fourteen *REE* compare favorably with the spectra using the peak-overlap corrections. Detection of *REE* by microprobe analysis is best accomplished by first collecting a wavelength-dispersion spectrum to identify interfering elements and locate the best wavelengths for background measurements. The *REE* phosphates were used as standards for wavelength-dispersion analysis of four silicate glasses prepared by Drake & Weill (1972), three silicate glasses prepared in the present study and some minerals previously analyzed for *REE* by wet-chemical method. The microprobe results of these samples are consistent with the known levels of *REE* in the samples.

Keywords: rare-earth analysis, *REE* microprobe analysis, microprobe standards.

SOMMAIRE

On mesure l'intensité relative des raies, $L\alpha_1$, $L\beta_1$, $L\beta_2$, $L\beta_3$, et $L\gamma_1$ dans dix phosphates de terres rares (*TR*). Ces données servent à calculer les corrections d'empiètement de raies pour les raies $L\alpha_1$ et $L\beta_1$ des *TR*. Les spectres *L* de quatorze *TR*, obtenus par dispersion de longeurs d'onde et par dispersion d'énergie, concordent avec les spectres calculés compte tenu de ces corrections. La détermination des terres rares à la microsonde est facilitée par l'obtention préalable d'un spectre par dispersion de longueurs d'onde, qui révèle les éléments en interférence et les longueurs d'onde à choisir pour mesurer le bruit de fond. Les phosphates de *TR* ont servi d'étalons dans l'analyse par dispersion de longueurs d'onde de quatre verres silicatés préparés par Drake et Weill (1972), trois verres préparés pour cette étude, et quelques minéraux dans lesquels on avait dosé les *TR* par voie humide. Les résultats que l'on obtient à la microsonde concordent avec les teneurs connues des *TR* dans ces échantillons.

(Traduit par la Rédaction)

Mots-clés: détermination des terres rares, analyse à la microsonde électronique, étalons pour microsonde.

INTRODUCTION

Electron-microprobe analysis of silicate minerals has become routine because of the relatively simple *K* series of X-ray spectra used for the major elements in silicates. The microprobe analysis of samples containing rare-earth elements is much more complicated because it is necessary to use the lower intensity and more complex *L* series of X-ray spectra. Thus the *L* line for one rare-earth element (*REE*) may interfere with the measurement of another element. As an example, *L* spectra for the phosphates of lanthanum, cerium and praseodymium are shown in Figures 1a, b, c, run under the conditions described in the next section. Thirteen peaks for lanthanum are identified in Figure 1a and illustrate the possible complexity for a sample containing more than one *REE*. The spectrum shown in Figure 1d pertains to a glass microprobe standard synthesized by Drake & Weill (1972); it contains almost equal concentrations (Table 1) of lanthanum (La), cerium (Ce) and praseodymium (Pr). The chemical symbol for the individual rare-earth elements will be used in the remainder of this paper. The lines for La$L\alpha_1$ and Ce$L\alpha_1$ in Figure 1d are almost of equal intensity, but the Pr$L\alpha_1$ is at almost the same wavelength as the La$L\beta_1$ line, and thus the measured X-ray intensity at this wavelength is due to both La and Pr. The peak overlap is a particularly serious problem for the evaluation of Pr, Eu, Gd, Ho, Er, Tm and Lu concentrations by microprobe. The two methods used to avoid this problem are to choose X-ray lines showing minimum interference (Exley 1980) or to use correction factors for peak overlap (Åmli & Griffin 1975, Haggerty 1983, Segalstad & Larsen 1978). The correction factors for overlapping peaks of different *REE* have been measured by Åmli & Griffin (1975), but the ones that they presented are dependent on the change in resolution and efficiency, over the wavelength region, of the spectrometer used in their microprobe. Other analysts who wish to use the results of Åmli & Griffin have to assume that their spectrometer shows the same resolution and efficiency change with spectrometer setting. The amount of peak overlap is very sensitive to the resolution of the spectrometer. Thus it is best to measure directly the overlap correction, but suitable standards are not always available. The major purpose of the present paper is to present data needed to calculate the peak overlap for a spectrometer of any resolution or efficiency and to present microprobe data for standard material.

The first part of this paper describes the measurement of the intensity of the major lines ($L\alpha_1$, $L\beta_1$,

$L\beta_2$, $L\beta_3$, $L\gamma_1$) for ten *REE*; a method is presented to use these peak intensities to calculate the overlap correction for each *REE*. These data are then used to calculate a spectrum that is compared to a measured spectrum. The second section describes the microprobe determination of fourteen *REE* in some glass samples prepared in the present study and the Drake & Weill glasses, which are used as *REE* standards by many microprobe analysts. Microprobe data are presented for some *REE* minerals and compared to wet-chemical results on these minerals.

EXPERIMENTAL PROCEDURE

All microprobe data were collected with an ARL SEMQ microprobe (take-off angle of 52.5°) at an excitation voltage of 15 kV or 25 kV. The wavelength-dispersion (WD) data were collected with a curved lithium fluoride crystal and an argon-filled detector. The energy-dispersion (ED) data were collected with a Princeton Gamma-Tech detector having a resolution (FWHM) of 155 eV for manganese. The WD data at 15 kV were collected at a beam current of 22 nA measured with a Faraday cage in a brass mount.

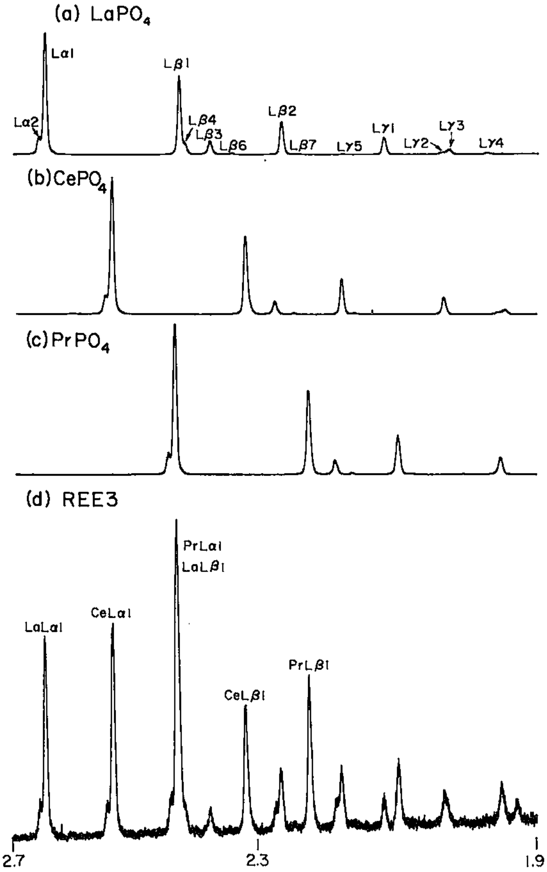

FIG. 1. Wavelength-dispersion spectra of *REE* collected with an LiF crystal from a λ of 2.7 to 1.9 Å at 15 kV: a) LaPO$_4$, b) CePO$_4$, c) PrPO$_4$, d) glass from Drake & Weill (1972).

The usefulness of the proposed peak-overlap correction procedure depends upon how well other analysts can measure the resolution and efficiency of their ED or WD spectrometers relative to the one used in the present study. This comparison is best made by measuring the peak width and count rate at the peak position for the *K* lines of common metals over the wavelength region used for the *REE*. The resolution or peak width at one standard deviation (60.6% height of the peak) for the WD spectrometer used in the present study is shown for the $K\beta$ line of some common metals in Figure 2. The peak width in ångström units is plotted against the wavelength of the lines as listed in White & Johnson (1979). Also shown in Figure 2 is the variation in count rate (only corrected for background) for the $K\alpha$ lines of some common metals. The matrix corrections of the intensity measurements were made using a ZAF correction program supplied by Tracor Northern and modeled after the MAGIC program of Colby (1968).

The samples used for the measurement of relative peak-height of the individual *REE* are a series of 10 *REE* phosphates prepared and supplied by L.A.

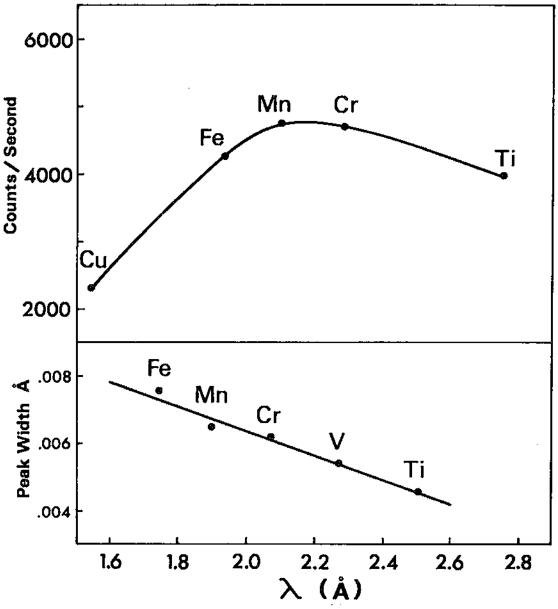

FIG. 2. a) Peak count-rate corrected for background for the $K\alpha$ line of the listed metals as a function of wavelength. b) The peak width in ångströms at one standard deviation (60.6% height) for the $K\beta$ line of the listed metals as a function of wavelength.

Boatner to A.N. Mariano. These samples are described by Boatner *et al.* (1980). The relative intensity of one *L* line relative to another *L* line for any one *REE* was checked using some *REE* metals supplied by Applied Research Laboratories and on oxides provided by A.N. Mariano. The *REE* glasses prepared and distributed by Drake & Weill (1972) were used as standards for Gd, Tb, Yb and Lu since no phosphates of these elements were available at the time this study was conducted. Three glasses were prepared in the present study in order to check the accuracy of the analytical and correction techniques.

These glasses (S-236, S-253, S-254) were prepared by carefully weighing predried $CaCO_3$ (600°C), Al_2O_3 (600°C) and silicic acid (1000°C). Predried CeO_2 and La_2O_3 were used in S-236, whereas predried Spexmix 1032 supplied by SPEX Industries was used in preparing samples S-253 and S-254. Spexmix 1032 is listed as containing scandium, yttrium and fourteen *REE* elements at the 5.28 el.wt.% level, and the glasses prepared using this mix were made such that they have a nominal concentration of 1.04% for each *REE* (S-254) or 0.08% for each *REE* (S-253). Each sample was carefully ground and mixed in an agate mortar and then fused twice at 1500°C for six hours with an intermediate grinding in a tungsten carbide ball-mill. The glass samples were analyzed for *REE* by two laboratories using neutron activation. These results, together with the nominal values for Ca, Al and Si, are shown in Table 1. The homogeneity of the glasses was checked by using the homogeneity index of Boyd *et al.* (1967). Limited amounts of these three glass samples are available from the author.

INTENSITY MEASUREMENT AND CALCULATION

The first information needed to calculate the overlap correction is the value of the intensity of any *REE* peaks relative to the intensity of the major peak of that same *REE* in a sample that contains no other *REE*. For example, if it is known that the $L\beta_1$ peak for La is 57% of the height of the $L\alpha_1$ peak, then the La contribution to the Pr$L\alpha_1$ peak shown in

TABLE 1. CHEMICAL COMPOSITION OF GLASS STANDARDS*

	Four Glasses of Drake & Weill			Glass S-254					Glass S-253				
		Probe			Probe					Probe			
	Nom.*	15kV(n=3)	NAA^1	Nom.*	15kV(5)	25kV(3)	NAA^2	NAA^3	Nom.*	15kV(3)	25kV(5)	NAA^2	NAA^3
La	3.65	3.60	3.91	1.04	1.04	1.05	0.92	0.82	0.08	0.07	0.06	0.090	0.100
Ce	3.42	3.33	3.67	1.04	1.06	1.06	0.91	0.76	0.08	0.08	0.06	0.079	0.100
Prα	3.79	3.71(4.12)	3.93	1.04	0.98	1.01			0.08	0.07	0.08		
Prβ	3.79	3.61	3.93	1.04	0.94	0.94			0.08	0.06	0.05		
Nd	3.65	3.65	3.60	1.04	1.03	1.10	0.78	0.51	0.08	0.06	0.08	0.067	0.100
Sm	3.67	3.77	3.72	1.04	1.01	0.99	0.96	0.70	0.08	0.06	0.06	0.087	0.097
Euα	3.80	3.76	3.90	1.04	1.06	1.04	0.85	0.70	0.08	0.07	0.08	0.077	0.088
Euβ	3.80	3.78	3.90	1.04	1.09	1.00	0.85	0.70	0.08	0.06	0.07	0.077	0.088
Gdα	3.87			1.04	1.09	1.03			0.08	0.10	0.08	0.095	
Tb	3.78		3.96	1.04	1.15	1.04	0.94	0.73	0.08	0.04	0.07	0.080	0.088
Dy	3.80	3.73		1.04	1.04	1.00	0.81		0.08	0.06	0.06	0.080	
Hoα	3.85	3.74	3.81	1.04	0.96	1.00	1.10		0.08	0.02	0.07	0.097	
Hoβ	3.85	3.65	3.81	1.04	1.16	1.01	1.10		0.08	0.13	0.10	0.097	
Erα	3.81	3.71		1.04	1.02	0.94			0.08	0.09	0.06		
Erβ	3.81	3.57		1.04	1.12	0.97			0.08	0.10	0.06		
Tmα	3.81	3.71		1.04	1.12	0.99	0.82		0.08	0.06	0.05	0.077	
Tmβ	3.81	3.46(4.78)		1.04	1.12	0.95	0.82		0.08	0.06	0.08	0.077	
Yb	3.74		3.58	1.04	0.98	0.97	0.84	0.63	0.08	0.09	0.06	0.080	0.088
Lu	3.75		3.75	1.04	1.15	0.98	0.91	0.69	0.08	0	0.06	0.080	0.086
Ca				16.90					20.80				
Al				12.90					16.26				
Si				15.09					18.09				

Glass S-236

		Probe		
	Nom.*	15kV	NAA^2	NAA^3
La	10.56	10.26	11.1	11
Ce	10.27	10.30	10.7	10
Ca	15.54			
Al	10.43			
Si	15.69			

*Composition expressed in wt. % elements, Nom. = Nominal wt. % from initial weighing.

[1] = Neutron activation analyses by Drake & Weill (1972).

[2] = Neutron activation analyses by GINA - Université de Montréal, Montréal, Quebec.

[3] = Neutron activation analyses by Neutron Activation Services, McMaster Nuclear Reactor, Hamilton, Ont.

Figure 1d can be calculated. It is possible to use the relative intensity of the peaks given in White & Johnson (1979); however, these values are given a nominal value ($L\beta_1$ 50, $L\beta_2$ 20, $L\beta_3$ 6, $L\gamma_1$ 5) for all the *REE*. The peak heights of the five major peaks for the 10 *REE* phosphates were measured by using a LiF crystal. The peak centroid was found by using an automatic peak-search routine that is part of the TASK software supplied by Tracor Northern. Each measurement involved three counts on different spots of 30 seconds duration (total 90 seconds). Background was measured at three different wavelengths and plotted as a function of wavelength. The intensity of each peak, minus the background, was divided by the intensity of the $L\alpha_1$ peak and multiplied by 100 to give percent intensity. The intensity of the various peaks relative to the $L\alpha_1$ peak is plotted as a function of atomic number in Figure 3. The measured values for the $L\beta_1$ line are shown by the crosses at the top on Figure 3 and show some irregularity (are too high) in the vicinity of Nd. This irregularity is because of $L\beta_4$ and $L\beta_1$ overlap; the $L\beta_4$ peak shifts in wavelength with respect to the $L\beta_1$ peak as the atomic number changes from La to Lu. There is complete overlap of these peaks for Nd. Thus, in Figure 1a, the $L\beta_4$ peak is shown at a lower wavelength than (to the right of) the $L\beta_1$ for La, and the two peaks can be almost completely discriminated with the spectrometer set at the $L\beta_1$ peak position. As the atomic number increases (Fig. 1b, c) there is greater overlap. The contribution of $L\beta_4$ to the $L\beta_1$ peak can be calculated using the peak positions given by White & Johnson (1979) and the relative intensity of the $L\beta_4$ given by White & Johnson. The calculated contribution of the $L\beta_4$ to $L\beta_1$ has been subtracted and is shown in Figure 3 by the position of the solid dots. Thus the crosses represent the measured values at the $L\beta_1$ peak postition, and the dots represent the corrected $L\beta_1$ intensity. The corrected $L\beta_1$ intensities show an approximately linear relation to atomic number. The $L\beta_2$, $L\beta_3$ and $L\gamma_1$ peaks have no interfering peaks, and the change of intensity relative to $L\alpha_1$ as a function of atomic number is also approximately linear. The calculation of peak-overlap correction assumes that the relative intensity of the peaks as shown in Figure 3 remains the same no matter what the material is or what other elements are in the matrix. The relative peak-intensity has been measured in some metals and simple glasses and found to be consistent with the intensities shown in the phosphates; the data for Sm are consistent with the data published by Bolon *et al.* (1979). Samples containing other elements with peaks in the $L\alpha_1$ to $L\gamma_1$ region for any particular *REE* may affect the relative intensities because of secondary fluorescence and absorption, but this effect will usually be small. For example, the *K* absorption edge for iron lies between the Dy$L\alpha_1$ and Dy$L\beta_1$ peaks and thus, if iron is present in the sample, the intensity of Dy$L\beta_1$ will be less relative to Dy$L\alpha_1$. The differential absorption of these two Dy lines by iron was calculated using the procedure of Corlett & MacDonald (1974) and the equations presented by Reed (1975). The intensity of Dy$L\beta_1$ relative to Dy$L\alpha_1$ is changed from 44% (from Fig. 3) in a sample with no iron to 42.5% in a sample with 50 wt.% iron, 50 wt.% dysprosium. This is within the experimental error of measurements made in the present study. There is also the possibility of the detector gas (*e.g.*, xenon) causing absorption edges between *L* lines (Smith & Reed 1981). Thus caution is recommended in using the relative intensities for calculating large corrections. Other analysts who wish to use the relative intensities shown in Figure 3 have to determine whether the change in spectrometer response over the wavelength interval is approximately the same as that (Fig. 2) in the present study. If it is different, the relative intensity

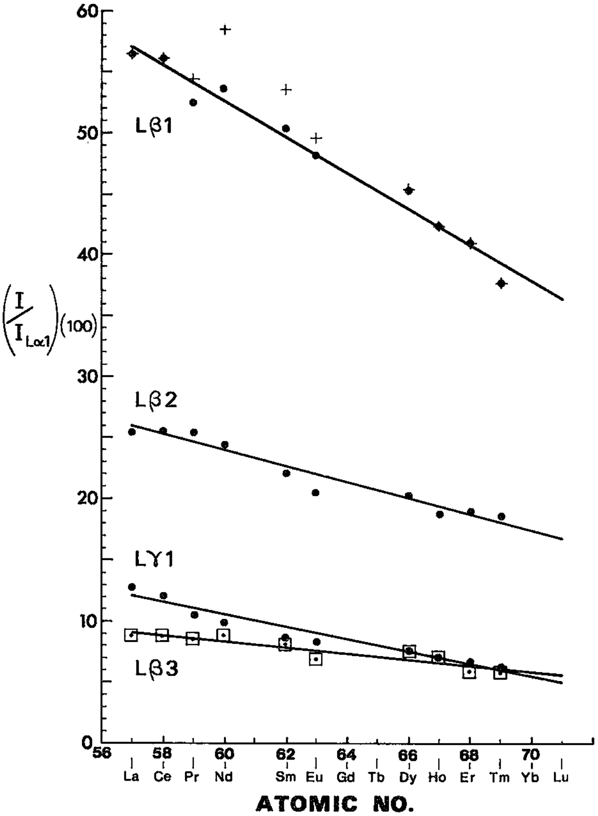

FIG. 3. The measured intensities of the $L\beta_1$, $L\beta_2$, $L\gamma_1$ and $L\beta_3$ lines of the *REE* relative to the $L\alpha_1$ line as a function of the atomic number of the *REE*. The crosses for the $L\beta_1$ line represent measured intensities, whereas the dots represent the intensities corrected for $L\beta_4$ overlap (see text).

of the peak relative to the $L\alpha_1$ peak will have to be changed accordingly.

The calculation of the contribution of X-ray counts of an interfering (i) peak to the measurement of the X-ray counts at the desired (d) peak-position requires knowledge of the intensity of the interfering peak, the accurate peak-position of both the interfering peak (λ_i) and the desired peak (λ_d) and the peak width (W) of each of the peaks. The contribution of one peak to another can be calculated assuming a Gaussian distribution of X-ray counts on either side of the position of the interfering peak. A Gaussian distribution was found to be a reasonable approximation to the shape of the peaks, except for a "tailing" on either side of the peaks that can only be represented by a much more complicated function (Suortti 1980). The following equations from Bolz & Tuve (1976) can be used to calculate the fractional contribution (F) of one peak to the measurement of another peak. The function X describes the amount of overlap expected between the desired peak and interfering peak. In the following relationships, λ_d is the wavelength of desired peak, λ_i, the wavelength of interfering peak, W, the width of peak at one standard deviation (60.6% of peak height), and F, the fraction of counts of interfering peak at the position of the desired peak.

$$X = \frac{(\lambda_d - \lambda_i)}{W/2} \qquad (1)$$

$$F = e^{-\left(\frac{X^2}{2}\right)} \qquad (2)$$

If the two peaks are very close in wavelength or if the peaks are broad (large W), the value of X will be low, and the peaks will overlap. It is thus possible to calculate the amount of peak overlap between the La$L\beta_1$ and the Pr$L\alpha_1$ peaks shown in Figure 1d. The calculated value for F is found to be 0.22 using a λ_d of 2.4630 (Pr$L\alpha_1$), a λ_i of 2.4589 (La$L\beta_1$), and a value of W of 0.0047 Å. The fractional contribution of La$L\beta_1$ is then multiplied by the intensity of this peak (57% from Fig. 3) in order to get an overlap correction of 12.4%. Åmli & Griffin (1975) measured a number of peak-overlap corrections directly on their ARL microprobe; for the La$L\beta_1$ interference with Pr$L\alpha_1$ they measured 12.7%. Thus if the Pr peak in the rare-earth glass standard shown in Figure 1d was measured at the Pr$L\alpha_1$ peak position, the actual number of counts due to Pr would be found by subtracting 12.7% of the net counts in the La$L\alpha_1$ peak position from those in the Pr$L\alpha_1$ peak position. The percentage correction can be calculated for a spectrometer of any resolution. For example, we have calculated the fraction overlap for our energy-dispersion spectrometer and found that because of its much poorer resolution, there is almost complete overlap of La$L\beta_1$ and Pr$L\alpha_1$. Thus F equals 1, and the overlap correction is equal to 57%. The analysis of a small amount of Pr in the presence of a large amount of La is very difficult, and small errors in the overlap correction will lead to large analytical errors.

TABLE 2. OVERLAP CORRECTIONS FOR $L\alpha_1$ AND $L\beta_1$ LINES USING WDS

Desired Line	Calculated % Overlap and Interfering Peak	Measured Overlap Åmli & Griffin (this study)
La$L\beta_1$	22.0 Pr$L\alpha_1$	
Pr$L\alpha_1$	12.4 La$L\beta_1$	12.7(13.6, 16.2)
Sm$L\alpha_1$	0.2 Ce$L\beta_2$	1.9
Eu$L\alpha_1$	21.7 Pr$L\beta_2$, 1.2 Nd$L\beta_3$	20.3Pr(23.3, 19.8)
Eu$L\beta_1$	9.9 Dy$L\alpha_2$, 0.3 Dy$L\alpha_1$	
Gd$L\alpha_1$	1.0 La$L\gamma_2$, 0.2 La$L\gamma_3$	2.8
	9.5 Ce$L\gamma_1$	11.8 (10.9)
Gd$L\beta_1$	87.5 Ho$L\alpha_1$, 0.3 Ho$L\alpha_2$	
Tb$L\beta_1$	11.7 Er$L\alpha_1$	
Dy$L\alpha_1$	0.1 Eu$L\beta_1$	
Ho$L\alpha_1$	40.8 Gd$L\beta_1$, 0.2 Gd$L\beta_4$	42.1
Ho$L\beta_1$	0.3 Eu$L\gamma_1$	
Er$L\alpha_1$	5.2 Tb$L\beta_1$, 4.2 Tb$L\beta_4$	3.0
Er$L\beta_1$	3.6 Gd$L\gamma_1$, 0.7 Eu$L\gamma_3$	
Tm$L\alpha_1$	9.3 Sm$L\gamma_1$, 1.5 Dy$L\beta_4$	8.7 Sm(9.1, 8.8)
Tm$L\beta_1$	1.0 Gd$L\gamma_1$, 0.8 Gd$L\gamma_2$	
	7.9 Tb$L\gamma_1$	
Yb$L\alpha_1$	0.3 Tb$L\beta_2$, 0.2 Dy$L\beta_3$	
Yb$L\beta_1$	1.0 Tb$L\gamma_2$, 0.7 Tb$L\gamma_3$	
	5.7 Dy$L\gamma_1$, 0.3 Tm$L\beta_3$	
Lu$L\alpha_1$	11.1 Dy$L\beta_2$, 6.5 Ho$L\beta_2$	9.0 Dy(12.2)
Lu$L\beta_1$	1.0 Dy$L\gamma_2$, 0.2 Dy$L\gamma_3$	
	2.8 Yb$L\beta_2$, 2.4 Ho$L\gamma_1$	

No correction is necessary for $L\alpha_1$ of La, Ce, Nd and Tb, and for $L\beta_1$ of Ce, Pr, Nd, Sm and Dy.

The peak positions for all *REE L* lines listed in White & Johnson (1979) have been included in a computer program written in BASIC that can be used to calculate the peak-overlap correction for all major peaks. The intensities of the $L\beta_1$, $L\beta_2$, $L\beta_3$ and $L\gamma_1$ peaks relative to $L\alpha_1$ used in the program were those taken from the best-fit lines given in Figure 3. The intensities of all other lines (*e.g.*, $L\gamma_4$, $L\beta_4$) were taken from White & Johnson. The correction factors, calculated with this program for the peak width shown in Figure 2, are given in Table 2 for all the $L\alpha_1$ and $L\beta_1$ peaks of the *REE* that have a correction greater than 0.1%. The correction factors for both the $L\alpha_1$ and $L\beta_1$ have been calculated because some analysts (*e.g.*, Exley 1980) use the $L\beta_1$ peak if the $L\alpha_1$ peak shows a large correction. The measured overlap-corrections of Åmli & Griffin (1975) are also shown in Table 2, and are reasonably close to the values calculated and measured (shown in parentheses) in the present study. The best spectral line for *REE* measurement on the microprobe would be one with as few interferences as possible and one where the correction factors are small and the interfering element is in low concentration. For example, Gd shows major interferences for both $L\alpha_1$ and $L\beta_1$, but $L\beta_1$ may be preferable because the major interference is from Ho, and this element is usually present at very low concentrations. Table 2 contains corrections due only to overlapping peaks for the *REE*; no consideration is given to peaks due to elements such as Mn and Fe that overlap some *REE* lines and can cause severe interference. The overlap correction for these elements can be calculated using the same spectrometer-data and the relative intensities from White & Johnson (1979), but it would be preferable to measure the overlap correction. It should be stressed that careful electron-microprobe analysis for *REE* involves a considerable investment of time and energy if the analytical levels are below 1%.

Spectral scan

The complexity of the *REE* X-ray spectrum is such that it is wise to conduct a WD spectral scan of any *REE*-containing mineral before attempting an analysis. The WD spectra of the glasses S–254 and S–253 are shown in Figures 4b and 4c. The spectrum in Figure 4b refers to a sample containing *REE* at the nominal 1.04% level; the sample for Figure 4c contains *REE* at the nominal level of 0.08%. These samples are unusual, compared to minerals, in the number and quantity of *REE,* but they demonstrate the potential complexities of the *REE* spectrum and the difficulty in measuring the background levels for heavy *REE.* A useful method for calculating the background in samples having a complex spectrum was described by Smith & Reed (1981). The spectrum in Figure 4c demonstrates the sensitivity of a spectral scan, even at levels of 800 ppm. A spectrum of a substance of known *REE* concentration can be calculated given a) the relative intensity of the $L\alpha_1$ lines of each *REE* in the sample, as calculated from a ZAF procedure, and b) the change in peak resolution over the spectral range. The peak-overlap corrections (Fig. 3) and data from White & Johnson (1979) were used with equations 1) and 2) to calculate (BASIC program) the spectrum shown in Figure 4a. This spectrum was calculated assuming a sample with equal intensity of the $L\alpha_1$ of the *REE*; it compares favorably with the measured scan shown in Figure 4b. The measured scan has a variable background and shows changes in the efficiency of X-ray generation and of the spectrometer as a function of wavelength. The underlined *REE* in Figure 4 are those that have a peak-overlap correction less than 1% for the $L\alpha_1$ line; thus the calculated $L\alpha_1$ peaks for these elements are at the same height. The similarity between the calculated and measured scan gives the analyst some confidence in the use of these corrections for analytical work.

The effect of changing spectrometer resolution is shown quite dramatically by comparing the WD spectrum in Figure 4b with the ED spectrum for the same glass sample in Figure 5. The major peaks in Figure 5c are due to aluminum, silicon and calcium, whereas the minor peaks are due to yttrium, scan-

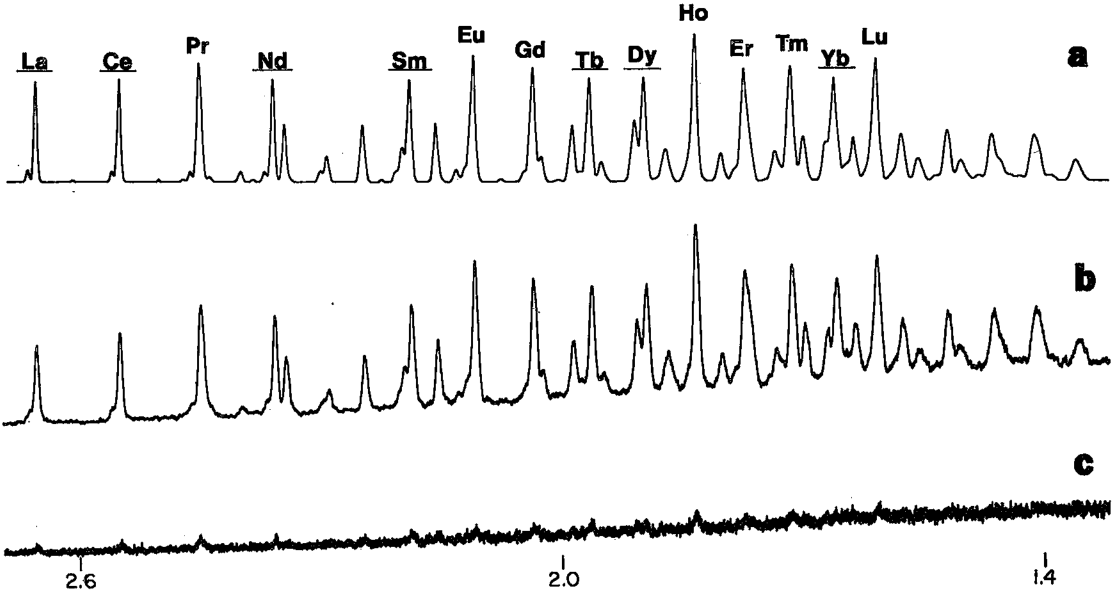

FIG. 4. Calculated and measured WD spectra for the wavelength region of 2.7 to 1.4 Å. a) Calculated spectrum, with the element symbol above the $L\alpha_1$ line; underlined symbols for elements where $L\alpha_1$ needs no overlap correction. b) Measured spectrum for glass S–254, with each *REE* at a nominal 1 wt.%. c) Measured spectrum for glass S–253 withe each *REE* at a nominal 0.08 wt.%.

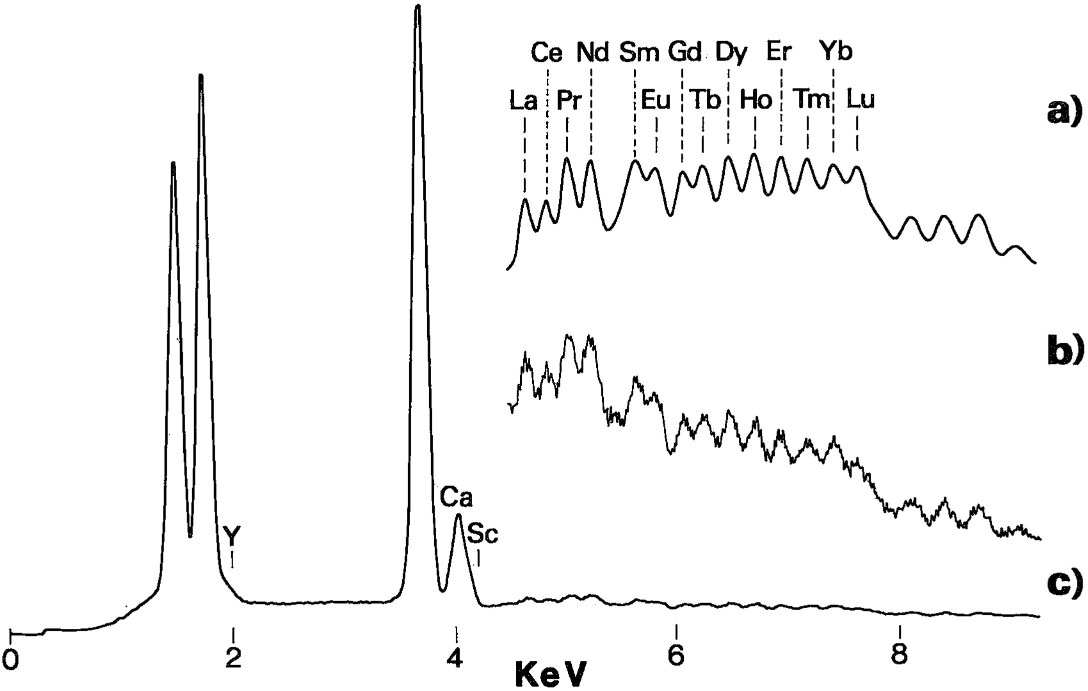

FIG. 5. Calculated and measured ED spectra for the glass samplei S-254. a) Calculated spectrum with $L\alpha_1$ peaks identified. b) Measured ED spectrum exaggerated eight times that in Figure 5c. c) Measured ED spectrum (0–9 kV) showing major peaks of Al, Si, Ca and minor peaks for Y, Ca$K\beta$, Sc and *REE*.

dium and the fourteen *REE*. The spectral region that includes the *REE* is shown separately in Figure 5b with an eight-fold vertical exaggeration. The measured ED spectrum was run for 1000 seconds in order to try to smooth some of the statistical variation that is apparent for a sample that contains each *REE* at only a 1% level. An ED spectrum (Fig. 5a) was calculated using the peak-width variation shown by our ED spectrometer and the same data as for the WD spectrum calculation. The calculated (Fig. 5a) and measured (Fig. 5b) ED spectra are very similar except for the changing background shown in the measured spectrum. The calculated WD spectrum (Fig. 4a) and the ED spectrum (Fig. 5a) cannot be exactly matched because the horizontal scale used on the WD spectrum is in wavelength units (Å), whereas the scale used for the ED spectrum is in energy units (eV). The La$L\alpha_1$ and Ce$L\alpha_1$ peaks are completely resolved using the WD spectrometer, but there is considerable overlap using the ED spectrometer. The calculated ED spectrum should show the $L\alpha_1$ peaks of all the rare earths at approximately the same height as the La$L\alpha_1$ and Ce$L\alpha_1$ peaks if the overlap corrections were low. Only La and Ce have small corrections by EDS, whereas seven *REE* (La, Ce, Nd, Sm, Tb, Dy, Yb) have a correction of less then 1% by WDS. It is obvious that *REE* analysis by EDS is very difficult or impossible unless one uses a multiple least-squares technique such as that developed by Tracor Northern. This has been used quite successfully by Robinson (1979) for *REE* at levels greater than 0.5% in zircon and monazite.

ANALYSIS OF MINERALS FOR THE *REE*

The microprobe analysis of minerals for the *REE* is difficult because of the scarcity of suitable standards, the problem of peak overlap, the difficulty of measuring the background in some samples, and matrix effects. The ten *REE* phosphates described earlier have been used as standards to analyze for *REE* in the four Drake & Weill glasses and also the glasses prepared in the present study. Since no *REE* phosphates for Gd, Tb, Eu or Lu were available at the time of this study, the Drake & Weill glasses were used as a primary standard for these elements. Drake & Weill (1972) gave the original weighed (nominal) concentration of *REE* in these glasses and also presented results of neutron-activation analysis for some of the *REE*. Both these values are listed in Table 1 together with the microprobe data from the present study. The analytical results for all four glasses of Drake & Weill are shown in one column. The $L\alpha_1$ line for the elements Pr, Eu, Ho, Er and Tm generally needs an overlap correction, so some analysts (Exley 1980) use the lower-intensity $L\beta_1$ line. Both lines for these elements were used in the present study in order to compare the results. The analytical results shown in Tables 1 and 3 were obtained during two microprobe sessions, one session at 15 kV and one at 25 kV, and only the normal precautions were taken for analyzing major elements. Each microprobe analysis was corrected for matrix effects and, if necessary, for peak overlap using the calculated corrections given in Table 2. Two examples are given in parentheses (Table 1) of values in weight % before peak-overlap corrections. Thus the nominal weight % Pr of the Drake & Weill glass is 3.79 and the overlap-uncorrected Pr value using the Pr$L\alpha_1$ line is 4.12, whereas the amount corrected for peak overlap is 3.71. The microprobe procedure used in the present study may not justify listing the second decimal place in Table 1, but it was thought useful to include it. Each microprobe analysis represents an average of a number (*n* shown in parentheses after kV) of 50-second counts at different positions on the sample. The glasses S-253 and S-254 were analyzed a sufficient number of times to justify calculating the homogeneity index of Boyd *et al.* (1967). All *REE* in these glasses have a homogeneity index less than 3, and most are less than 2. Samples S-254 and S-253 were also analyzed at 25 kV because of the low *REE* concentration, and more attention was paid to the measurement of background during the session at 25 kV. The background was measured at seven different positions (*i.e.*, wavelengths) which, by calculation, showed the least interference by *REE* peaks, and the best-fitting curved line through these points was used for the background. The glasses prepared in the present study (S-236, 253, 254) were sent to two laboratories for neutron-activation analysis. These results (NAA) are listed in Table 1, and no attempt has been made to reconcile these values with the nominal values or results of microprobe analyses.

The true test of any microprobe procedure lies in its suitability for minerals. The samples shown in Table 3 were analyzed at 15 kV during the same session as for the data in Table 1. The only difference in procedure was the addition of a Gd$L\alpha_1$ measurement, which was not done on the glass samples because of the high content of Ho. All the samples in Table 3 were analyzed by wet-chemical analysis of mineral separates. Many of the mineral grains contain inclusions (*e.g.*, biotite), which means that the microprobe data will not be directly comparable with the wet-chemical analytical data. The correction factors for peak overlap can be appreciable in natural samples because there is often a large amount of one or two of the light *REE*, such as La or Ce, and these major elements make a significant contribution at the peak positions for some of the heavier trace *REE*. A good example is the high uncorrected Gd content (shown in parentheses) for the bastnaesite, parisite and monazite because of the high La and Ce content. Thus large amounts of La and Ce make it almost impossible to analyze for minor amounts of Gd with any confidence using the $L\alpha_1$ line. The Gd$L\beta_1$ line is probably much better at very low concentrations, but only if there is no Ho present. It should be emphasized that the overlap corrections used in the present study may be quite different from those used by other investigators, and depend upon the resolution and efficiency of the spectrometers.

The microprobe data given in Tables 1 and 3 show that reasonable analyses of minerals for the *REE* are possible at levels greater than 1% if adequate preparation and care are taken. The microprobe determination of the *REE* in the Drake & Weill glass standards agrees well with the results given by Drake & Weill (1972). This agreement implies that the factors

TABLE 3. CONCENTRATION OF RARE-EARTH ELEMENTS IN SELECTED MINERALS

	Bastnaesite[1]		Parisite[2]		Monazite[1]		Allanite[3]		Apatite[4]		Apatite[5]	
wt. %	Probe	Chem	Probe	Chem	Probe	Chem	Probe	Chem	Probe	Chem	Probe	Chem
La	21.1	22.7	10.8	11.7	16.6	16.1	4.3	3.5	0.4	0.4	0.2	0.4
Ce	29.7	30.0	22.7	21.6	28.6	27.0	6.9	5.7	0.4	0.5	0.8	1.0
Prα	2.4(4.8)	2.6	2.6(3.8)	2.4	2.6(4.4)	2.6	0.9 (1.4)	0.6	0(0.1)	0.1		
Prβ	2.1	2.6	2.6	2.4	2.4	2.6	0.6	0.6				
Nd	6.7	6.5	10.1	8.6	8.3	7.6	2.0	1.7	0.1	0.2		
Sm	0.8	0.3	1.7	1.3	1.1(1.1)	0.6	0.3(0.3)	0.2				
Euα	0.1(0.6)	0.1	0.3(0.9)	0.1	0.2(0.8)	0.1	0 (0.2)	0				
Euβ	0	0.1	0.1(0.2)	0.1	0	0.1	0.4(0.4)	0				
Gdα	0 (3.6)	0.1	1.4(4.0)	1.1	0.2(3.6)	0.4	0.1(0.9)	0.1				
Gdβ	0.1	0.1	1.3	1.1	0.1	0.4	0.1	0.1				
Tb	0	0	0.1	0.1	0	0.1	0	0				
Dy	0	0	0.1	0.3	0	0	0.3	0				

[1]) Mountain Pass, California: Provided by A.N. Mariano and analyzed (Chem) by wet-chemical methods by M. Arnold of Molycorp Inc., Louviers, Colorado, U.S.A. [2]) Snowbird Mine, Montana, U.S.A. Analysis by M. Arnold. [3]) Prospect north of Timmins, Ontario, Canada. Analysis by M. Arnold. [4]) Cerro de Mercado, Durango, Mexico. Young et al. (1969).
[5]) Huddersfield Township, Quebec. Trzcienski et al. (1974).

involved in the ZAF correction procedure have worked well to correct for the difference in the matrix of the phosphate standards and silicate glasses. At levels of 0.1% to 1%, the analytical results are still reasonably good, but the problems of overlap correction and background measurement become increasingly important at the lower levels. The problem of accurate measurement of background (Smith & Reed 1981) and overlap correction for concentrations less than 0.1% are very significant, and results at this level should be viewed with a healthy scepticism.

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