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ROUTINE TRACE-ELEMENT CAPABILITIES OF ELECTRON-MICROPROBE ANALYSIS IN MINERALOGICAL INVESTIGATIONS: AN EMPIRICAL EVALUATION OF PERFORMANCE USING SPECTROCHEMICAL STANDARD GLASSES

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ABSTRACT

Using a Cameca CAMEBAX electron-microprobe, the performance of routine electron-microprobe analysis at concentrations from 50 to 500 ppm has been evaluated for 39 trace elements (in the range Sc to U) based on comparison with several independent methods. The samples used are fragments of granular glass originally prepared as spectrochemical standards for use in the analytical laboratories of the U.S. Geological Survey. Accurate measurement of background is the key to good trace analyses; the X-ray continuum in the vicinity of an analytical peak must be carefully investigated to avoid potential interference from other elements. Given this, the results indicate that using a beam current of 100 nA and counting times of 300 seconds on peaks and backgrounds, trace elements in a silicate matrix can be determined routinely (95% confidence level) at concentrations down to 50 ppm. Where the concentrations are known to be higher than 100 ppm, a beam current of 50 nA and counting times of 100 seconds on peaks and backgrounds can be used to minimize chances of beam damage and substantially increase the throughput of samples.

Keywords: electron microprobe, empirical evaluation, minerals, standard glasses, trace elements.

SOMMAIRE

Nous avons évalué le rendement d'une microsonde électronique Cameca CAMEBAX pour le dosage de 39 éléments-traces, dans l'intervalle de Sc à U, présents à des niveaux entre 50 et 500 ppm, par comparaisons avec plusieurs méthodes indépendantes. Les échantillons utilisés sont des fragments de verres qui avaient été préparés comme étalons spectrochimiques pour utilisation dans les laboratoires du U.S. Geological Survey. Une évaluation juste du bruit de fond est essentielle pour assurer le succès d'une analyse. Le profil continu des rayons X au voisinage d'un pic servant à l'analyse doit faire l'objet d'une étude soignée afin d'éliminer la possibilité d'une interférence avec les pics d'autres éléments. Avec un courant du faisceau de 100 nA et des temps de comptage des pics et du bruit de fond de 300 secondes, il est possible de doser, de façon routinière et à un niveau de confiance de 95%, ces éléments jusqu'à un seuil de 50 ppm. Dans les cas où leur concentration dépasse 100 ppm, l'utilisation d'un courant du faisceau de 50 nA et un temps de comptage de 100 secondes sur pics et bruit de fond peut minimiser le dommage causé à l'échantillon et augmenter de façon importante la productivité de l'analyste.

(Traduit par la Rédaction)

Mots-clés: microsonde électronique, évaluation empirique, minéraux, verres-étalons, éléments-traces.

INTRODUCTION

Quantitative information on the trace elements present in minerals is needed for a variety of applications, including: 1) the provision of constraints on petrogenetic hypotheses through studies of trace element partitioning behavior in natural and experimental systems, 2) the search for indicator elements in the minerals of potential host-rocks to mineralization, and 3) the economic evaluation of orebodies whose viability may depend upon the presence of trace metals, such as refractory gold, in specific host-minerals.

Microbeam techniques (for example, electron, ion and proton microprobes, high-resolution SIMS, and synchrotron X-ray fluorescence) are the only ones able to obtain such information *in situ*. Each has its advantages and disadvantages. The superior spatial resolution of the electron microprobe, however, means that this instrument must be used where the minerals are fine grained, intimately intergrown or complexly zoned, even though detection limits are generally poorer than with the other techniques.

A concentration of 100 ppm commonly is taken as the typical limit of detection for electron-microprobe analysis using wavelength dispersion (Reed 1975, Goldstein *et al.* 1981, Newbury *et al.* 1986). The literature contains many reports demonstrating that such levels and better (down to 10 ppm) can be determined by these techniques (Goldstein 1967, Buseck & Goldstein 1969, Smith 1971, Schneider 1972, Koppel & Sommerauer 1973, Rao 1973, Hewins & Goldstein 1974, Bishop *et al.* 1978, Hervig *et al.* 1980, Bizouard 1982, McKay & Seymour 1982, Solberg 1988). Such results, however, have been obtained for only a limited number of elements in specific minerals and, in general, have not called upon independent methods of analysis for verification. In most cases, the analytical procedures have been far from routine.

The aim of the present study has been to evaluate the performance of the electron microprobe for a wide range of trace elements (from Sc to U) using procedures that are routinely available and readily accessible to the average user in any mineralogically oriented laboratory. Since "...all results are a matter of opinion rather than fact..." (Lundell 1933), the "true results" have been taken to be those for which a variety of other methods show agreement (Myers *et al.* 1976), and the performance of the electron microprobe has been judged by comparison with these.

SAMPLES

Three glass standards (GSC, GSD and GSE), containing a wide range of trace elements at approximately 5, 50 and 500 ppm levels, respectively, form the basis of the present study. They comprise part of a suite of five glass reference standards prepared by Corning Glass Works to provide quality control for spectrochemical trace-element analyses of geological materials in analytical laboratories of the U.S. Geological Survey (Myers *et al.* 1970). A preliminary study of these glasses by electron microprobe (using 10-second counts) has been reported by Heidel (1971).

The samples analyzed in the present study comprise small (1 cm) fragments of the original granular glass that have been embedded in epoxy and polished for electron-microprobe analysis using diamond pastes. The composition and homogeneity of these standards (in powder form) have been thoroughly investigated by a variety of analytical techniques and interlaboratory comparisons (Myers *et al.* 1976). All the glasses contain major Na, Mg, Al, Si, K, Ca and Fe, so that with the exception of Ti and Mn, the effects of major-element interferences arising from the matrices of common silicate minerals are all represented.

Table 1 shows the average matrix compositions for GSC, GSD and GSE powders (Myers *et al.* 1976) and the compositions of the corresponding glass chips, as determined by electron-microprobe analysis in the present study. Agreement between the two sets of data is good. Small differences in matrix composition exist between the three glasses; these have been

TABLE 1. MATRIX COMPOSITION (WT%) OF THE STANDARD GLASSES

	GSE Glass		GSD Glass		GSC Glass	
	Probe	Myers et al.	Probe	Myers et al.	Probe	Myers et al.
SiO_2	61.53	61.50	62.52	61.80	62.39	62.05
Al_2O_3	13.28	13.60	14.01	14.40	13.72	14.20
Fe_2O_3*	6.20	6.56	7.17	7.10	7.06	7.17
MgO	3.68	3.63	3.94	3.90	3.92	3.90
CaO	5.27	5.26	5.17	5.01	5.21	4.92
Na_2O	4.58	4.56	4.22	4.08	3.97	4.09
K_2O	3.44	3.06	3.58	3.72	3.63	3.62
TiO_2	0.08	0.12	0.01	0.01	0.01	<0.01
P_2O_5	0.06	0.03	nd	0.02	nd	nd
MnO	0.09	0.09	0.05	0.04	0.03	0.03
CO_2	nd	0.02	nd	0.03	nd	0.04
Cl	nd	0.08	nd	0.01	nd	0.01
F	nd	0.03	0.02	0.02	0.04	0.01
H_2O^+	nd	0.22	nd	0.28	nd	0.33
H_2O^-	nd	0.06	nd	0.08	nd	0.08
Total	98.21	98.82	100.38	100.60	100.88	100.45

* Total iron as Fe_2O_3. nd:not determined. Standards: wollastonite (Ca, Si), kyanite (Al), forsterite (Mg), jadeite (Na), orthoclase (K), hematite (Fe), Mn metal (Mn), rutile (Ti), apatite (P), and CaF_2.

TABLE 2. ANALYTICAL CONDITIONS, MEASURED RESULTS (ELECTRON MICROPROBE) AND EXPECTED VALUES FOR GSE

	ANALYTICAL CONDITIONS							MEASURED		EXPECTED	
El.	Line	Xtal	Offset	Slope	kV	Beam (nA)	Time (s)	Mean (ppm)	2σ (ppm)	Median (ppm)	Range (ppm)
Ag	Lα	PET	+670	1.00	20	50	100	272	138	380 A	260 - 600
As	Lα	TAP	-150	1.07	20	150	100	437	100	450 S	320 - 700
Au	Lα	LIF	900	1.00	40	50	100	89	44	50 A	40 - 70
Ba	Lα	PET	+600	1.00	20	50	100	616	104	500 A	430 - 800
Bi	Lα	LIF	+500	1.00	40	50	100	408	184	480 A	350 - 600
Cd	Lα	PET	+640	1.00	20	50	100	414	160	420 S	250 - 700
Ce	Lα	LIF	500	1.00	20	50	100	520	146	550 S	450 - 780
Co	Kα	LIF	+400	1.00	20	50	100	470	108	450 A	350 - 700
Cr	Kα	PET	400	1.00	20	50	100	536	32	490 A	410 - 600
Cs	Lα	LIF	500	1.00	20	50	100	403	216	370 S	340 - 430
Cu	Kα	LIF	500	1.00	20	50	100	351	120	500 A	340 - 590
Ga	Kα	LIF	500	1.00	40	150	300	11	12	20 R	13 - 30
Ge	Kα	LIF	700	1.00	20	50	100	405	160	500 A	390 - 580
Hf	Lα	LIF	+500	1.00	20	50	100	584	240	500 S	220 - 600
In	Lα	PET	+500	1.24	20	50	100	460	130	500 S	420 - 600
Ir	Mα	PET	+500	1.00	20	50	100	81	158	140 S	61 - 150
La	Lα	PET	500	1.00	20	50	100	452	120	550 S	500 - 700
Mn	Kα	LIF	570	1.00	20	50	100	619	46	600 S	450 - 800
Mo	Lα	PET	500	1.00	20	50	100	380	128	500 A	300 -1000
Nb	Lα	PET	500	1.01	20	150	100	476	82	500 A	450 - 530
Ni	Kα	LIF	570	1.00	20	50	100	498	78	500 A	360 - 700
Pb	Mα	PET	670	1.00	20	50	100	480	216	500 S	430 - 600
Pd	Lα	PET	900	0.96	20	150	300	125	274	100 A	82 - 200
Pt	Mα	PET	-500	0.96	20	150	300	125	92	110 A	76 - 140
Rh	Lα	PET	-500	0.92	20	150	300	77	38	60 S	47 - 70
Ru	Lα	PET	+250	1.03	20	150	300	not detected		90 R	none
Sb	Lβ	PET	-250	0.98	20	150	100	475	125	470 S	330 - 510
Sc	Kα	PET	500	0.98	20	150	300	20	20	30 S	15 - 34
Sn	Lα	PET	+500/-300	1.01	20	150	100	415	52	440 A	390 - 530
Sr	Lα	PET	+740	1.00	20	50	100	533	192	500 A	410 - 700
Ta	Lα	LIF	+1000	1.00	20	50	100	525	208	480 S	400 - 530
Te	Lα	PET	-500	0.99	20	100	100	347	90	260 R	250 -<300
Ti	Kα	PET	+570	1.06	20	50	100	495	50	490 A	420 - 550
U	Mα	PET	+400	1.00	20	50	100	532	224	470 S	410 - 700
V	Kα	LIF	500	1.00	20	50	100	500	50	500 A	360 - 800
W	Lα	LIF	500	1.00	20	50	100	470	270	420 S	300 - 500
Y	Lα	PET	500	1.00	20	50	100	468	164	490 A	390 - 700
Zn	Kα	LIF	500	1.00	20	50	100	551	148	500 A	310 - 600
Zr	Lα	PET	500	1.00	20	50	100	431	104	480 A	360 - 540

Note: Time = Counting time on peak and background per point.
2σ calculated for the mean of ten analyses.
Expected values from Myers et al. (1976).
Confidence Level: A accepted, S suggested, R reservations.
Standards: Ag, Au, Bi, Cd, Co, Cr, Cu, Ge, Hf, Ir, Mn, Mo, Nb, Ni, Pd, Pt, Rh, Ru, Sb, Sc, Sr, Ta, Te, Ti, U, V, W, Y, Yb, Zn, and Zr, pure metals; As and Ga, gallium arsenide; Ba, barytes; Ce, cerium oxide; In, indium arsenide; La, lanthanum hexaboride; Pb, lead fluoride; Sn, cassiterite; Sr, strontium fluoride.

TABLE 3. ANALYTICAL CONDITIONS, MEASURED RESULTS (ELECTRON MICROPROBE) AND EXPECTED VALUES FOR GSD

	ANALYTICAL CONDITIONS							MEASURED		EXPECTED	
El.	Line	Xtal	Offset	Slope	kV	Beam (nA)	Time (s)	Mean (ppm)	2σ (ppm)	Median (ppm)	Range (ppm)
Ag	Lα	PET	+670	1.00	20	100	300	74	34	37 A	20 - 50
As	Lα	TAP	-150	1.09	20	100	300	12	20	42 S	<10 - 42
Au	Lα	LIF	900	1.03	40	150	300	not detected		14 A	10 - 15
Ba	Lα	LIF	500	1.00	20	100	100	68	161	90 A	50 - 200
Bi	Lα	LIF	500	1.00	40	150	300	25	50	41 S	30 - 52
Cd	Lα	PET	+640	1.05	20	100	300	27	32	30 S	25 - 40
Ce	Lα	PET	+800	1.06	20	100	300	60	42	50 R	30 - 76
Co	Kα	LIF	+400	1.05	20	100	300	32	22	35 A	26 - 50
Cr	Kα	PET	400	1.00	20	100	300	53	18	47 A	30 - 68
Cs	Lα	LIF	500	1.00	20	100	300	38	76	35 S	34 - 54
Cu	Kα	LIF	500	1.00	20	100	300	51	42	45 A	35 - 70
Ge	Kα	LIF	700	1.00	20	100	300	29	52	40 S	26 - 80
Hf	Lα	LIF	+600	1.00	30	100	300	65	54	45 R	16 - 50
La	Lα	PET	500	1.00	20	100	300	39	38	47 S	30 - 60
Mn	Kα	LIF	570	1.00	20	100	300	214	22	210 S	180 - 260
Mo	Lα	PET	500	0.94	20	100	300	41	54	46 A	20 - 70
Nb	Lα	PET	500	1.00	20	100	300	41	54	40 A	26 - 50
Ni	Kα	LIF	500	1.00	20	100	300	56	22	54 A	35 - 70
Pb	Mα	PET	670	1.00	20	100	300	38	68	52 A	35 - 70
Pd	Lα	PET	900	1.03	20	100	300	56	38	36 S	26 - 50
Sb	Lβ	PET	-250	0.97	20	100	300	72	66	37 R	25 -<500
Sn	Lα	PET	500/300	1.00	20	100	300	65	36	42 S	30 - 50
Sr	Lα	PET	+740	1.08	20	100	300	56	78	64 A	52 - 100
Ti	Kα	PET	+570	1.06	20	100	300	45	20	44 S	39 - 70
U	Mα	PET	+400	1.06	20	100	300	28	72	40 R	39 - 41
V	Kα	LIF	500	1.00	20	100	300	39	26	45 A	34 - 61
W	Lα	LIF	500	1.00	20	100	300	62	110	50 R	40 - 64
Y	Lα	PET	500	0.96	20	100	300	77	60	46 A	30 - 71
Zn	Kα	LIF	500	1.00	20	100	300	35	42	43 S	33 - 50
Zr	Lα	PET	500	0.97	20	100	300	65	44	48 A	36 - 53

Note: Time = Counting time on peak and background per point.
2σ calculated for the mean of ten analyses.
Expected values from Myers et al. (1976).
Confidence Level: A accepted, S suggested, R reservations.

taken into account when carrying out trace-element analyses with the electron microprobe.

The trace-element contents of GSE and GSD (in powder form), as reported by Myers *et al.* (1976), are summarized in Tables 2 and 3, respectively. These are the median results of interlaboratory comparisons based on several different analytical methods; Myers *et al.* (1976) have categorized them into accepted values (A), suggested values (S) and values that are included but with reservations (R).

GSE contains 49 elements ranging from B(5) to U(92), most of which are present at the target level of about 500 ppm. The exceptions are Cl (800 ppm), F (300 ppm), Te (250 ppm), Ir, Pd and Pt (about 100 ppm) and Au, Ga, Rb, Rh, Ru, Sc, Se, Tl and Yb (less than 100 ppm). GSD contains 47 of the same elements, most of which are at the target level of about 50 ppm. The exceptions are F (250 ppm), Mn (210 ppm), Ba and Cl (about 100 ppm), and Au, Ga, Pt, Rh, Ru, Sc, Te, Tl, Yb and Zr (less than 20 ppm). GSC contains 42 of the same elements, most of which are in the range 1 to 10 ppm. The exceptions are B (20 ppm), Ba (39 ppm), Cl (50 ppm), F (100 ppm), Mn (200 ppm), Ni (18 ppm), Pb (15 ppm), Sr (27 ppm), Ti (11 ppm) and Zn (12 ppm). This glass has been used as the "blank" for determination of nonlinear background-correction factors (see below).

ANALYTICAL PROCEDURES

Analyses have been carried out on a Cameca CAMEBAX automated electron-microprobe, equipped with four vertical wavelength-dispersion spectrometers using 90% argon–10% methane gas-flow proportional counters for measurement of X-ray intensities. Two of these spectrometers are equipped with PET and LIF crystals, a third with PET and TAP, and the fourth is equipped with TAP and ODPB (lead stearate). For most determinations, therefore, where PET or LIF can be used, at least three elements can be determined simultaneously. In favorable circumstances, where TAP also can be used on the fourth spectrometer, the simultaneous determination of 4 trace elements is possible. The instrument also is equipped with an argon gas-jet and cold-finger anticontamination device that can be used to minimize build-up of surface contamination during low-level trace-element analysis.

The original software for quantitative analysis with this instrument provided for background measurements to be made either symmetrically about the peak or at the positive side only, and with a count time half that used on the peak. This practice has been modified so that backgrounds can now also be measured asymmetrically on either side of a peak or only on the negative side of the peak, and the counting times increased to the same value as that used on the peak. In addition, where two backgrounds are measured the original software interpolated a background intensity under the peak using the arithmetic mean. This assumes a linear variation between the measured offset positions, whereas in reality, the continuum generally has a curvilinear profile that must be taken into account when performing trace-element analysis. Consequently, the software has been further modified to determine the deviation from linearity (nonlinear correction-factor) by measuring the background at the peak and offset positions on a blank of similar matrix composition.

Quantitative major-element analyses of the matrix compositions were carried out by averaging the ZAF-corrected results from 10 widely spaced points on each glass. These analyses were carried out at 15 kV with a beam current of 20 nA (measured by Faraday cup at the sample position, and regulated to better than 0.1%) and a counting time of 20 seconds. A defocused beam was used to avoid mobilization of Na. Data for the standards were obtained from a calibration file of stored peak-intensities. The relevant standards are shown in Table 1.

Before carrying out any trace-element analyses with the electron microprobe, the background in the vicinity of the analytical peak was investigated in order to establish whether any interferences were present and, if so, to design a strategy for avoiding them. This was done for each element by scanning the spectrometers under computer control from $-0.1 \sin\theta$ to $+0.1 \sin\theta$ of the analytical peak position, corresponding to angular ranges on the order of 2 to 4° 2θ (depending upon the element). For example, for Cr*Kα* (low 2θ on PET), the scan range is equivalent to 2.5° 2θ, and for Sr*Lα* (high 2θ on PET), the scan range is equivalent to 3.7° 2θ. GSE was used as the target since this glass contains all the elements of interest at their highest levels. Where an element could be analyzed with more than one crystal (LIF or PET or TAP), scans were obtained for all. The crystals and background offsets selected for quantitative analysis are summarized later (see Results).

Most scans were carried out with a beam current of 50 nA (measured by Faraday cup at the sample position, and regulated to better than 0.1% and an accelerating voltage of 20 kV. The exceptions were Pd*Lα*, Rh*Lα*, Ru*Lα* and Sb*Lα* (beam current 150 nA), Ga*Kα* (accelerating voltage 30 kV) and Au*Lα* and Bi*Lα* (accelerating voltage 40 kV). In addition to these routine investigations, several special scans were carried out to investigate specific difficult situations (see Discussion).

Rather than attempt to establish analytical conditions optimized to achieve a predicted detection-limit for each specific element, we have adopted general analytical conditions (kV, beam current and counting time) suitable for the routine on-line analysis for many elements. This allows considerable flex-

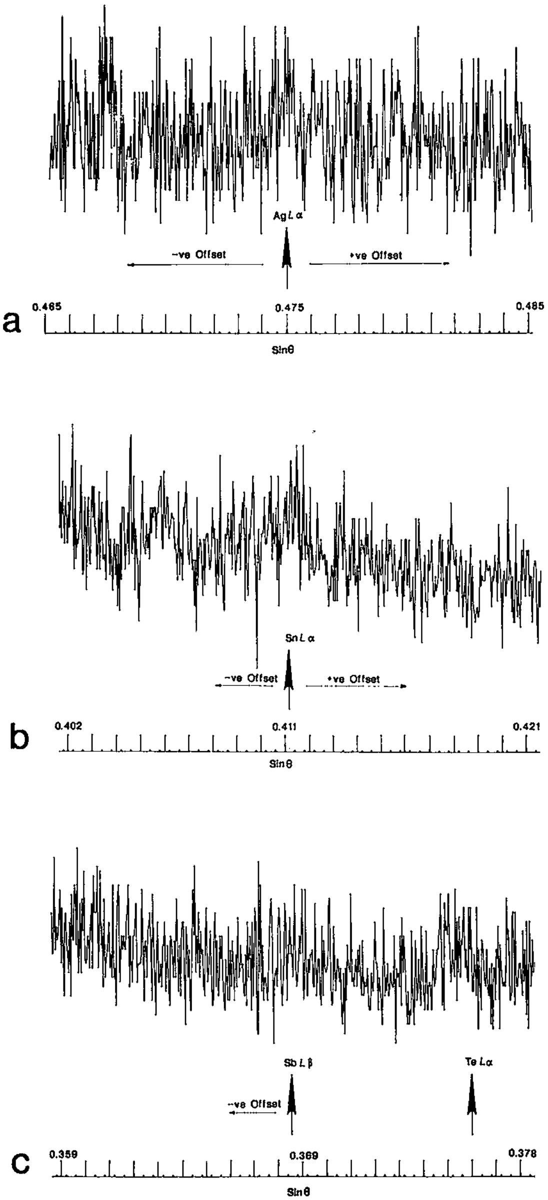

FIG. 1. Spectrometer scans from -0.1 to $+0.1$ sin θ of the analytical position for (a) Ag$L\alpha$ on PET, (b) Sn$L\alpha$ on PET and (c) Sb$L\beta$ on PET. Experimental conditions: 20 kV, 50 nA, 500 steps at 1 second counts/step. GSE glass.

ibility to be exercised in the analysis of minerals, where the requirement is often for meaningful reconnaissance studies prior to selection of specific elements for detailed investigations. For this reason, most analyses have been carried out at an accelerating voltage of 20 kV (except for Au, Bi and Ga, where a higher voltage is essential for efficient X-ray excitation), using a beam current not exceeding 150 nA (to minimize sample damage) and a counting time of not more than 300 seconds on peaks and background (to maintain a realistic time-frame). As for the major elements, all trace analyses were carried out with a defocused beam on the order of 5 μm in diameter to minimize damage to the glass. The anticontamination device, cooled to liquid nitrogen temperature, was used for analyses at levels less than 100 ppm. Under these conditions, the mean of 10 ZAF-corrected replicate analyses at the 50 ppm level can be obtained for three or four elements simultaneously in less than 2.5 hours. Where elements are known to be present at higher levels, the analyses can be carried out in less than 1 hour.

Of course, these estimates take no account of the time that must be devoted to prior investigation of the background. Such investigation must be carried out for each new problem, since the details of the continuum will vary from mineral to mineral, and no general rule can be adopted for placement of the background offsets. Using the CAMEBAX electron microprobe, spectrometer scans (for up to 4 elements simultaneously) can be carried out over a range from -0.1 to +0.1 sinθ of the analytical line at 0.0004 sinθ intervals in about 25 minutes. The data can then be archived for future reference so that the amount of pre-analysis time for a given mineral will decrease as such information accumulates.

Calibration was carried out on-line (rather than by accessing a stored calibration file) in order to ensure optimum peak-counts for the analyses. For each element, count rates (c/s/nA) were measured on the peak and on the background using the relevant standards listed in Table 2. Fixed (250,000) counts were obtained at the peak positions to provide a statistical precision of 0.2% for the calibration. Nonlinear background-correction factors were then determined by repeating these measurements for a fixed counting time on a blank of similar matrix composition (GSC glass). These correction factors were then subsequently applied to the measured backgrounds during on-line analysis of the particular glass (GSE or GSD) under investigation. For most calibrations, a fixed time of 100 s was used, but in certain difficult situations (see Results) the time was increased to 300 seconds to obtain more accurate measurement of the background slopes.

For analyses, the electron microprobe was programmed to step the sample stage automatically to 10 preselected arbitrary locations covering the whole area of the glass chip, and the average value for each element taken to be the "result". In addition, the homogeneity of distribution of selected elements on the micrometer scale was investigated by carrying out a series of point analyses along a 0.3-mm traverse across GSE.

RESULTS

Of the 49 elements known to be present in GSE, 39 have been determined with the electron-microprobe. Of the 47 elements known to be present in GSD, 30 have been determined with the electron microprobe. Concentrations of several elements could not be determined because they are beyond the range of the instrument (B, Be and Li) or at unrealistically low levels (Ga, Pt, Rh, Ru, Sc, Te and Yb in GSD), or because no suitable standards were available (Cl, Eu, F, Rb and Tl).

Tables 2 and 3 summarize the analytical conditions, and compare the trace-element results obtained by electron-microprobe analysis of GSE and GSD, respectively, with the "true results" reported by Myers *et al.* (1976). For most elements, the agreement is very good, even at levels less than 50 ppm. The electron-microprobe data, however, are characterized by comparatively large 2σ values (calculated for the mean of ten analyses). This can be attributed, at least in part, to sample inhomogeneity on the micrometer scale (see Discussion).

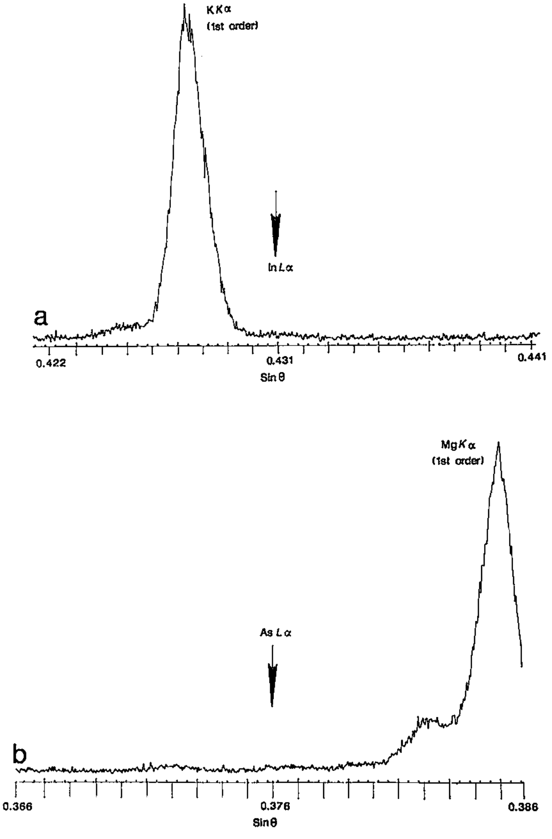

FIG. 2. Spectrometer scans from -0.1 to $+0.1$ sin θ of the analytical position for (a) In*Lα* on PET and (b) As*Lα* on TAP. Experimental conditions: 20 kV, 50 nA, 500 steps at 1 second counts/step. GSE glass.

In GSE, concentrations of all the elements present at the target level of about 500 ppm are readily determined, together with Ir, Pd and Pt at about 100 ppm. The only elements for which the mean values fall outside the ranges quoted by Myers *et al.* (1976) are those known to be present at less than 100 ppm, namely Au (50 ppm), Ga (22 ppm), Rh (60 ppm) and Ru (90 ppm). However, with the exception of Ru (which could not be detected), the values even for these elements are close to the "true results".

In GSD, results for most of the elements present at the target level of about 50 ppm also fall within the ranges accepted by Myers *et al.* (1976). Elements for which the mean values fall outside the ranges are Ag, Au, Bi, Hf, Pd, Sn, U, Y and Zr. However, with the exception of Au (which could not be detected at the 14 ppm level), the electron-microprobe values even for these elements are close to the "true results".

DISCUSSION

Interferences

The importance of careful investigation of the background is illustrated in Figures 1 to 4, where examples are given of the different problems that can be encountered. To some extent, the large number of trace elements present in GSD and GSE poses questions that would be unlikely to arise in natural silicate minerals, for not only must interference from major and minor elements of the matrix be considered, but the possibility of trace-element interference also needs to be avoided.

In favorable circumstances, there are few or no interfering lines, and the continuum will either be horizontal (as for Ag in Fig. 1a) or have only a minor positive or negative slope (as for Sn in Fig. 1b). In such situations, the background measurements can be located either symmetrically (as is the case for Ag) or asymmetrically (as is the case for Sn) about the analytical line.

In some situations (especially with TAP or PET crystals), an interference will be present. Although pulse-height selection may be used to eliminate interferences due to high-order reflections, it is not a routine procedure, and in most cases the effects can be avoided by judicious selection of the crystal and background offset. If this interference is minor and on only one side of the analytical line, then it can easily be avoided by careful placement of the background offset. If the interference is severe, then selection of a different crystal or analytical line (or both) can usually avoid the problem. This is the case, for example, with Zr and Sb. Using Roman numerals in parentheses to denote the order of the line, the Fe$K\alpha_1$(III) interferes on the low side and Ca$K\beta_1$(II) on the high side of the Zr$L\alpha$ line if using TAP; however, the background is free of interference if using PET. The K$K\beta_1$(I) line coincides with Sb$L\alpha_1$ on PET. No other crystal can be used for this element; therefore, the analysis must be attempted using the Sb$L\beta_1$ line (Fig. 1c), with a negative offset of background located to avoid possible interference from trace Te. Despite the reduced intensity of this line, satisfactory determinations of Sb-content were obtained at both 500 ppm (GSE) and 50 ppm (GSD) concentrations (Tables 2, 3).

In a few cases, major interference cannot be avoided. This is the case for In and As in the present study. The In$L\alpha$ line is dominated by the K$K\alpha$ line (Fig. 2a). The As$L\alpha$ line on TAP has major interference from Mg$K\alpha$ (Fig. 2b), but must be used since Pb$L\alpha$ coincides almost exactly with As$K\alpha$ on LIF, and the element is out of range on PET. These interferences make the determination of In and As very sensitive to differences in the Mg and K contents of the blank and sample matrix. It is only because these differences are small in the present investigation that it has been possible to analyze for both In and As at the 500 ppm level (Table 2). Realistically, it would be necessary to resort to overlap-correction procedures [see, for example, Okumura (1984)] to deal generally with these situations.

The trace analysis of Rh and Ru in GSE illustrates another problem that can arise if there is a significant difference in minor-element content between the unknown and the blank. GSE contains about 800 ppm Cl, whereas GSC contains only about 50 ppm Cl. Since the Cl$K\alpha$ peak is located between the analytical peaks for Rh and Ru (Fig. 3), it is essential that the Rh and Ru background offsets be located away from the tails of this peak, *i.e.*, on the negative side of the Rh$L\alpha$ and the positive side of the Ru$L\alpha$ lines, respectively. If not, and backgrounds are taken symmetrically about these peaks, then incorrect nonlinear background slopes will be determined from the blank owing to the absence of the Cl peak in GSC (Fig. 3a) and its presence in GSE (Fig. 3b).

The trace analysis of Au also is difficult in the present study. The Fe$K\alpha_1$(III) line interferes with Au$M\alpha$ on PET; hence it is necessary to use the Au$L\alpha$ line on LIF. This choice requires that the instrument be operated at an accelerating voltage of 40 kV, with the disadvantage of increasing the volume of X-ray excitation and thus degrading the spatial resolution achievable by microanalysis. Moreover, the continuum dips in the vicinity of the Au$L\alpha$ line (Fig. 4), making it very difficult to obtain a reliable measurement of background during routine, on-line analysis. The dip is not related to the sample composition, as it has been observed also with other materials

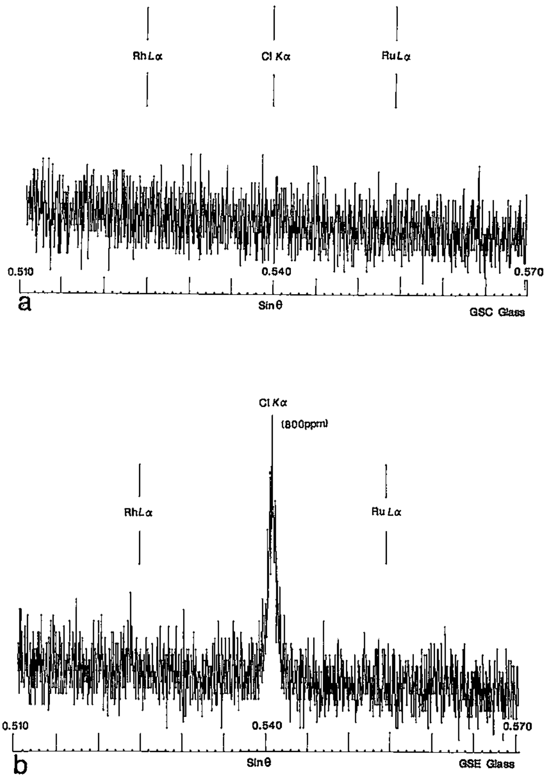

FIG. 3. Spectrometer scans from −0.3 to +0.3 sin θ of the Cl$K\alpha$ analytical position on PET showing (a) the absence of a Cl peak in the blank (GSC) and (b) its presence in the sample (GSE). The presence of Cl interference in GSE necessitates careful placement of the background offsets for Rh$L\alpha$ and Ru$L\alpha$ in order to determine the nonlinear correction-factors. Experimental conditions: 20 kV, 50 nA, continuous scanning, 1500 sampling intervals.

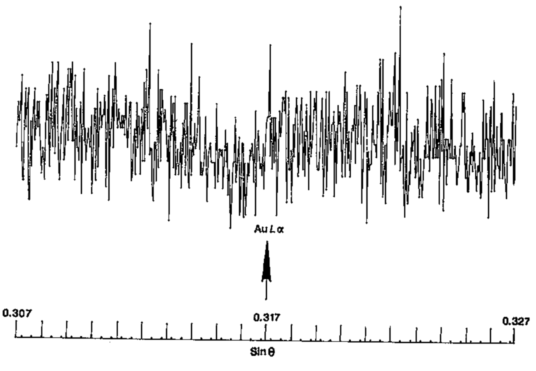

FIG. 4. Spectrometer scan from −0.1 to +0.1 sin θ of the Au$L\alpha$ analytical position on LIF showing a dip in the continuum. Experimental conditions: 40 kV, 100 nA, 500 steps at 1 second counts/step. GSE glass.

(*e.g.*, pyrite and arsenopyrite: Ramsden & Creelman 1984) and for other elements (*e.g.*, Sb in sphalerite when using a Ge analyzing crystal: Self *et al.* 1988). According to Self *et al.* (1988), such effects are an artefact of the analyzing crystal due to multiple diffraction.

Although beyond the scope of the present study, modeling of the background would probably be the best way of dealing with this problem, since once the sample-independent shape of the continuum has been established for a given spectrometer, the appropriate background-correction could then be calculated for any analytical condition.

Homogeneity

Because the results of the present study are being judged against results of "bulk" analyses of homogenized powders, we have chosen to carry out microprobe analyses at 10 widely spaced locations on the glass chips and average these, rather than take 10 replicate analysis at a single (5 to 10 μm) point. Given that the glasses are homogeneous on the macro scale (Myers *et al.* 1976), these averages should, therefore, be comparable with the bulk results. This procedure, however, can be expected to reveal inhomogeneity on the micro scale. Barnes *et al.* (1973) and Heinrich *et al.* (1977) have clearly demonstrated that such inhomogeneity can exist, even in NBS standard glasses that have been certified as homogeneous on the macro scale.

The present microprobe results also suggest that such micro-inhomogeneity is indeed present in GSE and GSD, as indicated by the relatively large 2σ values associated with the element means (Tables 2, 3). The variations that would be expected on the basis of the peak-count statistics if the element distributions were homogeneous are considerably less (Table 4). The basis for this calculation is that for a homogeneous sample, the measured deviations should fall within $3N^{\frac{1}{2}}/N$ of the mean concentration, where N stands for the mean peak-counts (Goldstein *et al.* 1981). It is evident that none of the 30 elements reported in GSD can be considered to be homogeneously distributed on the basis of this criterion, and that of the 39 elements reported in GSE, only Cr, Mn and V are homogeneously distributed.

TABLE 4. COMPARISON OF MEASURED STANDARD DEVIATIONS IN GSE AND GSD AND THEORETICAL VALUES CALCULATED FROM COUNT STATISTICS

El.	GSE Standard Deviation Measured	GSE Standard Deviation Theoretical	GSD Standard Deviation Measured	GSD Standard Deviation Theoretical
Ag	138	56	34	9
As	100	26	20	3
Au	44	5	--	--
Ba	104	44	161	19
Bi	184	39	50	3
Cd	160	70	32	6
Ce	146	103	42	6
Co	108	42	22	4
Cr	32	25	18	4
Cs	216	91	76	12
Cu	120	40	42	6
Ga	12	1	--	--
Ge	160	59	52	7
Hf	240	81	54	11
In	130	45	--	--
Ir	158	60	--	--
La	120	37	38	4
Mn	46	53	22	12
Mo	128	74	54	10
Nb	82	52	54	10
Ni	78	43	22	6
Pb	216	105	68	12
Pd	274	10	38	8
Pt	92	21	--	--
Rh	38	9	--	--
Sb	125	35	66	10
Sc	20	2	--	--
Sn	52	26	36	7
Sr	192	81	78	15
Ta	208	76	--	--
Te	90	27	--	--
Ti	50	26	20	4
U	234	110	72	15
V	50	57	26	6
W	270	74	110	11
Y	164	97	60	19
Zn	148	55	42	6
Zr	104	90	44	14

Concentrations in ppm.

TABLE 5. EMPIRICAL DETECTION LIMITS* UNDER THE CONDITIONS SPECIFIED ASSUMING THE MEASURED CONCENTRATIONS TO BE CORRECT

EL.	kV	Beam (nA)	Time (s)	Meas. (ppm)	Limit* (ppm)	EL.	kV	Beam (nA)	Time (s)	Meas. (ppm)	Limit* (ppm)
Ag	20	50	100	272	83	Nb	20	150	100	476	49
Ag	20	100	300	74	26	Nb	20	100	300	41	32
As	20	150	100	437	49	Ni	20	50	100	498	47
As	20	100	300	12	40	Ni	20	100	300	56	19
Au	40	50	100	89	25	Pb	20	50	100	480	130
Au	40	150	300	not detected		Pb	20	100	300	38	53
Ba	20	50	100	616	61	Pd	20	150	300	125	21
Ba	20	100	100	68	72	Pd	20	100	300	56	26
Bi	40	50	100	408	91	Pt	20	150	300	125	50
Bi	40	150	300	25	31	Rh	20	150	300	77	23
Cd	20	50	100	414	89	Ru	20	150	300	not detected	
Cd	20	100	300	27	33	Sb	20	150	100	475	71
Ce	20	50	100	520	128	Sb	20	100	300	72	53
Ce	20	100	300	60	28	Sc	20	150	300	20	10
Co	20	50	100	470	43	Sn	20	150	100	415	37
Co	20	100	300	32	18	Sn	20	100	300	65	24
Cr	20	50	100	536	28	Sr	20	50	100	533	84
Cr	20	100	300	53	15	Sr	20	100	300	56	52
Cs	20	50	100	403	102	Ta	20	50	100	525	143
Cs	20	100	300	38	57	Te	20	100	100	347	47
Cu	20	50	100	351	61	Ti	20	50	100	495	24
Cu	20	100	300	51	25	Ti	20	100	300	45	12
Ga	40	150	300	11	10	U	20	50	100	532	184
Ge	20	50	100	405	123	U	20	100	300	28	100
Ge	20	100	300	29	50	V	20	50	100	500	44
Hf	20	50	100	584	147	V	20	100	300	39	16
Hf	30	100	300	65	48	W	20	50	100	470	160
In	20	50	100	460	62	W	20	100	300	62	65
Ir	20	50	100	81	203	Y	20	50	100	468	89
La	20	50	100	452	64	Y	20	100	300	77	48
La	20	100	300	39	26	Zn	20	50	100	551	74
Mn	20	50	100	619	41	Zn	20	100	300	35	31
Mn	20	100	300	214	16	Zr	20	50	100	431	88
Mo	20	50	100	380	80	Zr	20	100	300	65	34
Mo	20	100	300	41	37						

Note: * based on 2 x (Av.Bk.Counts)$^{\frac{1}{2}}$
Time = Counting time on peak and background per point.

That micro-inhomogeneity is present also is substantiated by systematic evaluation of results of specific point-analyses. In one case, for example, duplicate analyses on two points less than 10 micrometers apart on GSE showed the Pd-content to be about 56 ppm and 390 ppm, respectively, although the mean of 125 ppm for 10 locations (Table 2) is close to the expected value of 100 ppm found by Myers *et al.* (1976). In another case, the results of a systematic line-traverse across the GSE chip show quite large variations in W and U at the micrometer scale (Fig. 5). Indeed, the overall U-content is lower for this traverse than if averaged over the chip as a whole, suggesting quite marked zonation in the distribution of this element.

Limits of detection

A detailed discussion of limits of detection is beyond the scope of the present paper. It should be noted, however, that a variety of procedures have been proposed for the calculation or prediction of detection limits in X-ray emission spectroscopy (Liebhafsky *et al.* 1960, Ziebold 1967, Pantony & Hurley 1972, Wintsch & Muster 1973, Wittry 1980, Tertian & Claisse 1982, Reimer 1985, Chappell 1987). As pointed out by Heinrich (1981), "One must conclude that there is no consensus as to what should be a reasonable statistical limit of detection".

The factors that determine the sensitivity of the electron microprobe used for analysis at the trace level are many and complex. They include: 1) the alignment of the electron beam and X-ray spectrometers, 2) the counting time, 3) the accelerating voltage, 4) the beam current, 5) the particular element and the line used to measure it, and 6) the composition of both the sample and the standards. Thus, the distinction between peak and background is limited not only by the statistical uncertainties in the measured X-ray intensities, but also by the systematic errors inherent in the procedures used to determine the background level. As pointed out by Heinrich (1981) "..the more carefully the analyst tries to eliminate the counting errors, the more prevalent the systematic errors become in determining the uncertainty of the intensity ratio. Hence it is incorrect in principle and in practice to define a limit of detection solely on the basis of statistical considerations as is so frequently proposed".

Detection limits reported in the present study are empirical and derived on the assumption that the

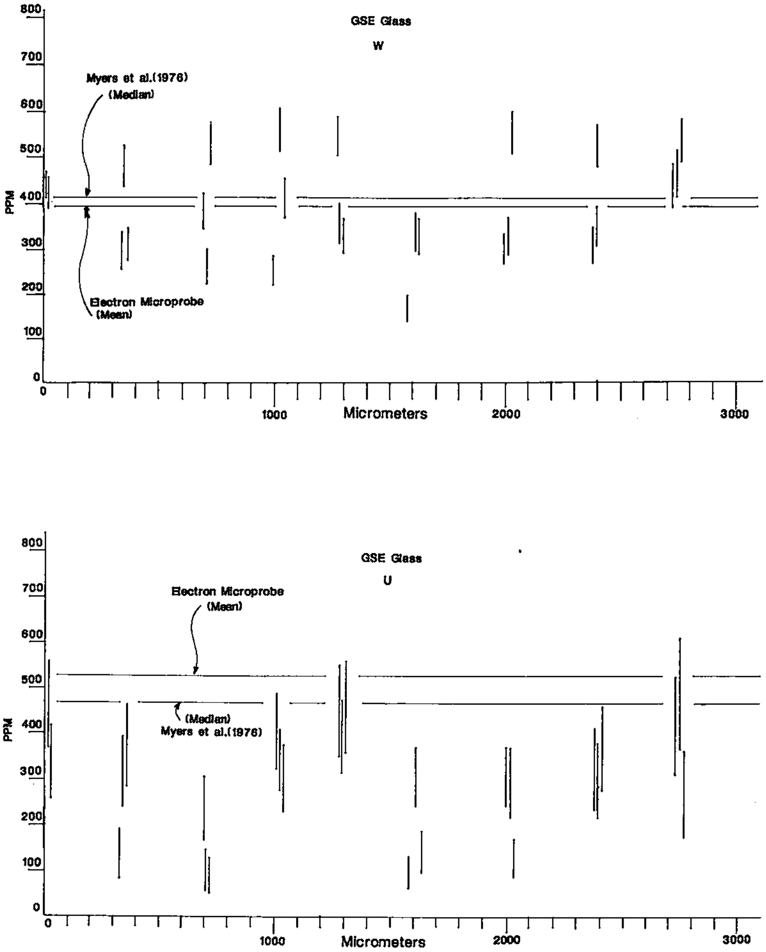

FIG. 5. Results of point analyses (100 second counts) for W and U along a 3000-micrometer traverse across GSE glass.

measured concentration (Tables 2, 3) corresponding to the peak height for each element is correct . It is then a simple matter to calculate the concentration corresponding to a specified level of confidence level above the mean background-count (N_b) for a given set of instrumental conditions.

The results of this approach can be seen in Table 5, in which detection limits calculated for a 95% confidence level (*i.e.*, $2N_b^{1/2}$) are compared for two different analytical conditions. As expected, they show that marked improvements in detection limits are obtained when the beam current is increased from 50 nA to 100 or 150 nA, and the counting times increased from 100 to 300 s. For the majority of elements, the detection limit is well below 50 ppm at the higher beam-current and counting time; apart from Ba, Ru, U and W, the remainder have detection limits close to 50 ppm.

For several elements (As, Cs, Ge, Ir, Pb and U), the measured concentrations in some cases are actually substantially below the detection limits quoted in Table 5. However, the results agree with the "true results" reported by Myers *et al.* (1976). Thus, although they would not be regarded as significant statistically (at the 95% confidence level), they are meaningful analytically. Bence *et al.* (1977) have likewise found that trace-element data obtained with an electron microprobe can be meaningful even where, from the statistical point of view, confidence in the result is low. In their studies, the values obtained from a single initial determination were found to be virtually identical to those obtained after up to 12 replications.

CONCLUSIONS

We conclude that the trace-element investigation of silicate minerals by means of electron-microprobe analysis can be readily carried out for a wide range of elements at levels of 50 ppm (and less) using routine procedures. To achieve this, however, it is very important that the background in the vicinity of each analytical line be carefully investigated. Because the procedures are routine, once the background investigations have been completed, it is possible to carry out such analyses in a comparatively short time-frame, typically involving counting times of 100 to 300 s on peaks and backgrounds, with reasonable precision and sensitivity. This practice allows reconnaissance studies on complex, fine-grained mineral assemblages, applicable to programs of mineral exploration and evaluation, to be undertaken with confidence.

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